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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 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 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 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 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.
Keyword: chelating resin, chitosan, determination of silver, environmental water samples, ICP-MS.

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 blockade the cones and deposit on ion lenses over a prolonged analysis run, which causes signal changes and hence degrade 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 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 (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 dithiocarbate – diethylammmonium 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. S. Cobianto *et al.* reported the polystryrene-divinylbenzene modified with ethylenediamine [21], A. A. Atia *et al.* prepared glycidyl methacrylate treatment with ethylenediamine [22], T. I. Tikhomirova *et al.* modified silica with ethylenediamine [23], while A. 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. D. E. Leyden *et al.* 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

Experimental

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 (4000-400 cm^{-1}) were recorded on a Jasco FT/IR-4100 (Jasco International Co. Ltd., Japan).

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 μg mL^{-1}) was prepared by diluting an analytical multielement standard solution, which contains 10 μg 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 μg 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 solutions for single element (1000 μg mL^{-1}) for AAS (Wako Pure Chemicals, Osaka, Japan) of Zr, Pd, Sn, Sb, Te, Hf, Au, Ge, Mo, W in 0.1 M of nitric acid solution. Working standard solutions were prepared by diluting the stock standard solution with nitric acid just before

column pretreatment, followed by an ICP-MS measurement. Accurate dilution of the standard solutions was carried out by weighing required amounts of the stock standard solutions and mixing them with water. Ultrapure grade nitric acid (60%, density 1.38 g mL^{-1}, Kanto Chemicals, Tokyo, Japan) was used and diluted with an ultrapure water to give a 0.1 M, a 1 M or a 2 M solution.

An internal standard solution was prepared by diluting a rhodium standard solution for AAS (Wako Pure Chemicals, Osaka, Japan) in 1 M nitric acid. This solution was added to blank, calibration standard solutions, and samples for correcting matrix effect [26, 27].

A stock solution of 4 M ammonium acetate buffer solution was prepared by mixing appropriate amounts of acetic acid (96%) and ammonia solution (29%). Both the acetic acid and the ammonia solution were of electronic industrial reagent grade (Kanto Chemicals, Tokyo, Japan). The buffer solution of 0.5 M ammonium acetate was prepared by diluting 4 M ammonium acetate stock standard solution and adjusting the pH with small amounts of ammonia or acetic acid.

The ultrapure water (18.3 MΩ cm^{-1} resistivity) was prepared by an Elix-3/ Milli-Q element system (Nihon Millipore, Tokyo, Japan).

All of sample solutions were acidified to pH 1 by adding nitric acid for storing, and the pH of the sample solutions was adjusted to 5 just before the column pretreatment by adding small amounts of ammonia solution.

CASS-4 near shore seawater reference material was purchased from Chemical Metrology, Institute for National Measurement Standards, National Research Council of Canada (Ottawa, Ontario, Canada).

Procedure

Synthesis of ethylenediamine-type chitosan resin

An ethylenediamine-type chitosan resin was synthesized in 2 steps, as shown in Fig. 1. In Step 1, the cross-linked chitosan having free amino groups was synthesized according to the previous work [28]. In Step 2, the cross-linked chitosan possessing ethylenediamine was synthesized by the following procedure. Five grams of cross-linked chitosan was suspended in 100 mL of the mixture of water – ethanol (1:1), and then 10 g of chloromethyloxirane was added to the suspension. The mixture was refluxed for 3 hours, and then cooled. The solid product was filtered on a filter paper, and then washed each three times with ethanol and water to remove chloromethyloxyrane remaining. The solid product was suspended in 100 mL of dioxane, and to this 10 g of ethylenediamine was added. Then, 40 mL of 1 M sodium hydroxide was added. The suspension was refluxed for 3 hours, and then cooled. The product was filtered, and washed each three times with ethanol and water.

Mini column procedure for collection and concentration of silver

Before the use of the resin for the collection / concentration of silver, the ethylenediamine-type chitosan resin was cleaned to remove metal impurities in the resin. Twenty milliliters of the wet resin was transferred to the plastic beaker, and to it, 80 mL of 2 M nitric acid was added. The mixture was carefully stirred at low speed for 6 hours. The aqueous solution was decanted, and the resin was rinsed with ultrapure water.

About 1 mL of ethylenediamine-type chitosan resin was packed in a mini column (5.0 mm i.d. x 50 mm, 1 mL of volume, Muromachi Chemicals, Kyoto, Japan). Through the column were passed 10 mL of 2 M nitric acid, 10 mL of ultrapure water for washing and 5 mL of buffer solution (pH 1-2: nitric acid; 3<pH<9: 0.5 M ammonium acetate buffer) for column conditioning. After the pretreatment of the column, sample solutions, the pHs of which were adjusted to appropriate pH, were passed through the column, and then 5 mL of the ultrapure water was passed for eliminating matrix ions. Finally, 10 mL of 1 M nitric acid

was passed through the column for recovering metal ions adsorbed on the resin. All of the effluents were collected in pre-cleaned screw-capped polypropylene bottles, and then analyzed by ICP-MS after adding Rh as the internal standard.

Throughout the column pretreatment, the flow rate of the rinsing solutions, samples, and the eluent were maintained at about 2 mL min^{-1}. The time required for the whole column pretreatment (for 10 mL of sample solutions) was about 25 min.

Results and discussion

Characteristics of the ethylenediamine-type chitosan resin

FTIR spectra were recorded and presented in Fig.2. The band at 825 cm^{-1} in Fig. 2A confirms the N-H wagging of amino group in the cross linked chitosan. This band intensity was decreased and new bands of C-Cl stretching appeared when the cross-linked chitosan were modified with chloro-methyl-oxyrane, as shown in Fig. 2B. The main changes on the FTIR spectra of ethylenediamine-type chitosan were increasing the intensity of N-H wagging at 825 cm^{-1} and disappearing the intensity of C-Cl stretching at 623, 700, and 751 cm^{-1}; due to the changing of chloro group to amino groups when ethylenediamine coupled to the cross-linked chitosan chloro-2-propanol, given in Fig. 2C. The decreasing intensity this band when silver loaded to the resin confirms the chelation of Ag with both of amino groups of ethylenediamine, as shown in Fig. 2D. The band at 1650 cm^{-1} confirms the N-H scissoring from the primary amine, due to the free amino groups of the cross-linked chitosan which not react with chloromethyloxirane, or from the ethylenediamine-type chitosan.

