Chemistry

Analytical Chemistry fields

Okayama University *Year* 2004

Synthesis of cross-linked chitosan possessing N-methyl-D-glucamine moiety (CCTS-NMDG) for adsorption/concentration of boron in water samples and its accurate measurement by ICP-MS and ICP-AES

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Synthesis of Cross-linked Chitosan Possessing *N*-Methyl-*D*-Glucamine Moiety (CCTS-NMDG) for Adsorption/Concentration of Boron in Water Samples and its Accurate Measurement by ICP-MS and ICP-AES

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Abstract

A chitosan resin derivatized with *N*-methyl-*D*-glucamine (CCTS-NMDG) was synthesized by using a cross-linked chitosan (CCTS) as base material. The *N*-methyl-*D*-glucamine (NMDG) moiety was attached to the amino group of CCTS through the arm of chloromethyloxirane. The adsorption behavior of 59 elements on the synthesized resin was systematically examined by using the resin packed in a mini-column, passing water samples through it and measuring the adsorbed elements in eluates by ICP-MS. The CCTS-NMDG resin shows high ability in boron sorption with the capacity of 0.61 mmol ml^{-1} (= 2.1 mmol g^{-1}). The sorption kinetics of this resin was faster than that of the commercially available resins. Other advantages of the synthesized resin are: (1) quantitative collection of boron at neutral pH regions, (2) complete removal of large amounts of matrices, (3) no loss of efficiency over prolonged usage, (4) effective collection of boron in wide range concentration using a mini column containing 1 ml resin, and (5) complete elution of boron with 1 mol l^{-1} nitric acid. The resin was applied to the collection/concentration of boron in water samples. Boron in tap water and river water was found to be in the range of 6 to 8 $\mu g\ l^{-1}$. The LOD of boron after pretreatment with CCTS-NMDG resin and measurement by ICP-MS was 0.07 $\mu g\ l^{-1}$ and the LOQ was 0.14 $\mu g\ l^{-1}$ when the volume of each sample and eluent was 10 ml.

Keyword : chitosan resin, N-methyl-D-glucamine, boron, adsorption, ICP-MS/AES

Introduction

Boron is widely distributed in surface and ground waters, occurring naturally or from anthropogenic contamination, mainly in the form of boric acid or borate salts [1]. Water contamination by boron is one of the widespread environmental problems, since even a few parts per million present in irrigation water can cause stunting of plant growth. Increasing attention has also been paid to microelectronic industries since the existence of trace amounts of boron in ultrapure water for cleaning and etching process can seriously influence the characteristics of semiconductor [2-3]. These facts show that the removal of ultra-trace, trace or large amount of boron is still a challenging problem, although a boron-specific resin was introduced in the mid-1960`s.

Several polymer resins for the removal of boron have been developed so far. Biçak *et al.* reported a sorbitol-containing polymer resin using crosslinked polystyrene-divinylbenzene as base material [4] and glycidyl methacrylate based crosslinked polymers containing *N*-methyl-*D*-glucamine (NMDG) [5-6]. Maeda *et* al. reported boric acid adsorbent, which was prepared by the addition of tris(hydroxymethyl)aminomethane to epoxy groups in macroreticular glycidyl methacrylate-divinylbenzene copolymer beads [7]. Much attention has been paid to the commercially available boron adsorption resins, such as Amberlite IRA 743, Diaion CBR02, etc. These resins have macroreticular crosslinked polystyrene matrices, on which NMDG is chemically fixed. However, their main disadvantage is slow kinetics in the boron uptake, despite their high specificity to boric acid in neutral pH regions [1,8]. Jyo *et al.* reported chelating fibers having poly-ol groups for boron adsorption [9]. In this case, tris(hydroxymethyl)aminomethane and NMDG were fixed to epoxy groups of poly (glycidylmethacrylate) chains, which were chemically bound to polyethylene coated polypropylene fiber (PPPE) by means of

electron beam irradiation induced graft polymerization method. This resin allowed faster sorption kinetics than a commercially-available boron resin. However, the adsorption capacity is low. Therefore, it is necessary to develop boron resin with both fast sorption kinetics and high capacity.

Chitosan, which possesses amino groups, is one of the excellent base substances for novel resin synthesis, because it has several advantages over synthetic polymer materials like poly(styrene-divinylbenzene), polyethylene and poly urethane[10,11]. In general, the resins made of chitosan as a base materials are more hydrophilic than synthetic resins such as polystyrene, poly (styrene-divinylbenzene), polyethylene, and polyurethane; therefore the sorption kinetic is very fast. We have already reported [10] a new-type cross-linked chitosan resins with ethyleneglycoldiglycidylether (EGDE) as crosslinker, which did not shrink even in a concentrated acidic solution. The adsorption behavior of metal ions on the resin were examined with a column treatment method [10,12]. By using the EGDE cross-linked chitosan (CCTS) as a base material, chelating resins possessing the iminodiacetate moiety, serine moiety, and leucine moiety, were synthesized and applied to the collection/concentration of trace amounts of elements [11,13,14].

In this work, NMDG moiety was introduced into CCTS through the arm of chloromethyloxirane. The adsorption behavior of boron, and other elements, was examined with the newly developed chitosan resin (CCTS-NMDG). The CCTS-NMDG resin provides some advantages, such as faster sorption kinetics and higher adsorption capacity of boron than commercially boron resin. Other advantages include collection of boron at neutral pH regions, complete removal of large amounts of matrix such as, Na, K, Mg, Ca, and no observable loss of

efficiency after long term use. The resin was applied to the collection of boron from tap, river, estuarine, and ground waters.

Experimental

Instrumentation

An ICP-MS system used for the measurement of elements was Model SPQ 8000H (Seiko Instruments, Chiba, Japan). An ICP-AES (Vista-PRO, Seiko Instruments) was also used for measuring boron in seawater. Boron was measured at m/z = 11 (ICP-MS) and at analytical line of 249.772 nm (ICP-AES). An automatic titration system, Model AT-310J (Kyoto Electronics Manufacturing Co., Kyoto, Japan), was used for the acid-base titration to estimate the pKa values of CCTS-NMDG resin.

Reagents and materials

Flake-type chitosan purchased from Tokyo Kasei Co. Ltd., Tokyo, Japan was used. All other reagents used for the synthesis of CCTS-NMDG resin were of analytical reagent grade.

