

Chemical behaviors of Fe, Ni, and Nb from low and intermediate radwaste samples based on spectrophotometric method

Tae-Hyeong Kim¹, Jong-Il Yun², Jung Bo Yoo¹, Hong Joo Ahn¹, Byeong-Kug Lee³, Kwang Yong Jee¹

¹Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 34057, 111 Daedeok-daero-989, Yuseong-gu, Daejeon, Republic of Korea; *E-mail: thkim@kaeri.re.kr

²Department of Nuclear and Quantum Engineering, KAIST, 34141, 291 Daehak-ro, Yuseong-gu, Daejeon, Republic of Korea

³Korea Hydro and Nuclear Power Co. LTD (KHNP), 1655, Bulguk-ro, Yangbuk-myeon, Gyeongju, Republic of Korea

A sequential separation of radionuclides such as ⁵⁵Fe, ^{59/63}Ni, ⁹⁰Sr, ⁹⁴Nb, and ⁹⁹Tc has been developed and applied to the evaluation of radionuclide inventory in radioactive waste. The process involves precipitation, anion exchange, and extraction chromatography for separation and purification of individual radionuclides. Although the present method shows over 92 % recovery, it is necessary to understand the chemical behavior of radionuclides during the process to enhance the efficiency. For this purpose, a photometric method based on the chelation with 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-3-sulfopropylamino) phenol (Br-PAPS) was used to determine the concentrations in the residue and washes. In order for solving overlapping absorption spectra of metal chelates, a partial least squares (PLS) regression analysis was adapted.

I. INTRODUCTION

According to the Nuclear Safety and Security Commission (NSSC), concentrations of radionuclides containing 95 % of total radioactivity must be determined. Several radionuclides are the subject of the assessment to classify the very-low, low, and intermediate radioactive waste for disposal. Of these, ⁶⁰Co and ¹³⁷Cs in bulk samples can be easily determined by gamma spectrometry; However, alpha-, beta-, and very-low-energy gamma-emitting radionuclides, such as ⁵⁵Fe, ^{59/63}Ni, ⁹⁰Sr, ⁹⁴Nb and ⁹⁹Tc must be individually separated for radioactivity measurements due to a high self-absorption of alpha particles in the sample matrix and a poor energy resolution of beta spectrometry. Therefore, a separation of the difficult-to-measure (DTM) radionuclides is necessary to provide reliable analytical results. A sequential separation and purification of those radionuclides including precipitation, anion exchange, and extraction chromatography have been developed and adopted for the evaluation of radionuclide inventory in the radioactive waste.^{1,2} Even though the present method shows over 92 % recovery, it is needed to comprehend chemical behaviors of radionuclides during the process for further purification. For this purpose, in this study, we used the simple and rapid spectrophotometric method based on the chelation of Br-PAPS to analyze iron, nickel, and niobium concentrations in the residue and washes, and a PLS regression analysis was performed with the SIMPLS algorithm for multi-component analysis.

II. EXPERIMENTAL

2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-3-sulfopropylamino) phenol (Br-PAPS) (Sigma-Aldrich) was used without additional purification, and Tris-HCl buffer to adjust the pH of the solution. Hydroxylamine hydrochloride was used as a reducing agent to keep the oxidation state of iron as the divalent valence. A non-ionic surfactant Triton X-100 was added to improve the solubility and stability of Br-PAPS and its metal chelates. All aqueous solutions were prepared using deionized water from a Milli-Q system. All absorption spectra were measured with a UV-Vis absorption spectrometer (MCS601 UV-NIR-C, Carl Zeiss,) using a 10 W halogen lamp (CLH600, Carl Zeiss). 1.0 cm quartz cuvette (Hellma) and 100 cm liquid waveguide capillary cell (LWCC-4100, World Precision Instruments) were connected with the spectrometer by an SMA optic fiber with a core diameter of 200 μm or 600 μm. The solvent degassing unit (AG-32, Gastorr) was installed to remove microbubbles generated by dissolved oxygen in the solution, which can lead to interferences in the absorbance. The SIMPLS algorithm using MATLAB (Mathworks) was applied for the PLS regression analysis³.

III. RESULTS AND DISCUSSION

Metal ions can form the 1:2 chelate with Br-PAPS with high molar extinction coefficients on the order of $10^5 \text{ M}^{-1}\text{cm}^{-1}$.¹ Figure 1 shows the absorption spectra of Br-PAPS and its divalent metal chelate with various metal ions. The absorption spectra of the chelates showed distinct double maxima between 500 nm and 600 nm. The maximum wavelength of iron, nickel, and niobium was 554, 557, and 603 nm, respectively, and the molar absorptivities were found to be 75,400, 141,000, and 76,200 $\text{M}^{-1}\text{cm}^{-1}$, respectively. An absorption band at 750 nm was observed for iron, the optical properties being distinguishable from others. Under optimized conditions, the detection limits (signal to noise ratio = 3) for iron, nickel, and niobium were determined as 0.021 ppb, 0.008 ppb, and 0.025 ppb, respectively.

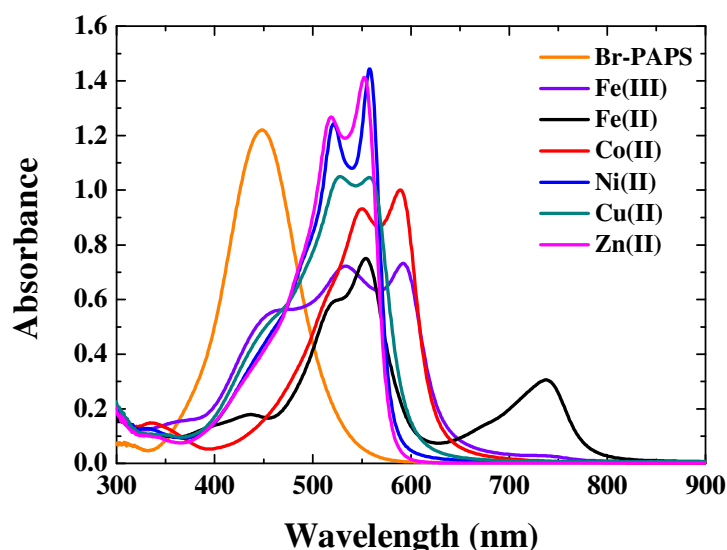


Fig.1. Absorption spectra of Br-PAPS and its divalent metal chelates at 10^{-5} mol/L and 10^{-4} mol/L, respectively.

The PLS regression analysis was used for the simultaneous spectrophotometric determination of metal ions. The difficulty imposed by overlapping the absorption spectra was overcome by the PLS regression analysis. The PLS regression mode was optimized by the predicted residual error sum of squares (PRESS) statistics and the F-statistics⁴. The average relative errors were less than 5 % and the relative errors were, in most cases, no greater than 7 %.

The average recovery of iron, nickel, and niobium was 93.3 ± 1.2 %, 93.3 ± 1.9 %, and 92.6 ± 0.6 %, respectively.¹ The combination of the proposed method was used to measure iron, nickel, and niobium in the residue and washes. The presence of up to 5 % of total metal ion concentration could be detected in the residue and the washes. The results of the proposed method corresponded well with the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

IV. CONCLUSIONS

In the present work, the concentrations of iron, nickel, and niobium in the residual solution were measured by spectrophotometric method based on the chelation of Br-PAPS as well as the PLS regression for the multi-component analysis. In the proposed simple and rapid method, the presence of up to 5 % of the total metal ion concentrations was detectable in the residue and the washes. Further investigations to improve the separation and purity of the recovered metals are underway.

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