Chelating agent separation analysis using a HILIC column

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1. Introduction

According to the Korea Radioactive Waste Agency (KORAD)'s acceptance criteria for low- and intermediate-level radioactive waste, the chemical name and amount of chelating agents in waste must be specified if more than 0.1% is present. The previous method for analyzing chelates in waste was based on UV-Vis spectrophotometry. This method was unable to separate and analyze ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), which have similar chemical properties. For this reason, new methods are required to separate and analyze the chelate agents. In this study, high performance liquid chromatography (HPLC) using a hydrophilic interaction chromatography (HILIC) column was used to analyze the separation of three commonly used chelating agents EDTA, diethylenetriaminepentaacetic acid (DTPA), and NTA in decontamination operations.[1]

2. Methods and Results

2.1 Sample Preparation

If chelating agents are present in the waste, they are expected to form multi-species complexes with many metals. To quantify the chelating agents more reliably, chelates that form complexes with many metals should be substituted with a single metal. We chose Ni-EDTA, Ni-DTPA, and Ni-NTA as our analytes following previous studies that analyzed chelates in waste by forming complexes with Ni.[2] EDTA, DTPA, and NTA were reacted with excess Ni and then filtered through 0.45 μm cellulose acetate filters.

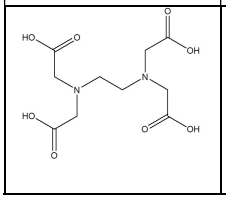
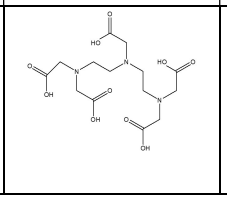
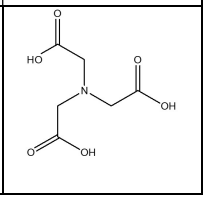
EDTA	DTPA	NTA
		

Table. 1. Chemical structure of EDTA, DTPA and NTA

2.2 HPLC condition

HPLC analyses were performed on a Shimadzu system. HILIC columns were used to analyze the polar compounds Ni-EDTA, Ni-DTPA, and Ni-NTA.[3] The mobile phase was consisted as follows A: 10 mmol L^{-1} ammonium buffer (pH 8.50 adjusted with ammonia solution)/ B: 0.1 mol L^{-1} ammonium buffer:ACN=1:9 (no pH adjustment). Gradient elution was performed at a flow rate of 1.0 mL min^{-1} and column temperature of 50℃ with A:B ratio of 0:100 linearly increasing to 40:60 for 10 min and decreasing 0:100 for 5 min. The injection volume was 10 μL.

2.3 Results and discussion

HPLC determination of 0.38 mM of Ni-EDTA, Ni-DTPA, and Ni-NTA showed three peaks expected to be complexes (Fig. 1.). LC-MS was used for qualitative confirmation of these peaks. The LC-MS results showed that the peaks were identified as m/z 347.00 (^{58}Ni+EDTA-3H)$^-$, m/z 245.95 (^{58}Ni+NTA-3H)$^-$, and m/z 448.05 (^{58}Ni+DTPA-3H)$^-$ from the previous results. The determination of each substance showed an accuracy of 96-109%.

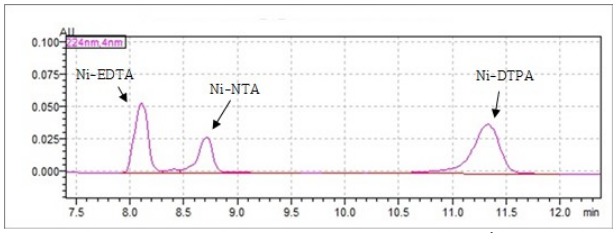


Figure. 1. HPLC measurements of 0.38 mmol L^{-1} Ni-Chelate

When measuring the sample, a high peak appeared early in the analysis (Fig. 2.). It is not clear exactly what this peak is, as the molecular weight was not identified in the mass, but we suspect it is a salt that was in the metal reagent. As the amount of salt increased, the peak at 2 min was stronger than the peak of the complex, suggesting the need to pretreat the sample further to remove it.

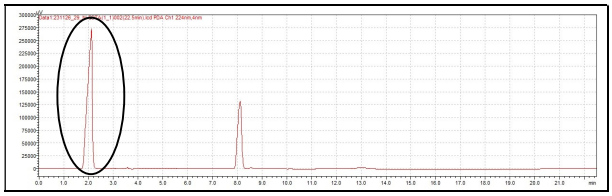


Figure. 2. HPLC measurements of Ni-EDTA (2min high peak)

3. Conclusions

The chelating agents were not separated by conventional methods, but HPLC using a HILIC column separated and analyzed the three chelating agents. However, there is a high peak expected to be a salt at the beginning of the elution, and a method to suppress this peak is needed. Further study will be conducted to suppress this peak and to investigate matrix effects in real samples (e.g. soil, paper, and concreate).

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