

## Development of Absorption and Fluorescence Analysis Methods of Lithium Ions in Seawater Using Metallohosts

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### Summary

In recent years, lithium (Li) has attracted much attention as the material used for secondary batteries, and the demand increases rapidly. At present Li is mainly extracted from an ore and salt lake salt water, but seawater is also expected as a future Li extraction source. When taking Li out from the natural salt water such as seawater, it is important to correctly evaluate (or analyze) the concentration of Li. But the analysis is difficult because the concentration of Li is generally much lower than that of sodium (Na). We recently created a new metallohost compound, (3,5-dimethylanisole)ruthenium trinuclear complex ( $[\text{Ru}(\text{DMA})(\text{pyO}_2)]_3$ ), which captures  $\text{Li}^+$  with very high selectivity. In this study, we applied this compound to an extraction - spectrophotometric or fluorescence analysis of  $\text{Li}^+$  and aimed at development of the new sensitive and accurate analytical method for  $\text{Li}^+$  in the natural salt water such as seawater.

When mixing an aqueous solution containing an alkali metal ion ( $\text{M}^+$ ) with a dichloromethane solution of the ligand ( $\text{L} = [\text{Ru}(\text{DMA})(\text{pyO}_2)]_3$ ) in the presence of a hydrophobic anion ( $\text{A}^-$ ),  $\text{M}^+$  is extracted as an ion-pair complex ( $\text{ML}^+\text{A}^-$ ). If using a dye ion or a fluorescent ion as  $\text{A}^-$ , the concentration of  $\text{M}^+$  in the initial aqueous solution can be determined by measuring the light absorption or emission of the organic phase. In this study, three kinds of dye or fluorescent ions were examined as  $\text{A}^-$ . From analysis of the extraction equilibria, the highest  $\text{Li}^+$  extractability and the highest  $\text{Li}^+/\text{Na}^+$  selectivity were observed when using 3',3'',5',5''-tetrabromophenolphthalein ethyl ester ( $\text{TBPE}^-$ ) as  $\text{A}^-$ . In addition, a small amount of  $\text{Na}^+$  co-extracted with  $\text{Li}^+$  could be removed by washing the organic phase with water. Then, the determination of  $\text{Li}^+$  in an aqueous sample was performed by extraction of  $\text{Li}^+$  with  $[\text{Ru}(\text{DMA})(\text{pyO}_2)]_3$  and  $\text{TBPE}^-$ , washing of the organic phase with water, and absorbance measurements of the organic phase. By this method,  $\text{Li}^+$  on the order of  $10^{-5}$  mol/L (ca. 100 ppb) can be determined even if 1000-fold excess of  $\text{Na}^+$  coexists in the sample. However, further improvement is necessary to apply this method to seawater that contains about 20,000-fold excess of  $\text{Na}^+$  over  $\text{Li}^+$ .