The stock solutions of an analytical standard for 59 elements were prepared by diluting single element standard solutions for atomic absorption spectrometry (1000 mg l^{-1}, Wako Pure Chemicals, Osaka, Japan) and a multi-element standard solution for ICP-MS (10 ppm, XSTC-13, Spex CertiPrep Inc., New Jersey, USA) with 1 mol l^{-1} nitric acid. The stock solutions were diluted by weight just before the column pretreatment with 1 mol l^{-1} nitric acid to give 10 μg l^{-1} of each element.

Ultrapure grade nitric acid (60 %, density 1.38 g ml^{-1}, Kanto Chemicals, Tokyo, Japan) was diluted with ultrapure water to give a 1 mol l^{-1} and a 2 mol l^{-1} concentration for column treatment. Acetic acid (minimum 96 %) and ammonia water (29 %) used for the preparation of ammonium acetate buffer solution were of

an electronic industrial reagent grade (Kanto Chemicals, Tokyo, Japan).

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

Synthesis of CCTS-NMDG resin

There are two main steps in this synthesis: the first step is the synthesis of CCTS with the crosslinker of ethyleneglycoldiglycidylether (EDGE), and the second step is the chemical bonding of NMDG to the CCTS through the arm of chloromethyloxirane. The CCTS was synthesized in a manner similar as the previous work as shown in Fig. 1 (scheme 1) [12]. The procedures are as follows: chitosan flake was ground to fine pieces and sieved to obtain chitosan particles of diameter, 100-300 μm, which were weighed (20 g) and suspended in 200 ml of ethanol. Benzaldehyde (80 g) was then added to the chitosan suspension. The mixture was stirred at room temperature for 12 h to protect amino groups of chitosan as Schiff base. After the reaction was completed, the product was filtered through glass filter and washed each 3 times with ethanol and water, respectively to remove unreacted benzaldehyde. The chitosan derivative, in which the amino groups are protected by benzaldehyde, was refluxed with ethyleneglycoldiglycidylether (EGDE, 30 g) in 300 ml of dioxane and 40 ml of 1 mol l^{-1} NaOH for 3 h. The product was filtered and washed each 3 times with ethanol and water, respectively. The Schiff base was cleaved to amino compound by twice stirring of the product in 1000 ml of 0.5 mol l^{-1} hydrochloric acid solutions at room temperature for 12 h, followed by filtration and washing 3 times with ethanol and water, respectively.

The CCTS-NMDG resin was synthesized in the procedure shown in scheme 2 of Fig. 1. The CCTS (5 g) was suspended in a mixture of water (50 ml) and

ethanol (50 ml), followed by the addition of chloromethyloxirane (10 g). The mixture was then refluxed for 3 h. After the reaction was completed, the product was filtered through a glass filter, and washed each 3 times with ethanol and water, respectively, to remove the unreacted chloromethyloxirane. After washing, the CCTS with the arm of chloromethyloxirane and NMDG (10 g) were suspended in dioxane (100 ml). To this suspension, 1 M NaOH (40 ml) was added, and then, the mixture was refluxed for 3 h in order to couple the amino group of NMDG with the terminal chloro group of the arm of the CCTS. The product was filtered through a glass filter and washed each 3 times with ethanol and water, respectively.

Procedures for the column pretreatment of sample solutions

Before being packed in the column, the CCTS-NMDG resin was purified to remove residual metal impurities as follows: 20 ml of the wet resin was transferred to a 100 ml plastic beaker, containing 80 ml of 2 mol l^{-1} nitric acid. The mixture was stirred carefully at a low speed for 6 h. The resin was then filtered on a filter paper, and rinsed with the ultrapure water. A 1 ml of the resin was then packed in polypropylene mini-columns (5 mm i.d. x 50 mm, Muromachi Chemical, Kyoto, Japan) for the examination of the collection/concentration of 59 elements.

The column pretreatment procedures are as follows: the resin, packed in the mini-columns, was washed with 10-ml aliquot of 2 mol l^{-1} nitric acid and ultrapure water, respectively. A 5-ml aliquot of a buffer solution (pH 1-2: nitric acid; pH 3-9: 0.5 mol l^{-1} ammonia-acetate solutions) was then passed through the column for column conditioning. A sample solution (10 ml), whose pH was adjusted with the same buffer as the one for the column conditioning, was passed through the column. A 5-ml aliquot of a 0.2 mol l^{-1} buffer solution (pH 1-9) was then passed through the column to remove matrix ions adsorbed on the resin such

as alkali and alkaline earth metals. To rinse the remaining buffer components in the column, a 5-ml aliquot of the ultrapure water was passed through the column. Finally, a 10-ml of 1 mol l^{-1} nitric acid was passed through the column to recover the elements adsorbed on the resin and the eluates were measured by ICP-MS.

Throughout column pretreatment, the flow rate of the sample, the rinsing solutions and the eluents was fixed at about 1 ml min^{-1}. The time required for whole column pretreatment was about 1 h.

Sampling and preserving of water samples

Tap water sample was collected from the faucet in the Venture Business Laboratory building located in Okayama University. River water sample was collected from Zasu river, which flows through Okayama University. Ground water was collected from Yubara spring water located in Okayama Prefecture. The estuarine water sample collected near Shin Okayama Port, was taken from an estuary at the location where the Asahi River meets the Seto Inland Sea. However, most of the samples came from Asahi River which flows to Shin Okayama Port. The natural pH of all samples was measured and found to be in the range of 6.5-7.1. The water samples were filtered through 0.45 μm membrane filter before introduction to the CCTS-NMDG resin column and measurement by ICP-MS/AES. Sampling and analysis were performed within the same day.

Result and discussion

Fundamental characteristics of CCTS-NMDG resin

Figure 2 shows the results of acid-base titration of the synthesized CCTS-NMDG resin (wet volume, 1 ml; dry weight, 0.29 g) in 30 ml of an acidic solution containing 2 ml 0f 0.1 mol l^{-1} HCl with a 0.10 mol l^{-1} NaOH solution. The pK_a values

calculated from the half points of the equivalent points, were about 9.1 and 10.6. As the obtained pKa values are a close, the pKa values of dimethylamine and trimethylamine can be referred to assign the pKa values of the amino groups in the CCTS-NMDG resin. The pKa of dimethylamine is 10.7, while that of trimethylamine is 9.8 [21]. Therefore the pKa of 9.1 in the CCTS-NMDG resin can be attributed to the tertiary amine of the arm of NMDG moiety, while the pKa of 10.6 can be attributed to the secondary amine of CCTS. To neutralize the protonated tertiary amine, 1.9 ml of 0.1 mol l^{-1} NaOH was required, which means that 0.19 mmol of the amine group exist in 1 ml of the CCTS-NMDG resin (Fig.2). One milliliter of the resin corresponds to 0.29 g (dry weight). If each NMDG moiety is attached to each unit of the CCTS, 0.58 mmol of amine group may exist in 1 ml of the resin. As the result, the mole ratio of each NMDG to each monomer unit of the chitosan resin can be calculated to be about 1:3 (=0.19:0.58).

