

# Synthesis of a chitosan-based chelating resin and its application to the selective concentration and ultratrace determination of silver in environmental water samples

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## Abstract

A novel chelating resin using chitosan as a base material, ethylenediamine-type chitosan, has been synthesized for the first time in the present study, and applied to the collection/concentration of ultratrace amounts of silver in environmental water samples. In the present study, ultratrace amounts of silver collected on the resin were eluted and determined by ICP-MS. The resin packed in a 1 mL mini column could adsorb silver selectively and quantitatively at a flow rate of  $2 \text{ mL min}^{-1}$  in the wide pH range from 1 to 8, and silver adsorbed on the resin could be easily recovered by passing 1 M nitric acid as an eluent into the column. High adsorption capacity for silver at pH 5,  $0.37 \text{ mmol mL}^{-1}$  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  $10^{-4}$  to 0.75 M; the results showed that the present resin can be used for the collection/concentration of ultratrace amounts of silver in natural waters, as well as seawater. To ensure the accuracy and the precision of the method, CASS-4 near shore seawater reference material from the NRCC has been analyzed. This is not a certified SRM for silver, but has been used for comparative silver analysis by several groups, who report very similar results to those that are reported here. The developed method using ethylenediamine-type chitosan resin gives  $0.7 \text{ pg mL}^{-1}$  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.

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## 1. Introduction

Determination of ultratrace elements in various complex samples has a lot of limitations because of high concentrations of sample matrix and very low concentrations of target analytes [1]. Although inductively coupled plasma mass spectrometry provides high sensitivity and selectivity for the determination of trace elements, direct analysis of samples containing highly concentrated matrices (e.g. seawater) is not recommended because highly dissolved solid elements in the samples can block the cones and deposit on ion lenses over a prolonged analysis run, which causes signal changes and hence degrades signal stability, and a mass detector can be damaged owing to high concentrations of ions. Matrix in samples also can cause polyatomic

interferences, isobaric interference with the determination of target analytes, which can give erroneous analytical results. Therefore, some pretreatment procedures for chemical separation and concentration are requisite.

In recent years, syntheses and analytical applications of chelating resins have studied widely for the collection and the concentration of trace and ultratrace amounts of elements in various samples.

Chitosan is an amino polysaccharide obtained by deacetylating of chitin. The main characteristics of chitosan are hydrophilicity, harmlessness for living things and biodegradability, easy chemical derivatization, and capability to adsorb a number of metal ions. Therefore chitosan seems to be very interesting starting material for chelating resins.

Silver is an important element that is widely used for human life. Because of its bacteriostatic properties, silver compounds are often used in filters and other equipments to purify water of swimming pool and drinking water, and used in the processing

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of foods, drugs, and beverages. In many countries, silver-impregnated filters are used for drinking water preparation [2].

In the past decade, the interest in measuring trace and ultratrace amounts of silver in natural waters has increased due to concerns over its toxicity to aquatic organisms. The biological purpose of silver found in the body of mammals has been unknown, while silver is suspected of being a contaminant. In mammals, silver usually interacts competitively with essential nutrients, especially with selenium, copper, Vitamin E, Vitamin B12 [2]. Soluble silver salts are in general more toxic than insoluble salts. In natural waters, the soluble monovalent species is in the form of environment concern and is controlled by the concentration of free silver ion ( $\text{Ag}^+$ ) and other silver complexes of chloride ion [2,3].

Silver is usually found at extremely low concentrations in natural waters because of its low crustal abundance and low mobility in water. It is obvious that for monitoring silver concentrations in natural waters to study silver toxicity effect on bio-organism in oceanographic research and survey work, highly sensitive and selective methods for silver determination are required.

Currently, some researches for the determination of silver in water have been reported; they propose some preconcentration procedures, including solid phase extraction (SPE) [4,5,9–17]. Solvent extraction is more familiar than SPE to separate and determine Ag in seawater samples: most of these methods used ammonium pyrrolidine dithiocarbamate–diethylammonium diethyldithiocarbamate (APDC–DDDC) as an extractant [6–8].

