

氏名 大 下 浩 司

授与した学位 博 士

専攻分野の名称 理 学

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学位授与の要件 自然科学研究科物質分子科学専攻

(学位規則第4条第1項該当)

学位論文の題目 Synthesis of Novel Solid Materials for Separation of Metals by Derivatizing Biomass
with Functional Moieties and Their Application to Analytical Chemistry
(官能基群を用いたバイオマスの誘導体化による金属分離のための
固体材料の合成とその分析化学的応用)

論文審査委員 教授 本水 昌二 教授 山本 啓司 教授 山本 峻三

学 位 論 文 内 容 の 要 旨

The concept and the principle of “Advanced Material Science” are of great importance in scientific fields and social fields. In an analytical chemistry field, “Advanced Material Science” which incorporates “Separation”, “Collection” and “Concentration”, has an important role in environmental, material, food and life sciences. By further extension, the “Advanced Material Science” can be applied to solve a number of problems in industry, medicine and environment.

In this work, the author's strategy was to apply the principle/ concept based on “Separation”, “Collection” and “Concentration” to develop novel solid materials. In order to accomplish the strategy, new solid materials were developed by using the chitosan as a base material. At the first step of this work, cross-linked chitosan was synthesized with ethylene glycol diglycidyl ether (EGDE). The cross-linked chitosan was then used for the development of the chelating resins. The cross-linked chitosan could adsorb anionic species, especially chloride complexes of Hg, Pd, Pt, Au. The resin could remove Hg existing as an impurity in concentrated hydrochloric acid. Therefore, the cross-linked chitosan developed is an effective material for removal of such an impurity. In order to develop specific chelating resins, the cross-linked chitosan was further chemically modified. In the analysis of trace elements in sea water, alkali and alkaline earth elements at high concentration levels interfere the trace analysis. Therefore, chelating resins are necessary for the elimination of alkali and alkaline earth elements. The synthesized chelating resin possessing iminodiacetate (IDA) group, HP/IDA-type chitosan, can adsorb almost 30 elements, whereas the resin can eliminate the alkali and alkaline earth elements. In general, the separation of rare earth elements is very difficult. To achieve their separation, IDP-type chitosan possessing iminodiphosphonate (IDP) group was developed. Rare earth elements could be separated using a column treatment packed with it. In addition, another series of more specific chelating resins were developed with amino acid, such as glycine, leucine, valine and serine. Amino acids are capable of forming chelates with some metals. By introducing the amino acid with steric hindrance, the selectivity of the metal collection on resin will be improved. The effect of steric hindrance of the functional group contained in such amino acids on metal collection was clarified by comparing with the adsorption behavior of metal ions on the developed resins. These specific resins were found to be suitable for the following metal collections: (1) the glycine-type chitosan, for Bi; (2) the leucine-type chitosan, for Mo; (3) the serine-type chitosan, for U. These resins can be used effectively for the collection/ concentration of such metal in sea water and river water. And these chelating resins could eliminate the matrix elements, such as alkali and alkaline earth metals. As the initial stage of the resin development, complex formation of calixarenes was examined by capillary zone electrophoresis. Since calixarenes can associate alkali metals and quaternary ammonium ions, the resin possessing calixarene has potential of improving separation of cationic species, such as optical isomers of amino acids, which has so far been difficult. The author developed some specific resin materials. The development of novel solid materials, such as chelating and ion exchange resins, was performed on the basis of “Advanced Material Science” concept. The developed resins have been used successfully in scientific and non-scientific fields (social field).

論文審査結果の要旨

The concept and the principle of “Advanced Material Science” are of great importance in an analytical chemistry field. “Advanced Material Science” which incorporates “Separation”, “Collection” and “Concentration”, has an important role in environmental, material, food and life sciences.

In this work, the author's strategy is to apply the principle/ concept based on “Separation”, “Collection” and “Concentration” to develop novel materials. In order to accomplish the strategy, new solid materials are developed by using the chitosan as a base material. The cross-linked chitosan (CL-CS) is synthesized with ethylene glycol diglycidyl ether (EGDE). The CL-CS is used for the development of the chelating resins. The CL-CS can adsorb chloride complexes of Hg, Pd, Pt, Au. The resin can remove Hg existing as an impurity in concentrated hydrochloric acid. To develop specific chelating resins, the CL-CS is further chemically modified. In the analysis of trace elements in sea water, matrix elements, such as alkali and alkaline earth elements, interfere the trace analysis. Therefore, chelating resins are necessary for the elimination of matrix elements. The HP/IDA-type chitosan possessing iminodiacetate (IDA) group and long spacer arm can adsorb almost 30 elements, whereas the resin can eliminate matrix elements. In general, the separation of rare earth elements (REEs) is very difficult. To achieve their separation, IDP-type chitosan possessing iminodiphosphonate (IDP) group was developed. REEs can be separated using a column treatment packed with it. In addition, another series of more specific chelating resins are developed with amino acid, such as glycine, leucine and serine. By introducing the amino acid, the selectivity of the metal collection is improved. These specific resins are found to be suitable for the following metal collections: (1) the glycine-type chitosan, for Bi; (2) the leucine-type chitosan, for Mo; (3) the serine-type chitosan, for U. These resins can be used effectively for the collection/concentration of such metal in sea water and river water. And these chelating resins can eliminate the matrix elements. Complex formation of calixarenes is also examined by capillary zone electrophoresis. Since calixarenes can associate alkali metals and quaternary ammonium ions, the resin possessing calixarene has potential of improving separation of cationic species, such as optical isomers of amino acids. The author develops some specific resin materials. The development of novel materials, such as chelating and ion exchange resins, is performed on the basis of “Advanced Material Science” concept.

In view of original contents and results obtained in this study, the committee evaluated this dissertation as doctor degree's worth of research.