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Development of a Simple Method for Determination of Lithium Ions Using Metallohost Compounds

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Summary

In recent years, lithium has attracted much attention as the material used for secondary batteries, and the demand increases rapidly. At present, lithium is mainly extracted from natural saline water such as salt lake, but seawater is also expected as a future extraction source. Relatedly, the determination of lithium in saline water is important. But it is generally difficult because saline water contains high concentration of sodium. We recently synthesized a macrocyclic metallohost, [{Ru(DMA)(pyO_2)}$_3$], which captures Li^+ with high selectivity. In addition, an extraction-spectrophotometric method using this metallohost for the determination of Li^+ in saline water was developed. However, this method has problems that it uses a flammable and harmful organic solvent and that the extraction of Li^+ is very slow. In this study, we prepared a solid-phase extractant by immobilizing the metallohost on a porous polymer resin and aimed at development of a simple and safe method for the separation and determination of Li^+.

A HP2MG resin was added to an EtOH solution of the metallohost, and the solvent was evaporated to prepare the solid-phase extractant. In a centrifuge tube, an aqueous solution of Li picrate (Li[pic]) or Na picrate (Na[pic]) was placed together with the extractant, and the tube was shaken at a constant temperature. The metal ion in the aqueous phase was determined by flame photometry to evaluate the extraction percentage.

When the extraction was conducted at 50 °C, Li^+ was quantitatively extracted by 15 min shaking. The shaking time is much shorter than that required for the solvent extraction of Li^+ with the metallohost and picrate (8 h). On the other hand, the extractability of Na^+ decreased with an increase of the shaking time. From the results, we fixed the extraction temperature of 50 °C and the shaking time of 30 min, which were suitable for quantitative extraction of Li^+ and separation of Li^+ and Na^+. After the extraction, the resin was washed with water and Li^+ was eluted from the resin with MeOH. Applying this method to artificial seawater, the molar concentration ratio of Na^+/Li^+ was decreased from 20,000 in the seawater to 700 in the eluent. By flame photometric analysis of the eluent, the Li^+ concentration in the seawater can be accurately determined.