The SPE methods for the enrichment pretreatment of silver employed chelating resins with sulfur as a coordinating group [9–14]. Generally, the resins with sulfur as a coordinating site are highly selective for noble metals, such as Hg, Ag and Au. Sulfur can make strong coordination with silver, because sulfur has ‘soft’ coordination site that possesses great affinity toward ‘soft’ cations such as silver [18]. However, thiosulfate or thiourea must be used for the desorption of silver from the resins. Other resins that contain no sulfur in functional groups are usually not selective for silver, which means that other elements can be also adsorbed on the resins [15–17]. One of the advantages of the resins having no sulfur in the functional groups is the easiness of silver elution with acid solutions. A colorimetric method coupled with SPE method was found to be selective for silver determination. The method, however, showed a poor detection limit [19,20].

Chelating resins with N-coordination sites, such as ethylenediamine, diethylenetriamine and EDTA, are highly specific for transition metal ions. Of these, ethylenediamine is a bidentate ligand that can coordinate silver ions through two nitrogen atoms: presumably it is more selective for silver ion than diethylenetriamine and EDTA.

There are some papers concerning about the use of ethylenediamine resin for preconcentration of trace elements. Cobianto et al. reported the polystyrene-divinylbenzene modified with ethylenediamine [21], Atia et al. prepared glycidyl methacrylate treatment with ethylenediamine [22], Tikhomirova et al. modified silica with ethylenediamine [23], while Syamal et al. used ethylenediamine to prepare polystyrene bound salen resin [24].

All of these resins were used for copper separation or other elements, except for silver. Leyden and Luttrell reported the chelating properties of ethylenediamine bound silica for preconcentration of Hg(II), Cu(II), Zn(II), Mn(II), and Ag(I) from perchlorate samples [25]. However there has not been any publication for the ethylenediamine chitosan resin, especially for collection and preconcentration of silver.

The purpose of this work is to develop a novel chelating resins for silver ion using chitosan as a base material and to determine ultratrace amounts of silver by ICP-MS coupled with the method for the selective collection/concentration of ultratrace amounts of silver in environmental water samples with the synthesized chitosan resin.

## 2. Experimental

### 2.1. Instruments

All measurements were carried out by an ICP-MS, a Model SPQ8000H System (Seiko Instruments Co., Tokyo, Japan). The operating conditions are listed in Table 1. An automatic potentiometric titration system was used for the acid base titration (Model AT-510, Kyoto Electronics Manufacturing, Co. Ltd., Japan). Infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded on a Jasco FT/IR-4100 (Jasco International Co. Ltd., Japan).

### 2.2. Reagents and solutions

The chitosan used in this work was a flake type (Tokyo Kasei Co. Ltd., Tokyo, Japan), and its deacetylated degree was about 80%. All other reagents used for the synthesis of ethylenediamine-type chitosan resin were of analytical reagent grade.

A multielement stock standard solution (58 elements,  $1\text{ }\mu\text{g mL}^{-1}$ ) was prepared by diluting an analytical multielement standard solution, which contains  $10\text{ }\mu\text{g mL}^{-1}$  of metal ions, such as Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi, T, and U (XSTC-13, Spex CertiPrep Inc.), an analytical multielement standard solution containing  $10\text{ }\mu\text{g mL}^{-1}$  of metal ions of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y (XSTC-1, Spex CertiPrep Inc.), and standard

Table 1  
The ICP-MS operating conditions

ICP-MS	Model Seiko SPQ8000 H quadrupole type
Plasma condition	
Forward power	1.1 kW
Reflected power	<5 W
Plasma gas	Ar $15\text{ L min}^{-1}$
Carrier gas	Ar $0.45\text{ L min}^{-1}$
Auxiliary gas	Ar $0.50\text{ L min}^{-1}$
Sample uptake rate	$1.0\text{ mL min}^{-1}$
Interface condition	
Sampling depth	10 mm from load coil
Sampling cone	Copper 1.1 mm i.d.
Skimmer cone	Copper 0.35 mm i.d.

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