For the titration of 1 mL ethylenediamine-type chitosan resin, 1.83 mL of 0.1356 M NaOH was used. One mililiter of the wet resin was equal to 0.27 g of dry resin; therefore if each unit of ethylenediamine attached to each monomer of the cross-linked chitosan, there would be 0.59 mmol ethylenediamine in 1 mL of resin. However, only 0.25 mmol of

ethylenediamine exists. Further, if each unit of ethylenediamine attached to the 2 units of cross-linked chitosan, there would be 0.32 mmol ethylenediamine in 1 mL of resin.

From the result of the titration, it could be estimated that the ratio of ethylenediamine and the unit of cross-linked chitosan was about 1 : 2. However, there was an original chitosan which did not react with chloromethyloxirane, as confirmed from IR band at 1650 cm^{-1} in Fig. 2B. Therefore from the synthesis result, there are two probabilities of the structure of ethylenediamine-type chitosan resin, as can be seen in Fig. 1.

Adsorption capacity of ethylenediamine-type chitosan resin

The ethylenediamine-type chitosan resin could be used for the collection of ultratrace amounts of silver at wide pH range. However, pH 5 was chosen to examine the adsorption capacity. At pH 1, the resin can adsorb silver selectively, but the chelation is seemed to be weaker.

The adsorption capacity of the ethylenediamine-type chitosan resin was determined by a batchwise method. One milliliter of the wet resin was equilibrated in 100 mL of 0.02 M and 0.01 M for Ag(I) and Cu(II) ion at pH 5. The result obtained for the adsorption of Ag(I) and Cu(II) on the ethylenediamine-type chitosan resin were 0.37 and 0.19 mmol mL^{-1} of the resin, respectively, with the $t_{1/2}$ of Ag(I) adsorbed is less than 5 min. As shown in Fig. 3, the capacity of Cu(II) adsorbed on the resin was lower than Ag(I), because Cu(II) could not adsorb completely on the ethylenediamine-type chitosan resin. Cupper has four coordination number and is one of the '*borderline'* cations, while silver has two coordination number and is a '*soft*' cation. Therefore Ag(I) possesses stronger affinity for intermediate (N) ligands than Cu(II) [18].

Adsorption behavior of metal ions on ethylenediamine-type chitosan resin

The ethylenediamine-type chitosan resin can adsorb Ag(I) at pH 1-8, Sn(II) at pH 4-9, Bi(III) at pH 3-9, and Th(IV) at pH 6-9 quantitatively through a chelating mechanism and /or an anion exchange mechanism. They could be recovered completely with 10 mL of 1 M nitric acid. The results obtained for the behavior of the adsorption of metal ions were shown in Fig. 4. Referring to the previous results [28], the ethylenediamine moiety on the cross-linked chitosan gave a specific characteristic on the adsorption of silver. A cross-linked chitosan itself could adsorb silver quantitatively only at pH 5-6, while the ethylenediamine-type chitosan resin synthesized in this work could adsorb silver quantitatively in wide pH range from 1 to 8. This is because Ag(I) can form stable chelate not only with N-sites of ethylenediamine, but also with N-sites of amino groups of the cross-linked chitosan. However, with ethylenediamine, a 5-membered ring chelate could be formed, which means that Ag(I) can form more stable chelate with ethylenediamine-type chitosan than that with cross-linked chitosan. These metal chelates are shown in Fig. 5.

The ethylenediamine-type chitosan resin was stable in acidic solutions and could be easily eluted with 2 M nitric acid. The resin was also stable for several-month usuage: even after using for more than 30 times, the adsorption property was the same as the first property.

Detection limit

The detection limit of the proposed method for the determination of silver was examined under the optimal experimental conditions. The instrumental detection limit (IDL) and the method detection limit (MDL), which includes IDL and the enrichment factor, were 8 and 0.7 pg mL^{-1}, respectively. IDL was calculated as the three times of the standard deviation of 10 replicates of 1 M nitric acid, while MDL was calculated as the three times of the standard deviation of 7 replicates of the blank solution obtained by the whole procedures for the enrichment factor of 50, in which 0.1 M nitric acid was used as the blank solution and the

procedure was carried out in the same manner as the sample solution.

Effect of chloride ion

For the determination of ultratrace amounts of silver in seawater samples, it was necessary to examine the effect of chloride ion on the recovery of silver from the samples. Solutions containing 0.1 ppb of silver and various concentrations of NaCl (from 10^{-4} to 0.75 M) were passed through the column packed with 1 mL of the ethylenediamine-type chitosan resin, and then silver collected on the column was recovered with 1 M nitric acid as an eluent. The effluents were then analyzed by ICP-MS. It can be seen from the results obtained in this work that the recoveries of silver from various concentrations of NaCl were quantitative and were 96.2-101.3%, as shown in Fig. 6. These results indicate that there are no interference with the determination of silver from sodium and chloride and the resin can be used for the quantitative collection of silver not only from river water samples which contain about 10^{-4} M of chloride, but also from seawater samples which contain about 0.5 M of chloride.

Speciation of silver in water and adsorption mechanism of silver on the ethylenediamine-type chitosan resin

Silver occurs naturally in several oxidation states, usually as Ag^0 or Ag^+; other possible oxidation states of silver are Ag^{2+} and Ag^{3+}. In surface freshwaters, silver may be present as a monovalent ion and its combination with sulfide, bicarbonate, chloride or sulfate [1]. By using the program **MINEQL**$^+$ (the aquatic geochemical equilibrium program, N. A. Webb *et al.*), the speciation of silver in waters was predicted [29]. Also, Y. Zhang *et al.* [6] and T. J. Ward *et al.* [30] predicted the speciation of silver by using thermodynamic models. R. H. Byrne reported the principal species as a function of pH for inorganic species of dissolved element in seawater [31].

