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Synthesis of novel chitosan resin derivatized with serine diacetic acid moiety and its application to on-line collection/concentration of trace elements and their determination using inductively coupled plasma-atomic emission spectrometry

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Abstract

A novel chelating resin functionalized with serine diacetic acid moiety was synthesized by using chitosan as base material, and applied to the collection/concentration of trace elements in environmental water samples, followed by the determination using inductively coupled plasma-atomic emission spectrometer (ICP-AES). The synthesized resin, crosslinked chitosan serine diacetic acid (CCTS-SDA), showed good adsorption behavior toward trace amounts of Cd, Pb, Cu, Ni, V, Ga, Sc, In, and Th in a wide pH range. Additionally, rare earth elements also can be retained on the resin at neutral pH region. The adsorbed elements can be easily eluted with $1 \, mol \, L^{-1}$ of nitric acid, and their recoveries were found to be 90–100%. The CCTS-SDA was packed in a mini-column, which was then installed in a computer-controlled auto-pretreatment system (Auto-Pret System) for on-line trace elements collection and determination with ICP-AES. Experimental parameters which related to the improvement of sensitivity and reproducibility were optimized. The limits of detection (LOD) for 13 elements were found to be in sub-ppb level. The proposed method with CCTS-SDA resin was successfully applied to the determination of trace elements in river water samples. The method was validated by determining a certified reference material of river water, SLRS-4.
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1. Introduction

Heavy metal ions in natural water can bring harmful effect to human health, as well as to animals and plants in aquatic environment. Therefore, monitoring these metals in environmental water samples at trace levels is very important. Accurate analysis of various complex samples containing elements at trace levels is one of the most challenging analytical tasks. Despite the rapid development of instrumentation which opens new path to trace analysis, accurate quantitative determination of a number of elements is still impaired to a greater or lesser extent by matrix and spectral interferences [1]. Moreover, some analytical techniques, such as flame atomic absorption spectrometry

and inductively coupled plasma-atomic emission spectrometry, do not have enough sensitivity to directly determine certain elements in a relative clean environmental water sample, and thus a preconcentration step is required before applying them to trace metal analysis.

In recent years, the importance of separation and concentration technique involving chelating sorbent in trace analysis has risen substantially. The pretreatment of aqueous solution by sorption technique not only can increase analyte concentration to detectable level, but also can eliminate matrix effects [2].

Several materials have been proposed as a sorbent for the collection/concentration of trace elements using solid phase extraction technique, such as activated carbon [3–5], Amberlite XAD [6–12], Diaion [13], Chromosorb [14], silica [1], and alumina [15]. Activated carbon may provide economical advantage. However, physical loading of a complexing agent on activated carbon suggested that such sorbent may have

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less durability due to the loss of complexing agent during sorption–desorption processes. The addition of a complexing agent to each sample prior to column treatment is considered to be disadvantageous due to high reagent consumption and more organic waste will be generated [3]. The utilization of *p*-dimethylamino-benzaldehyde-modified nanometer SiO_2 prior to inductively coupled plasma-atomic emission spectrometer (ICP-AES) measurement allows simultaneous determination of trace amount of Cu(II) and Pb(II) [1]; the detection limit indicates that the sensitivity of this method is not sufficient to measure Cu(II) and Pb(II) in relatively clean environmental water. The preconcentration method using Chromosorb-103 [13] provided a better detection limit for Pb(II). However, sample pretreatment by using 8-hydroxyquinoline is required before the preconcentration procedure can be carried out.

Though the pretreatment method which utilize a sorbent mentioned above can improve sensitivity in trace metal analysis, the operation of pretreatment step is usually tedious and time consuming because it must be carried out by manual batch-wise procedure, where stringent control of the laboratory environment is required to avoid sample contamination, especially if the determination of trace level of analytes is attempted. Such drawback can be overcome by utilizing an automated on-line preconcentration procedure, where less contamination and less reagent consumption can be done [15–19].

