Introduction

Solid-phase extraction using a chelating resin is one of the practical methods for separating and preconcentrating trace elements in an aqueous solution.1–3 Since a variety of chelating resins are commercially available, users are able to select an appropriate resin for their own purpose. The behavior of a chelating resin for solid-phase extraction of major, minor, and trace elements is generally governed by the complexing ability of a functional group immobilized on the resin. Aminocarboxylic acid, such as iminodiacetic acid (IDA) and nitrilotriacetic acid (NTA), is a popular functional group because aminocarboxylic acid can form complexes with various elements; many kinds of chelating resins immobilizing IDA, such as Chelex 100,4–11 Muromac A-1,12–14 Lewatit TP 207,11,15,16 and immobilizing NTA, such as NTA Superflow,8,17,18 can be purchased from various suppliers. However, these resins have some serious drawbacks. One is that Mg and Ca, which sometimes interfere with the determination of target elements, are extracted in significant amounts even under weakly acidic conditions. The efficiency of the extraction using the IDA-type chelating resin also considerably decreases with increasing flow rate during the solid-phase extraction.

To overcome these problems, some chelating resins that feature improvements in both selectivity and the efficiency have been developed. Nobias Chelate-PA119–29 has both IDA and ethylenediaminetriacetic acid (EDTriA) as functional groups. This resin is able to extract various elements simultaneously over a wide pH range, and Mg and Ca are captured in only small amounts at pH levels below 7. Such performance of this resin is highly attractive for analyses of real samples containing large amounts of Mg and Ca. Solid-phase extraction using this resin has been applied to separating and preconcentrating trace elements in various samples, including seawater,19–24,27–29 river water,19 salt,28 bone,25 blood,25 and urine.26 Recently, Presep® PolyChelate has also become commercially available. This resin contains carboxymethylated polyethyleneimine as a functional group.30 In general, the stability constant for a complex of a transition element with aminocarboxylic acid as well as the difference between the stability constant of alkaline earth elements and that of a transition element increases with an increase in the number of ethyleneamine units in aminocarboxylic acids.31 Based on this information and the performance of Nobias Chelate-PA1 and the chelating resin immobilizing carboxymethylated pentaethylenehexamine,32–34 Presep® PolyChelate is expected to show excellent potential for separating and preconcentrating trace elements. However, only a few reports including solid-phase extraction using Presep® PolyChelate have been published so far.35

In this paper, the potential of Presep® PolyChelate as a chelating resin is studied in detail. The chelating resin with extraction capacity for Cu of 0.30 mmol L–1 could quantitatively extract Cd, Co, Cu, Fe, Mo, Ni, Pb, V, and Zn at pH 4 or 5.5; however, only very scant amounts of Na, K, Mg, and Ca were captured at pH levels below 7. The quantitative extraction could be achieved in 100 – 1000 mL of artificial seawater and at a flow rate of 3 – 30 mL min–1. The performance of Presep® PolyChelate was compared to the other aminocarboxylic acid-type chelating resins, including Nobias Chelate-PA1, Chelex 100, Muromac B-1, Lewatit TP 207, and NTA Superflow, under the same conditions. The solid-phase extraction of the nine elements in the certified reference material (ES-L-1, ground water) and a commercially available table salt was also demonstrated.

Keywords Presep® PolyChelate, aminocarboxylic acid-type chelating resin, solid-phase extraction, trace elements, table salt

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Experimental

Apparatus
To measure the diameter of the chelating resin, a Hitachi High-Technologies (Japan) TM-1000 miniscope was used as a scanning electron microscope (SEM) and a Nikon (Japan) Eclipse TS100 inverted routine microscope was also used as an optical one. The infrared (IR) spectra of chelating resins were obtained using a Nicolet 6700 Fourier transform infrared spectrometer (Thermo Fisher Scientific, USA) equipped with a horizontal attenuated total reflectance (HATR) accessory (PIKE Technologies, USA); a ZnSe element was used for the measurement of ATR-IR. A PerkinElmer (USA) Optima 7300DV inductively coupled plasma atomic emission spectrometer (Thermo Fisher Scientific, USA) equipped with a three-channel ICP-OES detector was used for the solid-phase extraction experiments. The other reagents used were of extra-pure, guaranteed, or analytical grade.