It can be concluded that the main species of silver in freshwater are Ag^+ and a neutral complex, $AgCl_{aq}$, whereas the main species are chloro complexes of $AgCl_3^{2-}$ and $AgCl_2^-$ in seawater. The complex $AgCl_4^{3-}$ does not occur at seawater salinity [30], and the free ion Ag^+ and the complex of Ag^+ with organic ligands is negligible in seawater [6].

Silver ion can be retained on a strongly basic anion-exchange column as a chloro complex, and subsequently eluted with ammonia or an acetone-nitric acid-water mixture [32,33]. Ammonia solution was used for recovering silver from the anion exchange resin because silver-ammonia complex was more stable than silver-chloro complex. Similarly, silver-ethylenediamine (en) chelate was stronger than silver-chloro complex; that is K_f of $AgCl_3^{2-}$, $AgCl_2^-$ and $Ag(en)^+$ are 0.31, 1.81, and $5x10^4$, respectively [34,35]. As a result, it can be suggested that the adsorption mechanism of silver with ethylenediamine-type chitosan resin is based on the chelate formation mechanism with ethylenediamine moiety of the resin, as is shown in Fig. 5.

Determination of silver in CASS-4 nearshore seawater reference material

The accuracy and precision of the proposed column pretreatment using the ethylenediamine-type chitosan resin for the determination of ultratrace amounts of silver in seawater was examined by analyzing CASS-4 nearshore seawater reference material from the National Research Council of Canada (Ottawa, Ontario, Canada). The result of silver analysis performed using the ethylenediamine-type chitosan gave similar results for NRCC-CASS-4 to those reported by other workers [8,32]. 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, as was summarized in Table 2. Yang *et al.* used an isotope dilution / ICP-MS method and external calibration technique, while Ndung'u *et al.* enriched Ag using the solvent extraction with 1-pyrrolidine carbodithioic acid ammoinium salt/

diethyldithiocarbamic acid, diethylammonium salt (APDC/DDDC), and then measured Ag using a Finnegan MAT ELEMENT magnetic sector high-resolution ICP-MS.

Determination of silver in tap, river, and seawater samples

When artificial seawater samples were used to examine the stability of silver in a seawater sample, there was no difference in the recovery between the artificial seawater and the aqueous standard solution, as shown in Table 3.

The proposed method was successfully applied to the determination of silver in environmental water samples. The analytical data, as well as those of the recoveries of spiked silver, were shown in Table 4. The silver concentrations in fresh water are several ppt (10^{-9} g mL^{-1}), and those in seawaters 10-40 ppt.

Conclusion

A novel chelating resin using chitosan as a base material, ethylenediamine-type chitosan, has been developed. The resin has several advantages: high selectivity and adsorption capacity for silver, good stability for several months, easy recovery of silver from the resin and the elution of silver from the resin with 1 M nitric acid. The proposed resin can be used, not only for the separation of silver from high matrix solutions, but also for the preconcentration of silver.

The proposed method gives 0.7 pg ml^{-1} of the detection limit for 50-fold enrichment factor, and was applied to the determination of silver in tap, river, and seawater samples.

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References

1. T. R. Crompton, Analysis of Seawater, Butterwoth, England, 1989, p. 180-200.
2. R. Eisler, Silver Hazards to Fish, Wildlife and Invertebrates: A Sypnotic Review, Contaminant Hazard Reviews Report (Biological Report 32, September 1996), Patuxent Wildlife Research Center U.S. National Biological Service.
3. C. M. Wood, M. D. McDonald, P. Walker, M. Grosell, J. F. Barimo, R. C. Playle, P. J. Walsh, Aquat. Toxicol., 70 (2004) 137.
4. Q. Hu, G. Yang, Y. Zhao, J. Yin, Anal. Bioanal. Chem., 375 (2003) 831.
5. B. Wen, X. Q. Shan, Anal. Bioanal. Chem., 374 (2002) 948.
6. Y. Zhang, H. Amakawa, Y. Nozaki, Mar. Chem., 75 (2001) 151.
7. J. E. Conde, F. J. G. Montelongo, Bull. Environ. Contam. Toxicol., 73 (2004) 77.
8. K. Ndung'u, M. A.Thomas, A. R. Flegal, Deep-Sea Research II, 48 (2001) 2933.
9. G. Absalan, A. A. Goudi, Sep. Purif. Technol., 38 (2004) 209.
10. P. Liu, Z. Su, X. Wu, Q. Pu, J. Anal. At. Spectrom., 17 (2002) 125.
11. S. Zhang, Q. Pu, P. Liu, Q. Sun, Z. Su, Anal. Chim. Acta, 452 (2002) 223.
12. L. H. Babaei, Z. Ghasemi, F. Darviche, Anal. Sci., 17 (2001) 1305.
13. M. Shamsipur, M. Javanbakht, Z. Ghasemi, M. R. Ganjali, V. Lippolis, A.Garau, Sep. Purif. Technol., 28 (2002) 141.
14. S. Dadfarnia, A. M. Haji Shabani, M.Gohari, Talanta, 64 (2004) 682.
15. Q. Hu, G. Yang, Z. Huang, J. Yin, Microchim. Acta, 141 (2003) 191.
16. S. Pramanik, P. K. Dhara, P. Chattopadhyay, Talanta, 63 (2004) 485.
17. P. Chattopadhyay, C. Sinha, D. K. Pal, Fres. J. Anal. Chem., 357 (1997) 368.
18. V. Camel, Spectrochimica Acta Part B, 58 (2003) 1177.

19. M. P. Arena, M. D. Porter, J. S. Fritz, Anal. Chim. Acta, 482 (2003) 197.

20. D. B. Gazda, J. S. Fritz, M. D. Porter, Anal. Chem., 76 (2004) 4881.

21. S. Cobianto, A. Lezzi, R. Scotti, Reac. Func. Polym., 43 (2000) 7.

22. A. A. Atia, A. M. Donia, Saeda, A. E. Enein, A. M. Yousif, Sep. Purif. Technol., 33 (2003) 295.

23. T. I. Tikhomirova, V. I. Fadeeva, D. V. Kudryavtsev, P. N. Nesterenko, V. M. Ivanov, A. T. Savitchev, N. S. Smirnova, Talanta 38 (1991) 267.