Figure 3 shows the adsorbed amounts of boron and Cu (II) on CCTS-NMDG resin. To obtain the adsorption capacity, the resin (1 ml) was equilibrated with boron or Cu (II) for 24 h at pH 6.5 in the presence of an excess amount of each element. The adsorption capacities for boron and Cu (II) were found to be 0.61 and 0.51 mmol ml^{-1}, which correspond to 2.1 and 1.7 mmol g^{-1}, respectively. The adsorption capacities of both elements were larger than the amount of the NMDG moiety expected from the titration result, and boron adsorbed more rapidly than copper ion as shown in Fig.3. The sorption mechanism is discussed in the next section.

The sorption kinetics of CCTS-NMDG resin for boron uptake was compared with commercially available resin, Amberlite IRA 743. One gram of each resin, particle size of 100-300 μm, was placed in contact with 100 ml of boric acid solution (100 mg l^{-1} as boron), and the mixtures were stirred gently with a magnetic

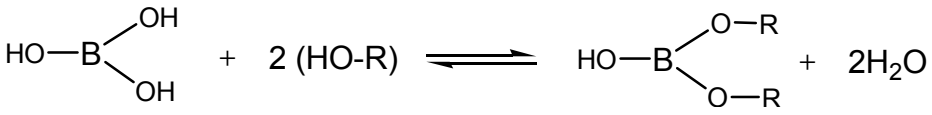
stirring bar. At appropriate time intervals, 5 ml of each aliquot was withdrawn, and after suitable dilution, the concentration of boron was determined by ICP-MS. From the concentration-time plot as shown in Fig.4, the CCTS-NMDG resin showed faster sorption rate than Amberlite IRA 743. The solution containing 100 mg l^{-1} boron goes down to almost zero within 10 min for CCTS-NMDG resin, while Amberlite IRA 743 needs almost 60 min. This is because chitosan is more hydrophilic than the styrene backbone of Amberlite resin.

Table 1 shows the comparison of sorption capacity and sorption rate of boron on several reported resins having poly-ol functional group. Usually, the functional groups containing tertiary amine and poly-ol moieties are attached to the base material polymer for boron resin. Such groups are suitable for boron's removal from aqueous solutions and for its complexation. From Table 1, it can be seen that CCTS-NMDG resin showed the fastest sorption rate and high capacity for the adsorption of boron. The capacity of CCTS-NMDG resin is similar to a resin prepared by glycidyl metacrylate as base material [5] and its modification [6].

Adsorption behavior of 59 elements on the CCTS-NMDG resin

Figure 5 shows the results of the recovery of each 10 μg l^{-1} of 59 elements at pH from 1 to 9 by using columns packed with the CCTS-NMDG resin. Most of the elements adsorbed on the resin were quantitatively recovered with 10 ml of 1 mol l^{-1} nitric acid as an eluent. The CCTS-NMDG resin can adsorb various kinds of elements, such as boron, vanadium, copper, gallium, arsenic, indium, tin, lead, bismuth, thorium, and uranium, etc. at suitable pHs. The recoveries of these elements were in the range of 93% to 103%. Of the elements examined, boron could be adsorbed completely at pH from 5 to 7. Since boron can adsorb at neutral pH region, it can provides benefit for the application to boron uptake in the

environmental water samples because pH adjustment of sample is not required. Boron can be adsorbed on the CCTS-NMDG resin according to the following mechanism; boric acid can form a complex with poly-ol groups (in NMDG moiety), as well as secondary and tertiary amine sites that can act as a weakly basic anion exchanger. This adsorption mechanism results in high sorption capacity of boron (0.6 mmol ml^{-1} = 2.1 mmol g^{-1}). The reaction can be expressed as:



where, HO-R represents hydroxyl groups attached to the NMDG moiety, glucamine ring of the chitosan base, and the arm of oxirane. The total number of HO-R is calculated to be 1.92 mmol ml^{-1} resin: (0.19 mmol ml^{-1}) x 4 + 0.58 mmol ml^{-1} + 0.58 mmol ml^{-1}. The first term corresponds to the hydroxyl groups of NMDG moiety, the second corresponds to the hydroxyl group of the glucamine of the base material, and the last one corresponds to hydroxyl group of the oxirane arm. Therefore, the number of HO-R(s) are enough for boron to form 1 : 2 complex with HO-R groups of the resin.

The reaction mechanism of boric acid with N-methyl-D-Glucamine (NMDG) in solution was clarified by Yoshimura *et al* [19]. The NMDG is an analogue to the functional group of boron resin (Amberlite IRA 743). The possible binding structure for complexes of borate with NMDG in aqueous solution is 1:1 tetradentate complex of borate with protonated glucamine and 1:2 bis-chelate complex with α, β-diol moieties of protonated glucamine. However, the binding mechanism of crosslinked polymer (Amberlite IRA 743) with boric acid is not yet clarified. According to that paper, boron species adsorb onto Amberlite IRA 743 resin at different pH, suggesting that only one chemical species of boron is adsorbed onto the resin. The equivalent molar ratios of boron adsorbed onto the resin to the total

fixed functional group, and the initial concentration of boron in aqueous solution indicated that boric acid/borate should bind to the fixed functional group of the resin with 1:1 stoichiometry. Thus, it was expected that boric acid/borate forms the 1:1 tetradentate complex with the anchor group of the resin. However, the binding structures of each 1:1 complex with NMDG are quite different in the aqueous solution and in the crosslinked polymer. Furthermore, the 1:1 tetradentate complex and 1:2 bis-chelate complex between boric acid/borate and NMDG are very stable even in acid solutions with the formation constants of $10^{4.9}$ and $10^{6.3}$ [19], respectively. Therefore, if the binding mechanism of boric acid with functional group of the resin is 1:1 tetradentate complex or 1:2 bis-chelate complex, the boron adsorbed on the resin would be very difficult to elute due to the high stability of the complexes. However, in our experiment, the boron adsorbed on the CCTS-NMDG resin is easily eluted using 1 mol l^{-1} nitric acid. Therefore, the alternative mechanism as explained earlier (esterification mechanism, similar as that with polyvinyl alcohol), was assumed to operate in boron`s adsorption.