Reagents
Deionized water obtained by a Milli-Q Gradient A10 (Millipore, USA) was used in all experiments. Presep® PolyChelate was purchased from Wako Pure Chemical Industries (Japan). For comparison, five kinds of commercially available chelating resins (aminocarboxylic acid-type), which have been applied for separating and preconcentrating trace elements, were also used; the information regarding the chelating resins, including Presep® PolyChelate, is summarized in Table 1. A standard solution containing 21 kinds of elements (ICP multi-element standard solution XVI, Merck, Germany) was used for the solid-phase extraction experiments. The other reagents used were of extra-pure, guaranteed, or analytical reagent grade.

Procedures
Microscope observation and measurement of IR spectrum. Presep® PolyChelate or the other chelating resin was washed with a mixture of methanol and deionized water, then placed in a beaker containing 1 mol L⁻¹ hydrochloric acid. The beaker was placed under ultrasonic irradiation for 20 min, and the resin was then washed with deionized water after the filtration. These operations were repeated. The resin was thoroughly washed with deionized water and then with methanol under ultrasonic irradiation. After the filtration, the resin was dried under vacuum. The obtained resin was used for SEM observation and measurement of IR spectrum. The observation of the resin using the optical microscope was conducted after immersing the resin in a 0.1 mol L⁻¹ sodium acetate solution and then left standing for 48 h at room temperature. Extraction capacity for Cu. A solution containing 5 mmol L⁻¹ Cu (pH 5) was prepared by dissolving copper(II) sulfate hexahydrate in deionized water. The commercially available chelating resin (approximately 0.05 g dry weight) was added to 20 mL of the solution, and the solution was then shaken at 120 rpm for 24 h at room temperature. The Cu remaining in the solution was determined.

Solid-phase extraction. For the evaluation of the solid-phase extraction potential of the chelating resin, a deionized water-based test solution (100 – 1000 mL) containing 10 μg of each element and 5 mmol L⁻¹ ammonium acetate solution were used; the solution pH was adjusted using nitric acid and aqueous ammonia. The artificial seawater-based test solution was also used to investigate the effect of coexisting ions. The artificial seawater was prepared according to the literature. The appropriate amount of each element and 50 mL of 0.1 mol L⁻¹ ammonium acetate solution were added to 1000 mL of the artificial seawater and the solution pH was adjusted before use.

Presep® PolyChelate or the other chelating resin (0.25 g dry weight) was packed in 6 mL of a reservoir for solid-phase extraction (GL Sciences, Japan). The resin was conditioned by passing 5 mL of methanol, 10 mL of 3 mol L⁻¹ nitric acid, 20 mL of deionized water, and 10 mL of a 0.1 mol L⁻¹ ammonium acetate solution through the reservoir, in that order. The test solution (100 – 1000 mL) was then passed through the reservoir at a flow rate of 3 – 30 mL min⁻¹. After the resin was washed using approximately 20 mL of deionized water, the extracted elements were eluted by passing 3 mL of 3 mol L⁻¹ nitric acid and then approximately 3 mL of deionized water through the reservoir-packed resin. The eluate was diluted to 10 mL with deionized water, and the elements in the solution were determined.

Analyses of certified reference material and table salt. To 300 mL of the certified reference material, EnviRoMAT™ ES-L-1 ground water (SCP Science, Canada), or a solution

<table>
<thead>
<tr>
<th>Chelating resin</th>
<th>Base polymer</th>
<th>Functional group</th>
<th>Diameter [μm]</th>
<th>Extraction capacity for Cu [mmol g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Presep® PolyChelate (Wako Pure Chemical Industries, Japan)</td>
<td>MA</td>
<td>CM-PEI</td>
<td>59.4 ± 5.9</td>
<td>0.30</td>
</tr>
<tr>
<td>Nobius Chelate-PA1 (Hitachi High-Technologies, Japan)</td>
<td>MA</td>
<td>EDTriA, IDA</td>
<td>65.2 ± 8.7</td>
<td>0.15</td>
</tr>
<tr>
<td>Chelex 100 (200 – 400 mesh) (Bio Rad Laboratories, USA)</td>
<td>ST/DVB</td>
<td>IDA</td>
<td>74.3 ± 15.3</td>
<td>0.75</td>
</tr>
<tr>
<td>Muromac B-1 (Muromachi Chemicals, Japan)</td>
<td>ST/DVB</td>
<td>IDA</td>
<td>505 ± 77</td>
<td>1.39</td>
</tr>
<tr>
<td>Lewatit TP 207 (LANXESS, Germany)</td>
<td>PS</td>
<td>IDA</td>
<td>504 ± 41</td>
<td>1.93</td>
</tr>
<tr>
<td>NTA Superflow (QIAGEN, Germany)</td>
<td>AG</td>
<td>NTA</td>
<td>52.8 ± 15.6</td>
<td>—d</td>
</tr>
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Table 1 Information regarding chelating resins used for this investigation