24. A. Syamal, M. M. Singh, D. Kumar, Reac. Func. Polym., 39 (1999) 27.

25. D. E. Leyden, G. H. Luttrell, Anal. Chem., 47 (1975) 1612.

26. H. Sawatari, E. Fujimori, H. Haraguchi, Anal. Sci., 11 (1995) 369.

27. M. Thomsen, R. E. Wolf, The Key to The Analysis of High Matrix Samples by ICP-MS, application note of PerkinElmer Instruments, Beaconsfield, UK.

28. K. Oshita, Y. Gao, M. Oshima, S. Motomizu, Anal. Sci., 17 Supplement (2001) a317.

29. N. A. Webb, C. M. Wood, Aquat. Toxicol., 49 (2000) 111.

30. T. J. Ward, J. R. Kramer, Comp. Biochem. Physiol. Part C: Toxicology & Pharmacology, 133 (2002) 75.

31. R. H. Byrne, Geochem. Trans., 3 (2002) 11.

32. L. Yang, R. E. Sturgeon, J. Anal. At. Spectrom., 17 (2002) 88.

33. Z. Marczenko, Separation and Spectrophotometric Determination of Elements, Ellis Horwood Limited, England, 1986, p. 524.

34. L. G. Sillen, A. E. Martell, Stability Constants of Metal Ion Complexes, The Chemical Society, London, 1964, p. 287, 519, 589.

35. G. D. Christian, Analytical Chemistry, 5th Edition, John Wiley & Sons, USA, 1994, p. 266.

Table caption

Table 1 The ICP-MS operating conditions

Table 2 Determination of silver in CASS-4 nearshore seawater reference material

Table 3 Recovery of silver

Table 4 Determination of silver in environmental water samples

Figure caption

Fig. 1 Reaction scheme for the synthesis of ethylenediamine-type chitosan resin.

Fig. 2 FTIR spectra: A. Cross-linked chitosan; B. Cross-linked chitosan chloro-2-propanol; C. Ethylenediamine-type chitosan; D. Silver-loaded ethylenediamine-type chitosan.

Fig. 3 Relationship between the time for the adsorption and the amount of Ag and Cu adsorbed on the ethylenediamine-type chitosan resin at pH 5. Ethylenediamine-type chitosan resin, 1 mL (0.27 g); concentration of metal ion, 0.02 M of Ag^{+} and 0.01 M of Cu^{2+}; metal ions solutions, 100 mL.

Fig. 4 Adsorption behavior of ethylenediamine-type chitosan for metals at various pH. Sample volume, 10 ml; concentration of each metal, 10 ng ml^{-1}; eluent, 10 ml of 1 M nitric acid.

Fig. 5 Predicted silver-chelate in ethylenediamine-type chitosan resin: A and B. Chelating with ethylenediamine moiety on the cross-linked chitosan; C. Chelating with amino group of the crosslinked chitosan.

Fig. 6 Effect of sodium chloride concentrations on the recovery of silver. Silver added to the solution is 0.110 ng mL^{-1}.

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 L min^{-1}
Carrier gas	Ar 0.45 L min^{-1}
Auxiliary gas	Ar 0.50 L min^{-1}
Sample uptake rate	1.0 ml min^{-1}
Interface condition	
Sampling depth	10 mm from load coil
Sampling cone	Copper 1.1 mm id
Skimmer cone	Copper 0.35 mm id

Table 2 Determination of silver in CASS-4 nearshore seawater reference material

Sample	Ag found (pg mL^{-1})			
	Proposed method[a]	ID / ICP-MS[b]	ICP-MS[c]	SE / ICP-MS[d]
CASS-4	5.6 ± 0.3	5.42 ± 0.10	5.55 ± 0.15	6.11 ± 0.90

[a] From 3 replicates, sample 50 mL (pH = 5), eluent 10 mL of 1 M nitric acid, evaporated and diluted in 1 mL of 1 M nitric acid.

[b] ID / ICP-MS; n = 3 [32].

[c] External calibration technique / ICP MS; n = 3 [32].

[d] Solvent extraction using APDC/DDDC-ICP MS; calculated from (56.55 ±8.34) pM; n = 7 [8].

Table 3 Recovery of silver

Sample	Concentration factor	Ag added ($ng\ mL^{-1}$)	% Recovery[a]
0.1 M HNO_3[b]	1	10	95.0 ± 1.0
0.1 M HNO_3	1	1	98.9 ± 2.8
0.1 M HNO_3	5	0.100	99.2 ± 3.8
0.1 M HNO_3	50	0.010	102.9 ± 1.9
0.1 M HNO_3	50	0.005	102.9 ± 3.0
Artificial seawater[c]	5	0.100	101.2 ± 3.7
Artificial seawater	5	0.075	93.4 ± 7.6
Artificial seawater	5	0.050	99.1 ± 1.9
Artificial seawater	10	0.025	97.7 ± 0.8

[a] Mean ± σ, from 3 replicates.

[b] Sample pH is adjusted to 5 by adding a small amount of ammonia solution.

[c] Sample contains 0.48 M Na^+, 0.05 M Mg^{2+}, 0.01 M Ca^{2+}, 0.01 M K^+,0.55 M Cl^-, 0.03 M SO_4^{2-}; pH is adjusted to 5 by adding a small amount of ammonia solution.