Copper (II) ion can adsorb on the resin in pH range of 5 to 9. In the previous work [12], the CCTS itself could adsorb Cu at neutral pH region by the chelation mechanism. Similarly, in the present resin, Cu can form five-membered chelate rings with nitrogen atoms of amino groups and oxygen atoms of hydroxyl groups of chitosan as well as hydroxyl groups of NMDG moiety. The resin contains 0.58 mmol ml^{-1} of the secondary amines and 0.19 mmol ml^{-1} of the tertiary amines, so that the total amines are 0.77 mmol ml^{-1} resin. Oxoanions, such as As, V, Ga, and Bi, may adsorb on the resin at the protonated amino groups by anion exchange mechanism, as they had been found to adsorb on CCTS itself [11,12]. The CCTS showed strong adsorption efficiency for Sn at pH>2 [11], as results also obtained on the CCTS-NMDG resin. Other elements, such as Th, U, Pb, and Ni, could adsorb

on the resin at pH region above 7. However, their optimum pH ranges are higher than the optimum pH region for boron adsorption. Since some elements mentioned above can adsorb on the cross-linked chitosan itself, which was used as a base material of the CCTS-NMDG resin, or adsorbed at higher or lower pH than optimum pH for boron (pH 5 to 7), it can be suggested that the functional moiety of NMDG in the CCTS-NMDG resin is more effective for adsorption/collection of boron and less competitive with other ions at around neutral pH region.

The commercially available resins (Amberlite IRA 743 and Diaion CRB02), which have macro porous polystyrene matrices, also showed high selectivity for boron adsorption. However, fast kinetic performance and high sorption capacity attributed to the CCTS-NMDG resin is more important from a practical viewpoint.

Application of the CCTS-NMDG resin for boron collection in water samples and its measurement by ICP-MS and ICP-AES

The CCTS-NMDG resin was applied to the collection of boron from tap, river, estuarine, and ground waters. Estuarine water, which contains more sea salts than freshwater, but less than the open sea, has similarity in matrices to sea water. The matrices, such as Na, K, Mg and Ca can interfere with the determination of trace elements, as well as can damage the detector of the ICP-MS system. Therefore, the matrices must be removed from the samples prior to the measurement by ICP-MS. In addition, it is difficult to measure boron at trace level by ICP-MS because of its memory effect. The injection of dilute hydrogen peroxide solution is efficient in removing memorized boron from the sample introduction system, nebulizer, spray chamber and plasma torch [20].

Table 2 shows the results obtained on examining the effect of matrices, such as Na, K, Mg and Ca, on the recovery of boron using column pretreatment. The results

indicated that the CCTS-NMDG resin is capable of adsorbing boron quantitatively even in the presence of large amounts of matrices, whereas almost all alkali and alkaline earth metal ions could be removed in the range of 99.98% to 100% after the column pretreatment. Due to its great ability to remove matrices, the resin can be applied effectively to the collection of boron in natural river water and estuarine water or seawater. Table 2 also showed the recovery of boron present at various concentration levels in the sample solutions using 10 ml of 1 mol l^{-1} nitric acid as an eluent. In the wide concentration range of boron from 1 μg l^{-1} to 1 mg l^{-1}, the CCTS-NMDG resin could adsorb boron quantitatively with excellent recoveries (99.2% – 101.4%). These results indicate that the CCTS-NMDG resin has high potential to be applied as column packing material for uptake of boron/boric acid from its highly concentrated in aqueous solutions.

. Boron can be adsorbed completely by the CCTS-NMDG resin in the pH range of 5 to 7 as shown in Fig. 5. Therefore the pH adjustment of water samples is not required during column treatment. Table 3 showed the analytical results of boron in tap, river, estuarine, and ground waters obtained by direct measurement and column pretreatment method containing 1 ml of CCTS-NMDG resin. To demonstrate the ability of the resin for boron collection, the preconcentration of the water samples up to 10 fold using CCTS-NMDG column was also performed. The analytical results of boron in water samples obtained by the direct measurement and the measurement coupled with column pretreatment method were in good agreement with each other. The latter method, however, exhibits better precision as indicated by lower standard deviation. Shao *et al* [2] and Motomizu *et al* [18] reported the concentration of boron in tap and river water to occur in the range of 5 - 15 μg l^{-1} and 4 - 14 μg l^{-1}, respectively. In the present method, the concentration of boron in tap and river water was found to be in the range 6.4 - 6.7 μg l^{-1} and 8.1 –

8.4 μg l^{-1}, respectively. Therefore, the concentration of boron in present method was comparable to results reported previously

While boron in estuarine water sample must be diluted before the direct measurement by ICP-MS, the dilution of samples is unnecessary for ICP-AES determination. In ICP-MS, the dilution is required not only because of high concentration of boron in the sample, but also because high concentration of matrices can cause potential damage to the detector of ICP-MS. From Table 3, the concentration of boron in estuarine water was found to be about 0.34 mg l^{-1} after column pretreatment. This concentration is quite low in comparison to the boron level in open seawater, which is about 3 - 4 mg l^{-1}. The comparatively low boron concentration may be attributed to the sampling location. The estuarine water sample was taken from the estuary at the location where the Asahi River meets the Seto Inland Sea. Most of the part of sampling area is river water. Therefore, the seawater is extensively diluted about one tenth with river water, as concentration of chloride was about 2208 mg l^{-1} (= 0.06 mol l^{-1}).

From Table 3, it also can be seen that the direct measurement resulted in higher concentrations of boron than the measurement coupled with the column pretreatment method. However, in the latter method, the concentration of boron in estuarine water showed good agreement for each preconcentrated sample. The difference in the results between the direct measurement and the measurement coupled with column method can be attributed to high concentrations of organic substances in estuarine water samples. Direct ICP-MS measurement of sample containing relatively high concentrations of organic substances has possibility of generating further polyatomic interferences. In this case, the carbon-based interferences can be considered. Boron at m/z = 11 can be interfered by carbon (m/z = 12, tail at low mass) [15]. To confirm the analytical results for the estuarine

water, the sample was spiked with 1000 μg l^{-1} of boron and then passed through the CCTS-NMDG column. The result (Table 4) showed that the recovery of boron added to the sample was almost 100%, determined either by ICP-MS or ICP-AES. Thus, the CCTS-NMDG resin is found to be favorable for the collection/concentration of boron in water samples, even in the presence of high concentrations of inorganic and organic matrices contained in the sample.