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containing 15 g of a commercially available table salt (Japan) and 0.1 mol L⁻¹ nitric acid, 15 mL of 0.1 mol L⁻¹ ammonium acetate solution was added. The solution pH was then adjusted to 4 or 5.5. Solid-phase extraction was conducted at a flow rate of 3 mL min⁻¹. The elements in the solution after the solid-phase extraction were determined; the limits of detection in this method are summarized in Table S3 (Supporting Information). For the analysis of the table salt, the recovery tests were also conducted using the solution spiked with 5 μg of each element.

Results and Discussion

The particle sizes of the chelating resins are summarized in Table 1. The diameter of dried Presep® PolyChelate (59.4 ± 5.9 μm) was similar to those of dried Nobias Chelate-PA1, Chelex 100, and NTA Superflow, whereas it was much smaller than those of dried Muromac B-1 and Lewatit TP 207. The particle sizes in 0.1 mol L⁻¹ sodium acetate solution were little changed for Presep® PolyChelate and Nobias Chelate-PA1, although for the other resins the diameters became 1.2 - 1.6 times larger than those of the dried particles. This was due to the difference in the base polymers (Table 1). The ATR-IR spectrum of Presep® PolyChelate was almost the same as that of Nobias Chelate-PA1 (Fig. S1, Supporting Information). Similar spectra were also obtained in Chelex 100, Muromac B-1, and Lewatit TP 207 (Fig. S1).

The extraction capacities for Cu are also appended in Table 1. NTA Superflow was not investigated because the amount of the resin available for this investigation was not enough. For Presep® PolyChelate, the extraction capacity was 0.30 mmol g⁻¹, which was 2 times larger than that for Nobias Chelate-PA1. Chelex 100, Muromac B-1, and Lewatit TP 207 had large extraction capacities compared to Presep® PolyChelate.

The effect of pH on the solid-phase extraction using Presep® PolyChelate was investigated using 100 mL of the test solution at a flow rate of 3 mL min⁻¹. The obtained results are shown in Fig. 1 (for eight elements) and Figs. S2 and S3 (for the others, Supporting Information). The elements Cd, Cu, and Pb were recovered over a wide pH range. The recovery of Mn increased with an increase in the solution pH, and high recoveries were obtained at pH levels above 5.5. The element V was quantitatively recovered in the pH range from 2 to 7. The recovery of Mo, which is present as oxoanion in the solution, was almost 100% under acidic and neutral conditions. This result would indicate that the CM-PEI as a functional group has the ability to extract elements based on the anion exchange mechanism as well as chelation. The elements Co, Fe, Ni, Ti, and Zn were also quantitatively recovered as shown in Figs. S2 and S3. On the other hand, Mg, Ca (Fig. 1), and Sr (Fig. S3) were barely recovered at pH 7 or below. For comparison, the solid-phase extraction behavior using the other chelating resins are also shown in Fig. 1 and Figs. S2 and S3. Similar tendencies were obtained for Cd, Cu, Pb, V (Fig. 1), Co, Fe (Fig. S2), Ni, Ti, and Zn (Fig. S3) when Nobias Chelate-PA1, Chelex 100,
and NTA Superflow were used. For Cd, Cu, Co, Ni, and Zn, the recoveries at pH 2 were insufficient when using all of the resins; however, Presep® PolyChelate gave the highest recovery. This may be due to the high complexing ability of the immobilized functional group, carboxymethylated polyethyleneimine. For Mn, almost the same results were obtained in Presep® PolyChelate and Nobias Chelate-PA1; however, Chelex 100 and NTA Superflow were able to recover Mn at pH above 3. When Muromac B-1 and Lewatit TP 207 were used, the recoveries of these elements were insufficient. As shown in Table 1, the diameters of these resins were much larger than those of the others. Increasing the amount of resin and/or decreasing the flow rate would improve recovery of the elements. For Mg and Ca, the behavior using Presep® PolyChelate was almost the same as that using Nobias Chelate-PA1; however, the other chelating resins also captured these elements even at pH 3. The effect of flow rate was then investigated using 100 mL of the test solution at pH 5.5. The obtained results for Cd and Cu are shown in Fig. 2. For Presep® PolyChelate, the recoveries were not affected at flow rates of up to 30 mL min⁻¹. Nobias Chelate-PA1 gave similar tendencies (Fig. 2). For NTA
Superflow, the recoveries were quantitative at flow rates of up to 10 mL min\(^{-1}\); however, it was difficult to flow the test solution at higher than 10 mL min\(^{-1}\). This may be because of the relatively small particle size (Table 1) and the swelling effect. For the other chelating resins, the recoveries considerably decreased with increasing flow rate. Such performance can be attributed to the difference in the hydrophobicity of the base polymer, the particle size of the resin, and/or the complexing ability of the functional group. The effect of volume of the test solution was also investigated at the flow rate of 3 mL min\(^{-1}\) and pH 5.5. In this investigation, 100 - 1000 mL of the test solutions spiked with 10 \(\mu\)g of each element were used. As shown by the results for Cd and Cu in Fig. 3, the quantitative recoveries were obtained without any influence from the solution volume. Nobias Chelate-PA1, Chelex 100, and NTA Superflow were also able to recover these elements quantitatively in solution volumes of up to 1000 mL. In these investigations, similar results were obtained for the other elements.