Chitosan, an *N*-deacetylated product of chitin which can be obtained in large quantity from crustacean shells, has become an important natural polymer because of its unique properties, such as higher chelating ability compared with other natural polymers obtained from seafood-industries waste, easy derivatization, and biodegradability [20]. The reactive amino group in chitosan can provide easy derivatization of this material with some chelating moiety for wider application in solid phase extraction. Compared with other synthetic polymers, chitosan possesses higher hydrophilicity thus providing faster adsorption rate in aqueous medium.

Several researchers have reported the synthesis of cross-linked chitosan to improve its chemical durability against acid medium along with its application [21–25]. Cross-linked chitosan itself has been derivatized with several functional groups, and has been applied to solid phase extraction techniques; For example, cross-linked chitosan derivatized with serine moiety for U collection [26], leucine moiety for Mo collection [27], dithiocarbamate [28] and iminodi(methylphosponic acid) [29] moieties for trace elements collection, *N*-methyl-D-glucamine moiety for B collection [30], 3,4-diaminobenzoic acid moiety for As and Se collection [31], and ethylenediamine moiety for Ag collection [32].

In this work, cross-linked chitosan (CCTS) was chemically functionalized with serine diacetic acid moiety through the extension arm of chloromethyloxirane. The synthesized resin was then packed in a mini-column, and the mini-column was installed in a laboratory-assembled auto-pretreatment system (Auto-Pret AES System) coupled with inductively coupled plasma-atomic emission spectrometer for the collection/concentration and determination of 13 trace elements. Experimental variables of the system and pretreatment proce-

dure, which are related to the improvement of sensitivity and reproducibility, have been optimized. The proposed method provides effective automated on-line preconcentration with high sensitivity (ppt level for several analytes), good reproducibility, less reagent consumption, less waste, and less time-consuming.

2. Experimental

2.1. Instruments

The adsorption behavior of cross-linked chitosan functionalized with serine diacetic acid (CCTS-SDA) resin toward various trace elements was examined by inductively coupled plasma mass spectrometer SPQ8000H System Seiko Instruments (Chiba, Japan). Infrared spectra (4000–400 cm^{-1}) were recorded on Jasco FT/IR-4100 Jasco International Co. Ltd. (Tokyo, Japan). A modular digital syringe pump Cavro (San Jose, CA, USA), a selection valve and a switching valve Hamilton (Reno, NV, USA) were used as a part of Auto-Pret AES system. This Auto-pret AES system was coupled with ICP-AES Vista-pro Seiko Instruments (Chiba, Japan). The operating condition of ICP-AES is shown in Table 1.

2.2. Reagents

Flake type chitosan with 80% deacetylation degree was purchased from Tokyo Kasei Co. Ltd. (Tokyo, Japan). All other reagents used for the synthesis of CCTS-SDA resin were of analytical reagent grade.

Multi-element standard solutions were prepared from several kinds of single element standard solution for atomic absorption (1000 μg mL^{-1}) purchased from Wako Pure Chemicals (Osaka, Japan). Two multi-element stock solutions for ICP-MS, XSTC-13 and XSTC-1 provided by Spex CertiPrep Inc. (Metuchen, NJ, USA) were mixed with the single element solutions to give a multi-element standard solution containing 63 elements. The XSTC-13 contains 10 μg mL^{-1} of 31 elements, namely Th, Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, TL, V, Zn, U, and Hg, and XSTC-1 contains 10 μg mL^{-1} of 16 elements, namely Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y. The

Table 1
Operating conditions of ICP-AES

Spectrometer	VISTA PRO
Plasma conditions	
RF power	40 MHz, 1.2 kW
Plasma gas flow rate (L min^{-1})	Ar 15.0
Auxiliary gas flow rate (L min^{-1})	Ar 1.50
Nebulizer gas flow rate (L min^{-1})	Ar 0.75
Spray chamber	Glass cyclonic spray chamber
Nebulizer	K-style concentric glass nebulizer
Torch	One-piece low flow extended torch in the axial view mode
Data acquisition	
Measurement mode	Time scan mode