Analytical merits

The preferable working range for boron measurement was 0-20 μg l^{-1} (ICP-MS), and 0-10 mg l^{-1} (ICP-AES). Therefore, if the concentration of boron over these ranges, it had to be diluted to reach the working range concentration.

The limit of detection (LOD) was calculated from the sum of average concentration of reagent blank and 3σ of reagent blank (LOD : blank + 3σ , σ : standard deviation of reagent blank), while limit of quantification (LOQ) was calculated from the sum of average concentration of reagent blank and 10σ (LOD : blank + 10σ). The LOD of boron after pretreatment with CCTS-NMDG resin and measurement by ICP-MS was 0.07 μg $l^{-1}$and the LOQ was 0.14 μg l^{-1} when the volume of each sample and eluent was 10 ml. The standard deviation and relative standard deviation from 10 measurements of 1 μg l^{-1} boron using ICP-MS (after column pretreatment) was 0.018 and 1.8%, respectively.

The LOD of boron using ICP-AES was 0.05 mg l^{-1}, while the LOQ was 0.15 mg l^{-1} when the volume of each sample and eluent was 10 ml. The standard deviation and relative standard deviation from 10 measurements of 1 mg l^{-1} boron using ICP-AES (after column pretreatment) was 0.045 and 4.5%, respectively.

Conclusions

The CCTS-NMDG resin showed a reasonably high ability in boron sorption with the adsorption capacity of 2.1 mmol g^{-1} of the resin. To the best of our knowledge, the CCTS-NMDG resin has the fastest rate of boron sorption compared to other resins previously reported. Because of the fore mentioned advantages of the resin, it can be applied as a column packing material for the collection of boron/boric acid from aqueous solutions containing high concentration of these species. Other advantages of the resin developed in this work are its ability to (1) quantitatively collect/adsorb boron at neutral pH regions, (2) completely eliminate large amounts of Na, K, Mg, Ca matrices by passing the solution through a small resin column, (3) retain its optimum performance despite long term usage (at least 20 times), (4) effectively collect boron in many water samples such as tap, river, estuarine, and ground waters using 1 ml resin in a mini column accompanied easy dilution with 1 M nitric acid.

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Acknowledgements

The present work was partially supported by the Grant-in-Aid for Scientific Research (C) no 15550138 from Japan Society for the Promotion of Science (JSPS).

References

1. M.O Simonnot, C. Castel, M. Nicolai, C. Rosin, M. Sardin, H. Jauffret, *Wat. Res.*, 2000, 34, 109.
2. C. Shao, S. Matsuoka, Y. Miyazaki, K. Yoshimura, *Analyst*, 2002, 127, 1614.
3. L.E, Vanatta, D.E., Coleman, R.W., Slingsby, *J. Chromarogr.A,* 1999,850,107.
4. N. Biçak, B.F., Senkal, *J. Appl. Polym. Sci.,* 1998, 68, 2113

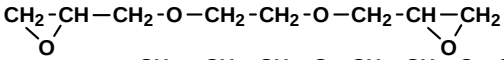
5. N. Biçak, H.O, Özbelge, L. Yilmaz, B.F. Senkal, *Macromol. Chem. Phys.,* 2000, 201, 577.
6. N. Biçak, N. Bulutçu, B.F., Senkal, M.Gazi, *React. Funct. Polym.,* 2001, 47, 175.
7. H. Maeda, H. Egawa, A. Jyo, *Sep. Sci. Technol.,* 1995, 30, 3545.
8. B.M. Smith, P. Tood, C.N. Bowman, *Sep. Sci. Technol.,* 1999, 34, 1925
9. A. Jyo, S. Aoki, M. Uchimura, K. Yamabe, T. Sugo, *Anal. Sci.(Supplement),* 2001, 17, i1211
10. K. Oshita, M. Oshima, Y. H. Gao, K. H. Lee, S. Motomizu, *Anal. Sci*., 2002, *18*, 1121.
11. Y. H. Gao, K. Oshita, K. H. Lee, M. Oshima, S. Motomizu, *Analyst*, 2002, *127*, 1713.
12. K. Oshita, Y. H. Gao, Oshima M, S. Motomizu, *Anal. Sci. (Supplement)*, 2001, *17*, a317.
13. K. Oshita, M. Oshima, Y. H. Gao, K. H. Lee, and S. Motomizu, *Anal. Chim. Acta*, 2003, *480*, 239.
14. K. Oshita, J. Xu, Y. H. Gao, K. H. Lee, M. Oshima, and S. Motomizu, *Bull. Chem. Soc. Jpn*., 2003, *76*, 1555
15. http://www.chem.agilent.com/cag/other/EKC_article.pdf
16. http://www.sigmaaldrich.com/Brands/Aldrich/Technical_Bulletins/AL_142/Amberlite___Amberlyst.html#A2
17. http://www.diaion.com/Diaion_Tables/Diaion_CRtable_R_E.htm
18. S. Motomizu, M. Oshima, Z. Jun, *Anal. Chim. Acta*., 1991, 251, 269
19. K. Yoshimura, Y. Miyazaki, F. Ota, S. Matsuoka, H. Sakashita, *J. Chem. Soc., Faraday Trans.,* 1998, 94, 683
20. I. Kano, D. Darbouret, *Ultrapure Water for Boron and Silica Sensitive Laboratory Applications*, The R&D Notebook, a publication of the laboratory

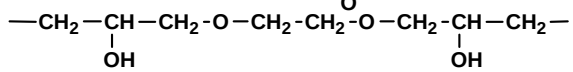
Water Division of Millipore, RD003,1999, p.4.

21. David R. Lide, *Handbook of Chemistry and Physics*, CRC press, New York, 81st edition, 2000, p 8-50

Figure captions

Fig. 1 Scheme for the synthesis of the CCTS-NMDG resin.

EGDE: 

Cross-linking: 

CCTS-NMDG : cross-linked chitosan possessing N-methyl-D-glucamine moiety

Fig. 2 Acid-base titration curve of the CCTS-NMDG resin.

A sample used for the titration consists of 1 ml of the CCTS-NMDG resin (wet volume), 2 ml of 0.1 mol l^{-1} hydrochloric acid and 28 ml of the ultrapure water.

A: the inflection point of hydrochloric acid; B C: the inflection points of CCTS-NMDG resin; D, E: half point of each equivalent point.

Fig. 3 Relationship between the time and the adsorption amounts (mmol ml^{-1}) of B and Cu adsorbed on the CCTS-NMDG resin at pH 6.5.