Table 4 Determination of silver in environmental samples

Sample	Concentration factor (CF)[a]	Ag (ng mL^{-1})			% Recovery
		Found	Added	Total found	
Asahi River	50	0.005 ± 0.000	0.010	0.014 ± 0.001	98.3 ± 3.3
Nishi River	50	0.008 ± 0.000	0.010	0.018 ± 0.001	101.7 ± 2.7
Zasu River	50	0.006 ± 0.001	0.010	0.016 ± 0.001	96.5 ± 1.8
Tap water A[b]	50	0.008 ± 0.000	0.010	0.018 ± 0.000	99.0 ± 3.1
Tap water B[c]	50	0.012 ± 0.001	0.010	0.022 ± 0.001	99.7 ± 2.9
Seawater at Ushimado	5	0.042 ± 0.001	0.050	0.092 ± 0.002	97.9 ± 1.4
	10	0.042 ± 0.001	0.010	0.052 ± 0.002	102.3 ± 3.5
	50	0.041 ± 0.002	0.010	0.050 ± 0.001	99.3 ± 4.2
Seawater at Shibukawa	5	0.031 ± 0.001	0.050	0.079 ± 0.002	97.0 ± 4.0
	10	0.030 ± 0.001	0.010	0.040 ± 0.001	100.6 ± 8.1
	50	0.031 ± 0.001	0.010	0.042 ± 0.002	105.5 ± 5.8
Seawater at Kojima	5	0.022 ± 0.003	0.050	0.069 ± 0.003	98.5 ± 5.6
	10	0.019 ± 0.001	0.010	0.028 ± 0.001	101.1 ± 8.7
	50	0.019 ± 0.001	0.010	0.027 ± 0.001	91.9 ± 9.0
Seawater at Muroto	50	0.008 ± 0.000	0.005	0.013 ± 0.001	102.2 ± 4.4
	50	0.008 ± 0.000	0.010	0.018 ± 0.001	100.3 ± 9.4

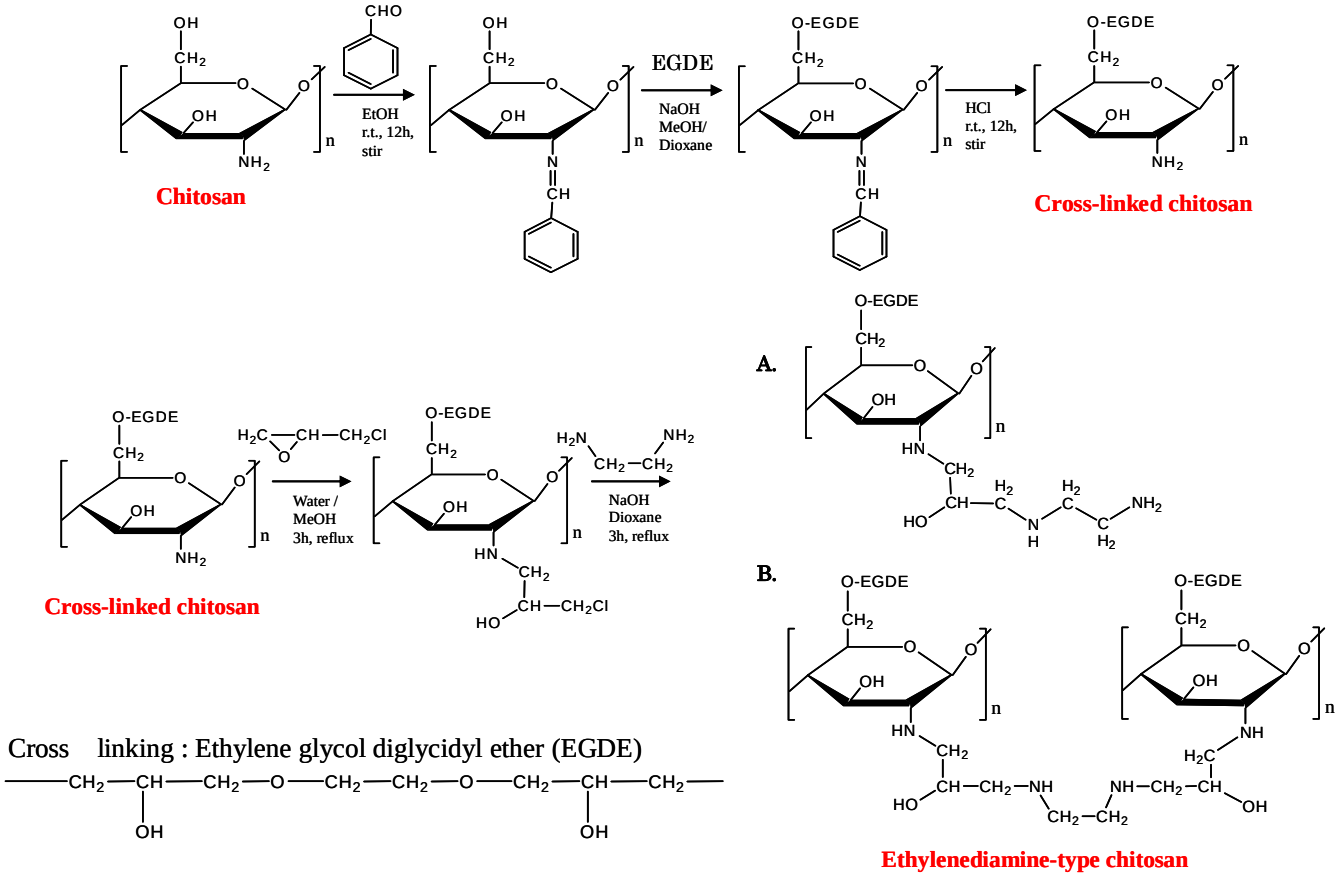
[a] CF 50 : sample 100 mL(pH=5), eluent 10 mL of 1 M HNO_3, evaporated and diluted in 2 mL of 1 M HNO_3;

CF 10 : sample 100 mL, eluent 10 mL of 1 M HNO_3;

CF 5 : sample 50 mL, eluent 10 mL of 1 M HNO_3.

[b] Tap water samples at VBL, Okayama University.

[c] Tap water samples at Fac. of Science, Okayama University.



