Development of novel analytical method of uranyl ions in environmental samples using supercritical CO_2 with fluorogenic sensor

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A novel fluorogenic sensor consisting of crown ether and naphthalimide moieties, called as BPN-DCE, was designed and synthesized for rapid, simple, environmentally-friendly analysis of uranyl ion in environmental samples. The physicochemical properties of BPN-DCE were evaluated by ^{1}H-NMR and fluorescence spectroscopic techniques. Moreover, supercritical CO_2 extraction of uranyl ion from solid matrix and the fluorometric detection were demonstrated.

Keywords: Crown ether, Fluorogenic sensor, Supercritical CO_2, Environmental sample, Uranyl ion

1. Introduction

From the viewpoint of waste management of nuclear facilities, analysis of trace amount of uranium has been required for preventing radiological and toxic chemical risks. In general, uranium analysis process based on solvent extraction and ICP-MS detection was used, but the chemical operations were time-consuming and produced large amount of secondary wastes. Therefore, in this study, we aimed to develop a novel analytical method using supercritical CO_2 ($scCO_2$) with fluorogenic uranyl ion sensor, BPN-DCE, and evaluated their extraction and detection performance.

2. Experimental

BPN-DCE was synthesized by reacting 4-bromo-1,8-naphthal-imide with 4,13-diaza-18-crown-6 ether (see Figure 1). The BPN-DCE was dissolved in acetonitrile and mixed with 10 equivalent concentration of metal (Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, La^{3+}, UO_2^{2+}) perchlorates. After that, ^{1}H-NMR and fluorescence spectra of each sample were recorded. For evaluating the suitability of BPN-DCE on $scCO_2$ extraction of solid matrix, BPN-DCE and 10 equivalent concentration of metal perchlorates were added into a container, and the $scCO_2$ extraction was performed in 35 °C, 25 MPa for 1 hour. The concentrations of the extracted UO_2^{2+} were analyzed by fluorescence intensity changes. In the same way, $scCO_2$ extraction of simulated soil samples was performed.

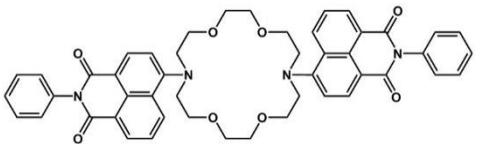

Figure 1 Structure of BPN-DCE

3. Results and Discussions

We found that the addition of UO_2^{2+} into an acetonitrile solution containing BPN-DCE induced not only drastic shift of ^{1}H-NMR peaks of BPN-DCE but also fluorescence quenching. The relationship between the quenching percentages and concentration ratios of UO_2^{2+} and BPN-DCE indicated that the one BPN-DCE coordinated with two UO_2^{2+}. Moreover, the $scCO_2$ extraction and fluorescence detection results showed that sub-μM of UO_2^{2+} could be detected by the combination with BPN-DCE.

4. Conclusion

A novel uranyl ion sensor, BPN-DCE, was successfully synthesized, and the superior extraction and detection abilities for UO_2^{2+} were confirmed. We believe that this sensor will contribute to improve environmental monitoring of uranium.