CCTS-NMDG resin: 1 ml (wet volume); concentration of each element : 0.01 mol l^{-1} ; volume of the solution: 100 ml.

Fig.4 Sorption kinetic of boron on the CCTS-NMDG and Amberlite IRA 743 resins.

Sample: 100 ml of 100 mg l^{-1} B at pH 6.5; amounts of each resin: 1 g.

Fig. 5 Adsorption behavior of trace elements at various pHs on the CCTS-NMDG resin.

Sample: 10 ml, concentration of each element :10 μg l^{-1}, column: 1 ml of the CCTS-NMDG resin, eluent :10 ml of 1 mol l^{-1} HNO_3 .

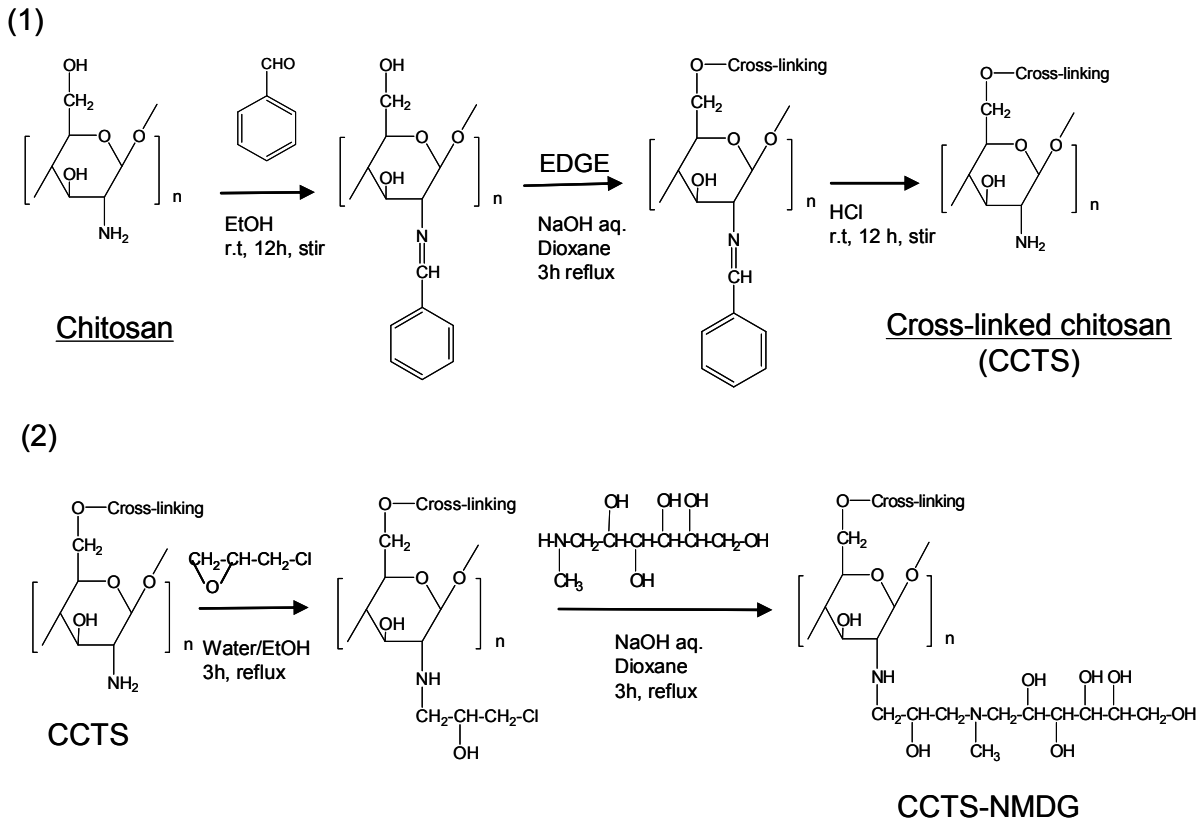


Figure 1

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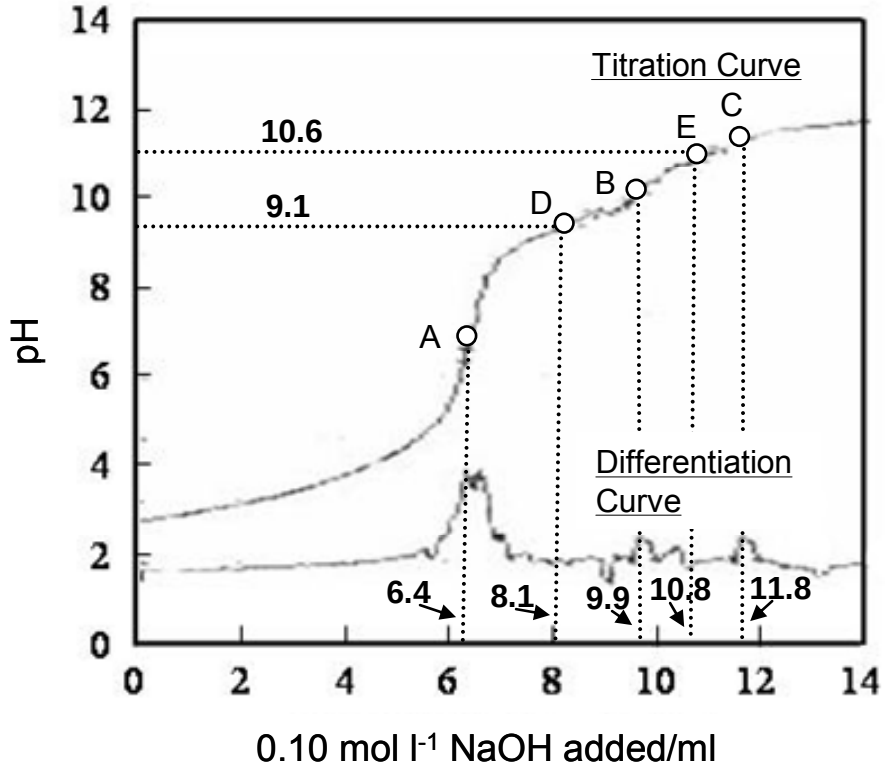