Cross linking : Ethylene glycol diglycidyl ether (EGDE)

Fig. 1

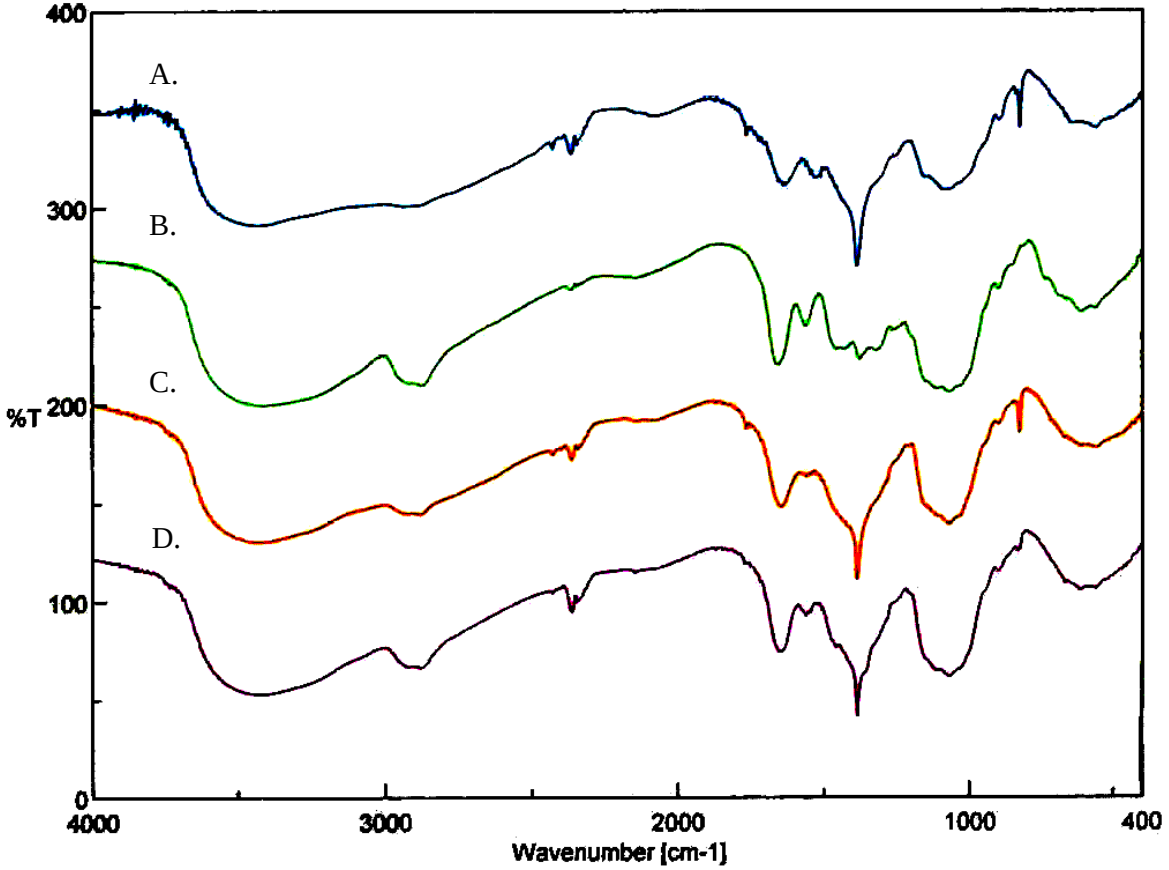

400
300
200
100
0
%T
A.
B.
C.
D.
4000
3000
2000
1000
400
Wavenumber [cm-1]

Fig. 2

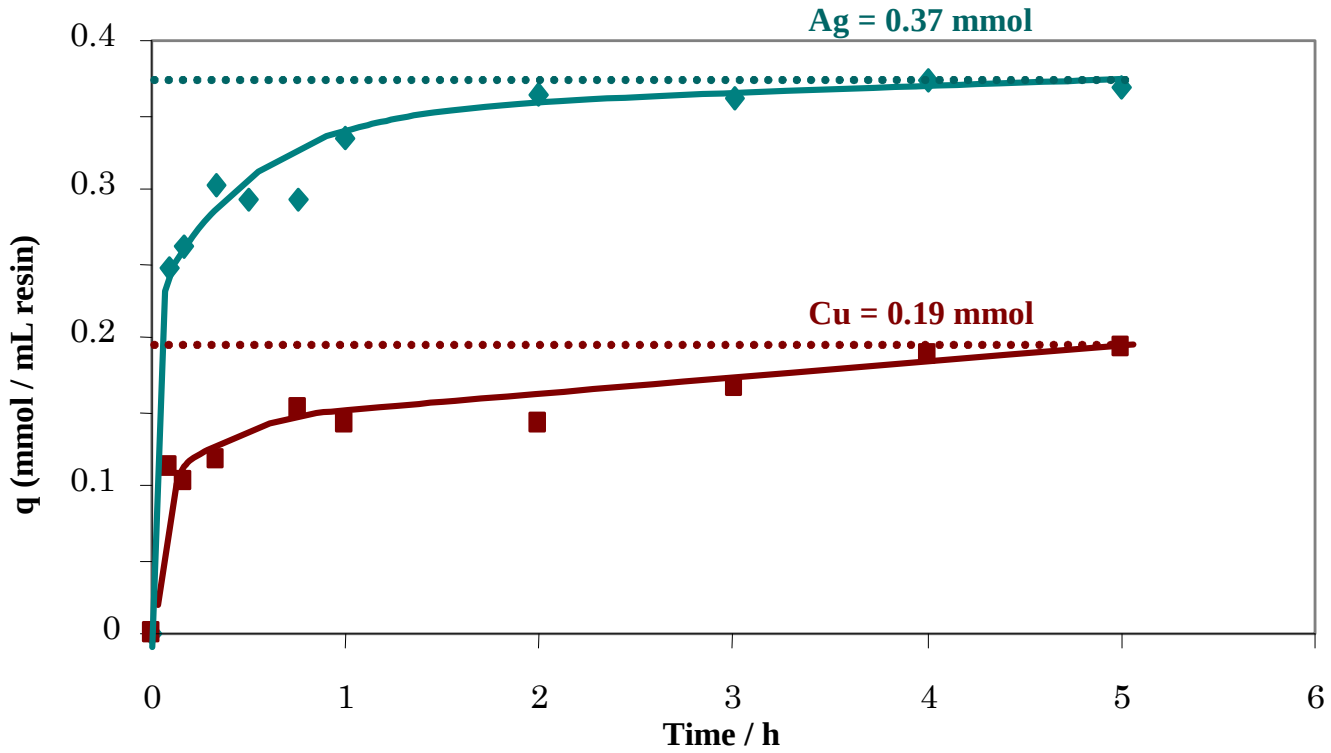

Ag = 0.37 mmol
Cu = 0.19 mmol
q (mmol / mL resin)
Time / h
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6

