| | |
|---|---|
| 氏　　名 | ROSI KETRIN KATARINA |
| 授与した学位 | 博　士 |
| 専攻分野の名称 | 理　学 |
| 学位授与番号 | 博甲第３８９７号 |
| 学位授与の日付 | 平成２１年　３月２５日 |
| 学位授与の要件 | 自然科学研究科　機能分子化学専攻<br>（学位規則第５条第１項該当） |
| 学位論文の題目 | Study on Synthesis of Chitosan-Based Chelating Resins and Their Application to Trace Metal Analysis<br>（キトサン基材キレート樹脂の合成とその微量金属分析への応用に関する研究） |
| 論文審査委員 | 教授　本水　昌二　　教授　山本　峻三　　准教授　大島　光子 |

## 学位論文内容の要旨


This study describe the synthesis of novel chitosan-based chelating resins for collection / concentration of trace metals in environmental water samples prior to their measurement by ICP-MS or ICP-AES.

Several amino-series chitosan resins were synthesized and compared. It was obtained that ethylenediamine-type chitosan has the best adsorption for Ag and can be used for the collection / concentration of Ag in water samples and detected by ICP-MS. High adsorption capacity for silver at pH 5, 0.37 mmol $mL^{-1}$ of the resin, was achieved, and $t_{1/2}$ of the adsorption is less than 5 min. The effect of chloride on the collection of silver was examined by varying chloride concentrations from $10^{-4}$ M to 0.75 M; the results showed that the present resin can be used to the collection / concentration of ultratrace amounts of silver in natural waters, as well as seawater. The developed method using the resin gives 0.7 pg $mL^{-1}$ of the detection limit when 50-fold enrichment was used. The proposed method was successfully applied to the determination of silver in tap, river, and seawater samples.

Among the aminocarboxylate-series chitosan resins that were synthesized, it was obtained that ethylenediamine N,N,N'-triacetate-type chitosan (EDTriA-type chitosan) and N-(2-hydroxyethyl) glycine-type chitosan are the best resins for adsorption of a number metal ions. Both resins showed very good adsorption for transition and rare-earth metals. The resin did not adsorb both of alkali and alkaline-earth metals in an acidic media. The EDTriA-type chitosan was used for the simultaneous determination of trace metals in seawater samples by ICP-MS. The method was evaluated by the analysis of NASS-5 seawater reference materials for trace metals. Good agreement was obtained for most metals, which indicates that by the proposed pretreatment using the synthesized resin, seawater samples can be favorably measured by ICP-MS.

Several automated on-line sample preparation systems (Auto-Pret AES system) coupled with ICP-AES were developed. The performance of the systems were examined using a commercially iminodiacetate chelating resin, Muromac A-1. The Auto-Pret AES system was successfully applied for determining trace metals, including such toxic metals as Be, Cd, Cr, Cu and Pb. The enrichment factors for metal ions were about 19 times, when 5 mL of samples were used. The sample throughput was 11 $h^{-1}$. A Multi-Auto-Pret AES system that consists of triply-synchronized Auto-Pret system, one more selection valve and a switching valve was developed for the rapid determination of trace metals in water samples. The Multi-Auto-Pret AES system proposed here consists of 3 mini-columns that can be used for the preconcentration of trace metals sequentially, and can reduce analysis time and running cost of argon gas and labor. Under the optimum conditions, the repeatability in the same mini-column and the different mini-columns gave similar results, in which were less than 10% the relative standard deviations (RSD). When 5 mL of sample solution was used, the sample throughput was about 30 $h^{-1}$. The proposed system was very useful for analyzing a number of samples and applied to the rapid determination of 11 trace metals in river water samples.

The Multi-Auto-Pret system using EDTriA-type chitosan and N-(2-hydroxyethyl) glycine-type chitosan were applied for the collection / concentration of transition and rare-earth metals prior to their measurement by ICP-AES. Only 5 mL of samples could be used for the determination of transition metals, while 20 mL of samples was necessary for the determination of rare-earth metals. The proposed method was evaluated by the analysis of SLRS-4 river water reference materials for trace metals. Good agreement with certified and reference values was obtained for most of the metals examined; it indicates that the proposed method using the synthesized resins could be favorably used for the determination of transition and rare-earth metals in water samples by ICP-AES.

## 論文審査結果の要旨

This study describes the synthesis of novel chitosan-based chelating resins for collection / concentration of trace metals in environmental water samples prior to their measurement by ICP-MS or ICP-AES.

Several amino-series chitosan resins were synthesized and compared. It was obtained that ethylenediamine-type chitosan has the best adsorption for Ag and can be used for the collection / concentration of Ag in water samples and detected by ICP-MS. High adsorption capacity for silver at pH 5, 0.37 mmol $mL^{-1}$ of the resin, was achieved, and $t_{1/2}$ of the adsorption is less than 5 min. Among the aminocarboxylate-series chitosan resins that were synthesized, it was obtained that ethylenediamine N,N,N'-triacetate-type chitosan (EDTriA-type chitosan) and N-(2-hydroxyethyl)glycine-type chitosan are the best resins for adsorption of a number metal ions. Both resins showed very good adsorption for transition and rare-earth metals. To increase chelating sites of the N-(2-hydroxyethyl)glycine-type chitosan resin, EGDE as a cross-linker was replaced with CMO. It can increase the adsorption capacity to about 40 % per g resin, compared to that with EGDE, and can decrease the synthesis process.The EDTriA-type chitosan was used for the simultaneous determination of trace metals in seawater samples by ICP-MS. The method was evaluated by the analysis of NASS-5 seawater reference materials for trace metals. Good agreement results were obtained for most metals, which indicate that by the proposed pretreatment using the synthesized resin, seawater samples can be favorably measured by ICP-MS.

Automated on-line sample preparation systems (Auto-Pret AES system) and Multi-Auto-Pret AES system coupled with ICP-AES were developed. The Auto-Pret AES system was successfully applied for determining trace metals, including such toxic metals as Be, Cd, Cr, Cu and Pb. The Multi-Auto-Pret AES system that consists of triply-synchronized Auto-Pret system, one more selection valve and a switching valve was developed for the rapid determination of trace metals in water samples. Since it consists of three mini-columns that can be used for the preconcentration of trace metals sequentially, it can reduce analysis time to one-third and running cost of argon gas and labor. Under the optimum conditions, the repeatability in the same mini-column and the different mini-columns gave similar results, in which were less than 10% the relative standard deviations (RSD). The Multi-Auto-Pret system using EDTriA-type chitosan and N-(2-hydroxyethyl)glycine-type chitosan were applied for the collection / concentration of transition and rare-earth metals prior to their measurement by ICP-AES. Only 5 mL of sample could be used for the determination of transition metals, while 20 mL of sample was necessary for the determination of rare-earth metals. The proposed method was evaluated by the analysis of SLRS-4 river water reference materials for trace metals. Good agreement with certified and reference values was obtained for most of the metals examined; it indicates that the proposed method using the synthesized resins could be favorably applied to the determination of transition and rare-earth metals in water samples by ICP-AES.

As the result of the evaluation of the thesis and the oral presentation, the thesis submitted to the committee was decided to be worthy of a doctoral thesis (Doctor of Philosophy in Science).