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学位論文の題目	Studies on Novel Collection/Concentration Resins for Trace Elements Using Chitosan as Polymer Base and Their Analytical Applications （キトサンをポリマー基材とする微量元素の濃縮／捕集用樹脂及びその分析的応用に関する研究）
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学位論文内容の要旨

The study describes the development of novel chelating resins using chitosan as polymer base and their applications in the analytical chemistry field, especially to the collection/concentration of trace elements in environmental water samples by batchwise and automated on-line column methods.

Some functional moieties, containing nitrogen and oxygen groups existing in aliphatic and aromatic ring chelating agents, were chemically attached to cross-linked chitosan (CCTS).

The moiety of N-methyl-D-glucamine attached to cross-linked chitosan (CCTS-NMDG resin) has excellent ability and selectivity for the adsorption of boron in aqueous samples even in the presence of high matrix concentrations.The CCTS-NMDG resin provides some advantages, such as faster sorption kinetics and higher adsorption capacity of boron than any other commercial boron resins. A di-2-propanolamine functionalized to cross-linked chitosan (CCTS-DPA resin) exhibits excellent ability for the adsorption of germanium at pH 5 to 9. The resin can successfully remove chloride, selenium and other matrices that can interfere with the direct determination of germanium by ICP-MS, which result in accurate determination of germanium in environmental water samples.

The moiety of 3,4-diamino benzoic acid introduced to cross-linked chitosan (CCTS-DBA resin) showed a great ability for the adsorption of arsenic (V) and selenium (IV) and selenium (VI). Therefore, this resin is very useful for removal as well as the speciation of toxic elements in water system, which is becoming one of the most interesting research topics in environmental analysis. Chitosan resin functionalized with 4-amino-3-nitro benzoic acid (CCTS-NABA resin) gave excellent adsorption for molybdate. The adsorption capacity of the resin for Mo (VI) was found to be 380 mg g^{-1} at pH 4, which is much higher than other molybdenum resins reported so far. The moiety of 3,4-dihyroxy benzoic acid moiety attached to amino group of chitosan (CCTS-DHBA resin) was applied to collection/concentration and determination of uranium in water samples. Further application of CCTS-DHBA resin was demonstrated by packing the resin in mini-column, and was installed to flow injection system to allow on-line collection/concentration of copper, nickel, silver, bismuth, gallium, uranium, indium, and molybdenum. The moiety of 2-amino-5-hydroxy benzoic acid attached to cross-linked chitosan (CCTS-AHBA), which was packed in a mini-column and installed into a laboratory-assembled automated pretreatment system (Auto-Pret System), offers excellent collection efficiency for on-line determination of Ag, Be, Cd, Co, Cu, Ni, Pb, U, V, and rare earth elements (REEs) by inductively coupled plasma-atomic emission spectrometry. The cross-linked chitosan functionalized with 3,4,5-trihydroxy benzoic acid (CCTS-THBA) and 4-hydroxy phthalic acid (CCTS-HPA) has great ability for the adsorption of chromium (VI), which is very toxic and carcinogenic. Furthermore the resin could be applied to the speciation of chromium in environmental water samples. In addition, the alkali and alkaline earth matrices in environmental samples, which can cause interferences to direct determination of trace elements by analytical instrumentations, could be removed completely by the recent developed resins. Selective resin for lead, Analig Pb-01, was packed in a mini-column and coupled with Auto-Pret System to allow determination of trace amounts of lead in water sample by ICP-AES. Excellent sensitivity and selectivity for lead were achieved.

論文審査結果の要旨

This thesis aims at developing novel collection/concentration resins for trace metals and non-metals, and their application to trace analysis. Several novel resins using chitosan as a base material have been synthesized and examined. Their applications to analytical chemistry were exploited by using batchwise and automated on-line column pretreatment methods. Further, the speciation of toxic elements, such as arsenic, selenium, and chromium, using the chitosan-based chelating resins developed in this research were also established.

A chelating resin consists of two components, such as chelating moiety and the polymeric base material. In this work, chitosan, which is cross-linked with ethyleneglycoldiglycidylether, was selected as a base material due to its typical properties, such as (1) easy derivatization of its amino group, (2) hydrophilic character, (3) high porosity, and (4) safety to living organism and human. The functional moieties studied mainly contain two types; aliphatic chains and aromatic rings chelating agents. An aliphatic chains chelating moiety, which is more flexible than aromatic rings, tends to accept several binding partners. Although sacrificing selectivity, it has the advantage of transmitting conformational information. The aromatic structures of the functional moieties used in this study are due to their ability to restrict conformation of flexibility, which may result in selective adsorption of the chelating resins toward target elements.

The aliphatic chain chelating moieties of N-methyl-D-glucamine (NMDG), and di-2-propanolamine (DPA) were chemically immobilized to the cross-linked chitosan (CCTS) through the arm of chloromethyloxirane. Furthermore, chitosan resins, which contain aromatic rings, were systematically synthesized. The moieties of 3,4-diamino benzoic acid (DBA), 4-amino-3-nitro benzoic acid (NABA), 3,4-dihyroxy benzoic acid (DHBA), and 3,4,5-trihydroxy benzoic acid (THBA), were chemically attached to CCTS through the amide bond formation, whereas 2-amino-5-hydroxy benzoic acid (AHBA) and 4-hydroxy phthalic acid (HPA) were chemically bonded to CCTS through the arm of chloromethyloxirane.

A functional moiety of N-methyl-D-glucamine moiety attached to the cross-linked chitosan (CCTS-NMDG resin) showed excellent ability and selectivity for the adsorption of boron. Boron as boric acid can form a complex with poly-ol groups (in NMDG moiety. The CCTS-NMDG resin provides some advantages, such as faster sorption kinetics and higher adsorption capacity of boron than any other commercial boron resins. The resin was applied to the collection and preconcentration of boron in tap, river, estuarine and ground waters prior to their measurement by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The present thesis can greatly contribute to improve the trace and ultratrace analysis for metals and non-metals, and to create a new frontier of the solid-phase separation chemistry in analytical science. In view of original contents and creative results obtained in this research, the committee evaluated this dissertation as PhD degree's worth of research.