Fig. 3

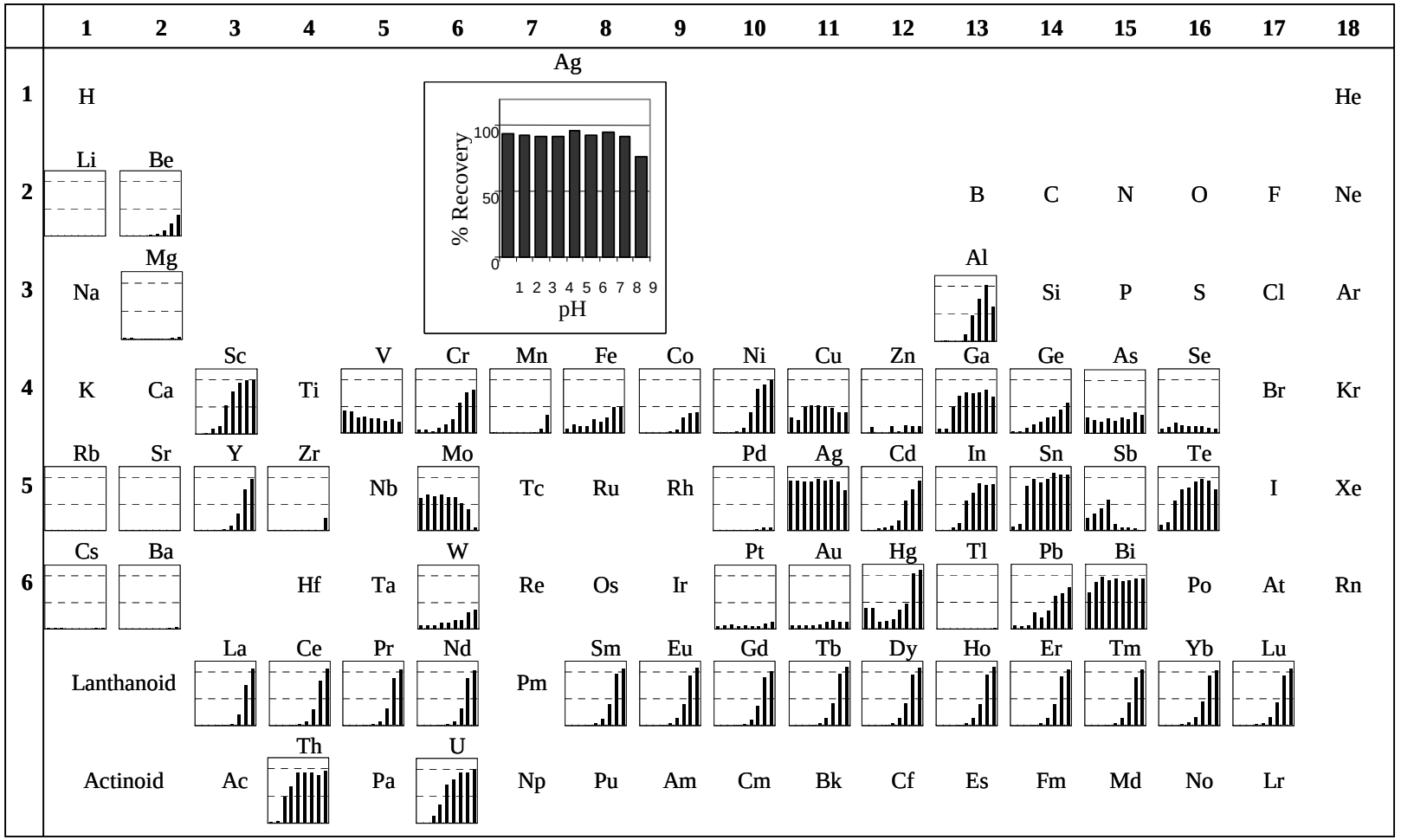

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
1 2 3 4 5 6
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Lanthanoid La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinoid Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Ag
% Recovery
100
50
0
1 2 3 4 5 6 7 8 9
pH