The investigations for Presep\textsuperscript{®} PolyChelate and Nobias Chelate-PA1 were also conducted using the artificial seawater-based test solution. The obtained results are shown in Figs. 1 and 4 and Figs. S2 and S3. The recoveries of Mn and Mo decreased under weakly acidic and neutral conditions, respectively; however, for the other elements, the obtained results were almost the same as those using the deionized water-based test solution. For Mn, the stability constant of the complex with aminocarboxylic acid is lower than those for the other elements, such as Cd, Cu, and Pb;\textsuperscript{11} the extraction of Mn was more easily affected by the presence of coexisting ions compared with the other elements. The presence of coexisting anions in large amounts may also interfere with the extraction of Mo, if the extraction obeys the anion exchange mechanism. On the other hand, Na, K, Mg, Ca, and Sr, which were contained in the artificial seawater-based test solution at high concentration levels, were scarcely recovered at pH up to 7. The effect of flow rate and solution volume was also investigated. As appended in Figs. 2 and 3, no significant influence was observed. These results were comparable to those using Nobias Chelate-PA1 (Figs. 1 - 4 and Figs. S2 and S3).

The solid-phase extraction of nine elements (Cd, Co, Cu, Fe, Mo, Ni, Pb, V, and Zn), which could be efficiently recovered using Presep\textsuperscript{®} PolyChelate, in the certified reference material, ES-L-1 (ground water), and a commercially available table salt was then demonstrated. For the certified reference material, the obtained values at both pH 4 and 5.5 were nearly equal to the certified values (Table S4, Supporting Information). For the table salt, some elements in the salt could be determined (Table S5, Supporting Information). When the solution pH was adjusted to 5.5, the recovery of Mo was insufficient. However, the recovery improved by adjusting the pH to 4. The recoveries of Mg and Ca were less than 1%. Only 5 \(\mu\)g (pH 5.5) or 0.9 \(\mu\)g (pH 4) of Mg was recovered from the solution dissolving 15 g of the table salt, which contained 2.4 mg of Mg. The recovered amount of Ca was also only 5 \(\mu\)g at pH 5.5 or 0.5 \(\mu\)g at pH 4, although the solution before the extraction contained 9.6 mg of Ca.

**Conclusions**

From the obtained results, it can be seen that Presep\textsuperscript{®} PolyChelate shows excellent potential for the solid-phase extraction of the nine elements Cd, Co, Cu, Fe, Mo, Ni, Pb, V, and Zn. Extraction can be achieved even at a flow rate of 30 mL min\(^{-1}\). The elements Na, K, Mg, and Ca, in contrast, were barely captured on the resin at pH levels below 7. Such performance is comparable to that of Nobias Chelate-PA1 and is superior to those of the other commercially available aminocarboxylic acid-type chelating resins used for this study. Solid-phase extraction using Presep\textsuperscript{®} PolyChelate is applicable to analyses of the certified reference material (ground water) and commercially available table salt. This method would also be useful for analyses of various real samples.

**Acknowledgements**

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Supporting Information

Additional information and data, including operating conditions for ICP-AES, ATR-IR spectra of the chelating resins, effect of pH on the solid-phase extraction of some elements, the limit of detection, and the results for analyses of the certified reference material and the commercially available table salt, are given as Supporting Information. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References