Figure 2
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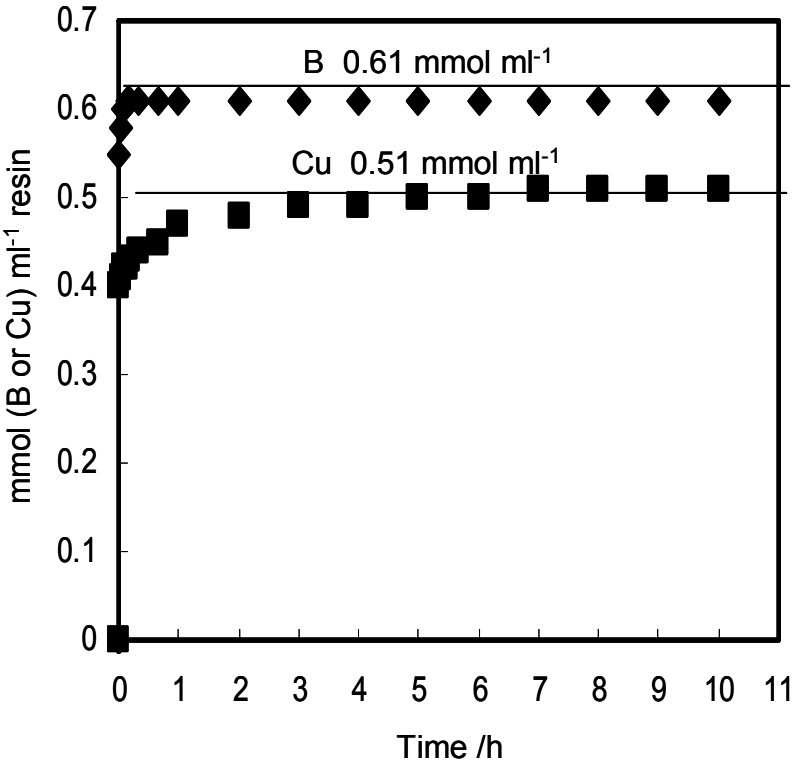

Figure 3
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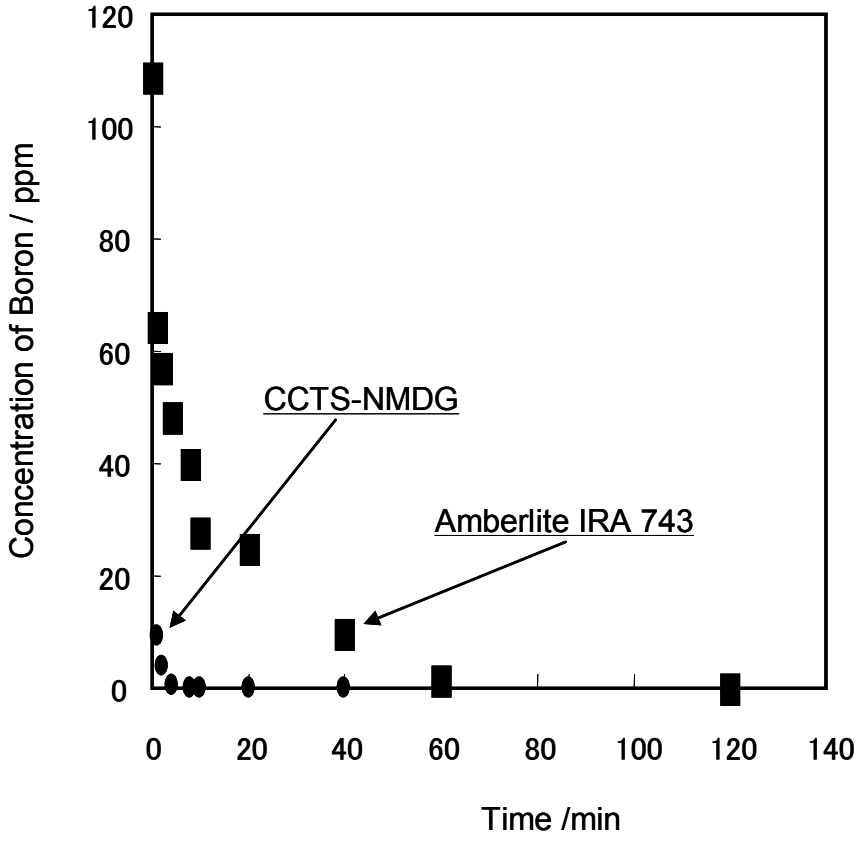

Figure 4
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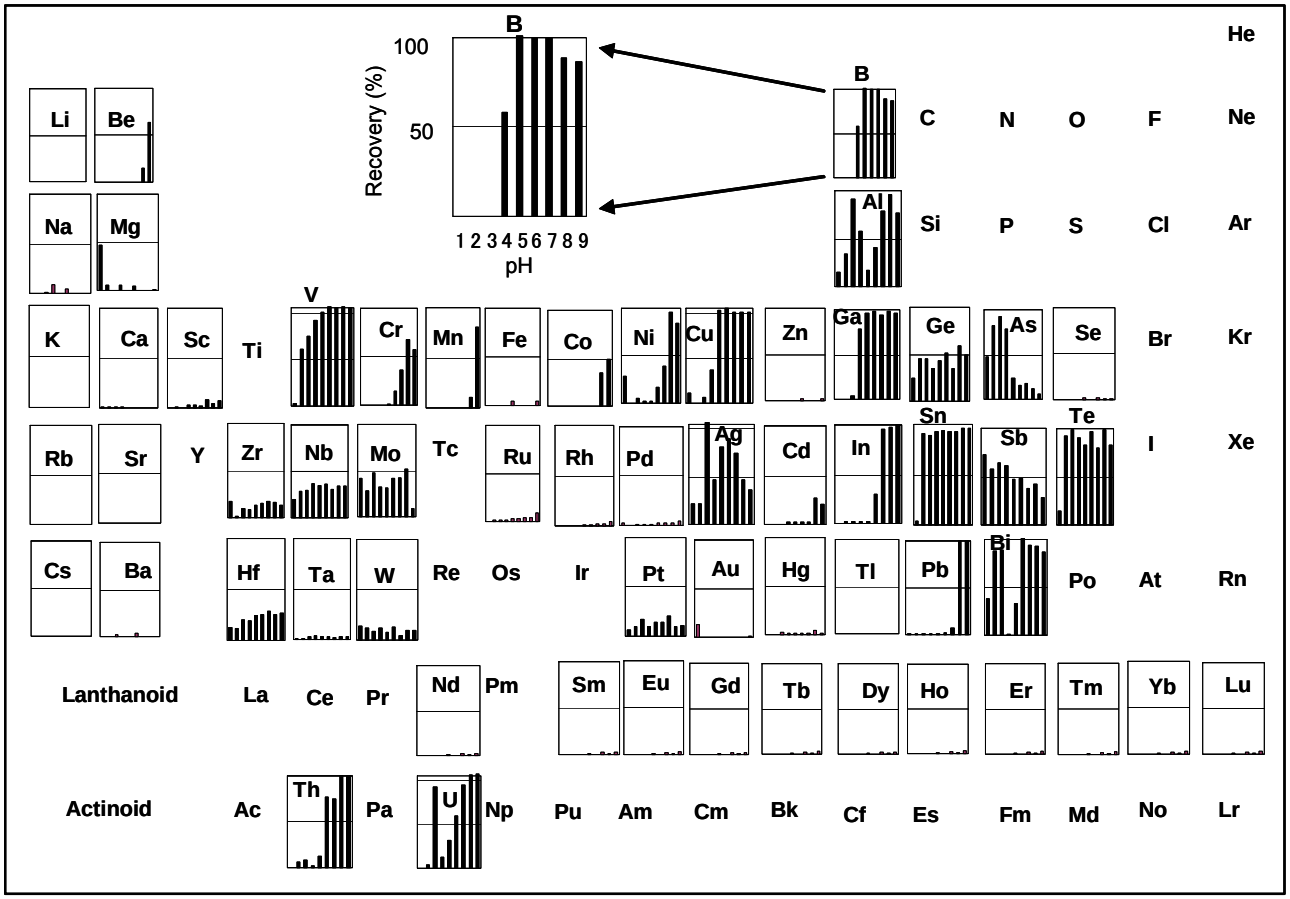