Fig. 4

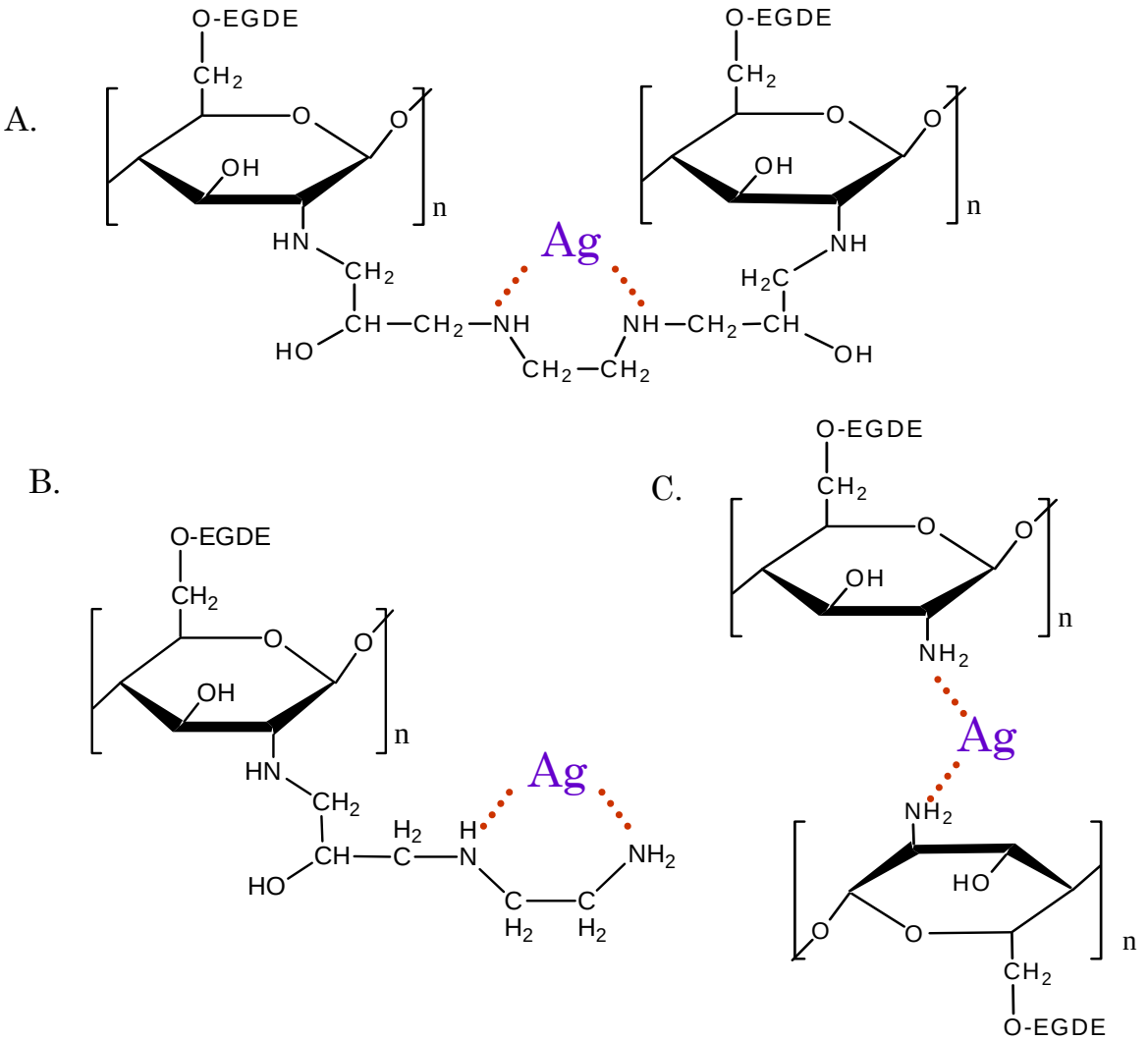

A.
O-EGDE
CH2
O
O
OH
n
HN
CH2
CH
CH2
NH
Ag
NH
CH2
CH
HO
CH2
CH2
NH
H2C
OH
B.
O-EGDE
CH2
O
O
OH
n
HN
CH2
CH
H2
C
H
N
Ag
NH2
HO
C
H2
C
H2
C.
O-EGDE
CH2
O
O
OH
n
NH2
Ag
NH2
HO
O
O
n
CH2
O-EGDE

Fig. 5

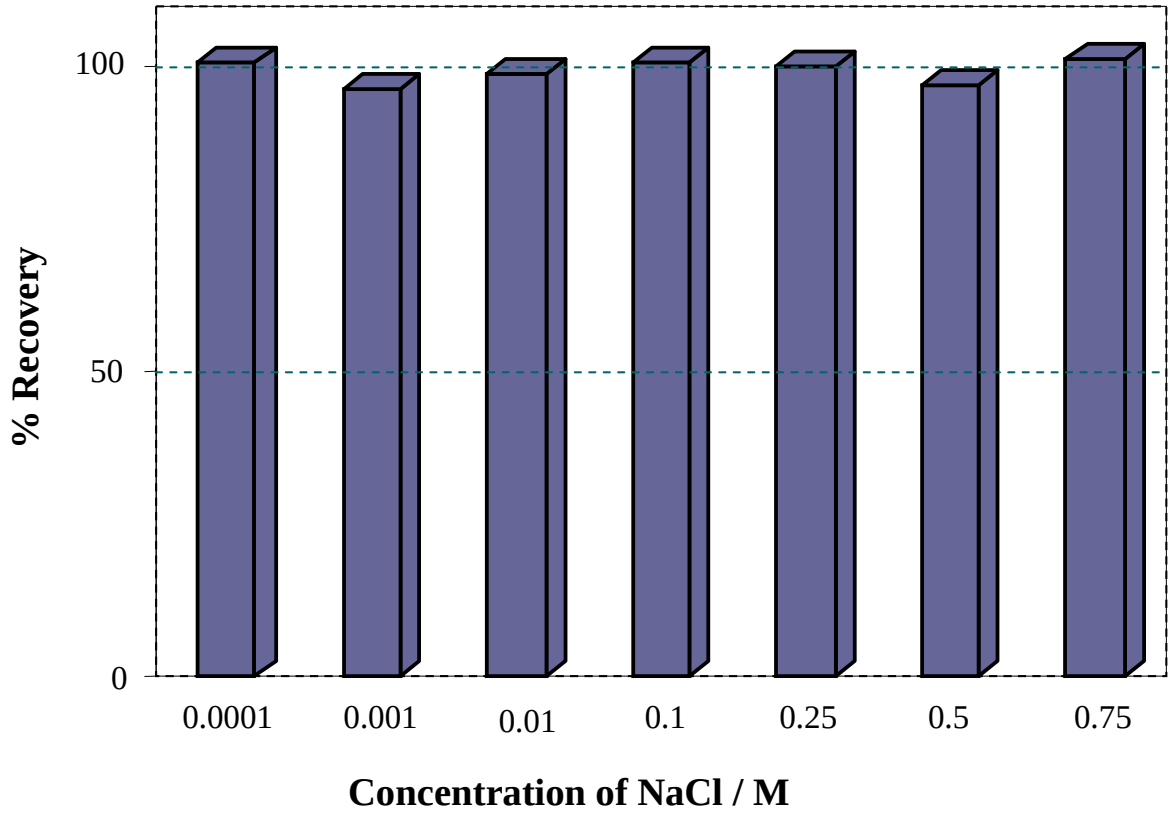

100
50
0
% Recovery
0.0001
0.001
0.01
0.1
0.25
0.5
0.75
Concentration of NaCl / M

Fig. 6

50