Figure 5
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Table 1 Comparison of sorption capacity and sorption kinetic of boron on several resins having poly-ol functionality

Resin	Base material	Moiety	Sorption capacity mmol g^{-1}	Sorption rate	Reference
Amberlite IRA 743	Polystyrene	NMDG	0.6 (meq ml^{-1})	Slow[a*a]	9, 16
Diaion CBR02	Polystyrene	NMDG	>0.6 (meq ml^{-1})	-	9, 17
FNmg-f	GMA-grafted PPE-f	NMDG	1.3	-	9
FTris-f	GMA-grafted PPE-f	Tris	1.0	-	9
Sorbitol-modified polymer	Polystyrene	sorbitol	1.2	Slow[*b]	4
GMHP polymer	Polyethylene	NMDG	2.1	Slow[*c]	5
GMA-modified polymer	Cross-linked GMA-MMA-DVB	NMDG	2.2	Moderate[*d]	6
CCTS-NMDG	CCTS	NMDG	2.1	Fast[*e]	this work

NMDG : N-methyl-D-Glucamine; Tris : tris(hydroxymethyl)amino methane; GMA: glycidyl metacrylate; MMA: methyl metacrylate; DVB: divinylbenzene; CCTS: cross-linked chitosan; GMHP; N-glucidol-N-methyl-2-hydroxypropyl metacrylate; PPE-f: polyethylene coated polypropylene fiber.

[*]a : 100 mg l^{-1} of boron goes down to zero within 60 min

*b : 33 mg l^{-1} of boron goes down to zero within 30 min

*c : 31 mg l^{-1} of boron goes down to zero within 15 min

*d : 100 mg l^{-1} of boron goes down to zero within 30 min

*e : 100 mg l^{-1} of boron goes down to zero within 10 min

Table 2 Recovery of boron adsorbed on the CCTS-NMDG resin at pH 6.5

	Boron added[a]					
	1 μg l^{-1}	2 μg l^{-1}	10 μg l^{-1}			1 mg l^{-1}
	Standard[b]	Standard[b]	Standard[b]	Artificial river water[c]	Artificial sea water[d]	Standard[b]
Recovery (%)[f]	101.3 ± 1.8	100.9 ± 0.3	101.1 ± 0.1	101.4 ± 1.6	99.2 ± 2.9	100.2 ± 1.4[e]

[a] Samples, 10 ml, were treated at pH 6.5 with the column (CCTS-NMDG resin: 1 ml). Eluents, (1 mol l^{-1} HNO_3): 10 ml. The eluents were measured by ICP-MS.

[b] The sample contains boron without addition of Na, K, Mg, and Ca matrices

[c] The samples contains boron and metal ions: Na, 20 mg l^{-1}; K, 10 mg l^{-1}; Mg, 15 mg l^{-1}; Ca, 50 mg l^{-1}.

[d] The sample contains boron and metal ions: Na, 11500 mg l^{-1}; K, 3900 mg l^{-1} m; Mg, 1200 mg l^{-1}; Ca, 400 mg l^{-1}.

[e] The sample is measured by ICP-MS after appropriate dilution

[f] Average from three measurements.

Table 3 Analytical results of boron in water samples

Sample	Boron found ($\mu g\ l^{-1}$)[a]			
	Direct	Column pretreatment[b]		
		1-fold preconcentration	5-fold preconcentration	10-fold preconcentration
Tap water[c]	6.5 ±0.3	6.6 ±0.2	6.4 ±0.2	6.7 ±0.1
River water[c]	8.1 ±0.2	8.3 ±0.1	8.3 ±0.1	8.4 ±0.1
Ground water[c]	19.5±0.4	19.6 ±0.0	19.7 ±0.2[e]	19.4 ±0.1[e]
Estuarine water[c]	405 ±12[e]	336±4[e]	338 ±8[e]	338 ±3[e]
Estuarine water[d]	427±24	341±4	343±8	337 ±1

[a] Means with ± standard deviation (σ)

[b] Each sample, 10 ml, 50ml, 100 ml was passed through the column (CCTS-NMDG resin: 1 ml). Eluent was 10 ml of 1 mol l^{-1} HNO_3.

[c] Measured by ICP-MS

[d] Measured by ICP-AES

[e] Measured by ICP-MS after appropriate dilution

Table 4 Analytical results of spiking boron in estuarine water samples with column pretreatment

Sample[b]	Boron added ($\mu g\ l^{-1}$)	B Found ($\mu g\ l^{-1}$)[a]	
		ICP-AES	ICP-MS[c]
Estuarine water	-	341 ± 4	336 ± 4
	1000	1339 ± 4	1337±1
Recovery (%)		99.4	100.3

[a] Means with ± standard deviation (σ)

[b] Sample, 10 ml, was passed through the column (CCTS-NMDG resin: 1 ml). Eluent was 10 ml of 1 mol l^{-1} HNO_3.

[c] Measured after appropriate dilution