Phosphomethylated Polyethyleneimine-immobilized Chelating Resin: Role of Phosphomethylation Rate on Solid-Phase Extraction of Trace Elements

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Abstract

Chelating resins immobilizing phosphomethylated polyethyleneimine (PM-PEI) that had different phosphomethylation (PM) rates were prepared by using the different amounts of both phosphonic acid and paraformaldehyde in the phosphomethylation of PEI immobilized on a methacrylate resin as a base resin. The extraction of many elements improved with increasing the PM rate; REEs, Be, Fe, Mo, Ti, and V were quantitatively extracted at pH 2. The elution of the elements tended to become difficult with increasing the PM rate. When a PM-PEI resin with a PM rate of 0.26 was used, REEs and Be could be eluted using 0.2 mol L⁻¹ EDTA solution adjusted to a pH of 7 and 3 mol L⁻¹ nitric acid, respectively, although the elution of Fe, Mo, Ti, and V was insufficient. The PM-PEI resin could be reused at least 10 times to recover REEs and Be without the influence of any other elements. The PM-PEI resin could be applied to a recovery test using artificial seawater spiked with REEs, except for Sc, Tm, Yb, and Lu, and the separation of the REEs in NIST SRM 1515 Apple Leaves.

Keywords: Solid-phase extraction, chelating resin immobilizing phosphomethylated polyethyleneimine, phosphomethylation rate, aminophosphonic acid, trace elements, rare earth elements
Introduction

Chelating resin immobilizing aminophosphonic acid as a chelating group is one material useful for the solid-phase extraction of trace elements, including rare earth elements (REEs). Since this type of chelating resin can be purchased from some suppliers, commercially available chelating resins as well as self-made chelating resins were applied to the recovery, removal, and preconcentration of the elements. The chelating resin immobilizing aminophosphonic acid has a strong affinity for alkaline earth elements, such as Ca. However, this feature is often troublesome when the chelating resin is used for separating and preconcentrating trace elements. Various samples contain alkaline earth elements at relatively high concentrations; the presence of the elements sometimes suppresses the extraction of trace elements and interferes in their subsequent determination by atomic spectroscopy.

Recently, it has been found that a chelating resin immobilizing carboxymethylated polyethyleneimine (CM-PEI), which is classified as an aminocarboxylic acid group, is a material capable of achieving a selective extraction of some trace elements. The CM-PEI resin is prepared by immobilizing PEI on a methacrylate resin and then carboxymethylating the PEI on the resin with sodium monochloroacetate. The carboxymethylation (CM) rate, which is defined as the ratio of the amount of the carboxylic acid group to that of the amino group in the PEI, can be controlled by the amount of monochloroacetate used for the carboxymethylation process. The CM rate considerably affects the solid-phase extraction behavior of trace elements. Both the aminocarboxylic acid group and the amino group are on the chelating resin having a low CM rate. It is thought that the aminocarboxylic acid group mainly functions to extract elements, and the amino group, which is protonated under acidic and neutral conditions, suppresses the extraction of some cations, such as alkaline earth elements, which are weakly complexed with aminocarboxylic acid.

The amino group in the PEI can also be phosphomethylated using phosphonic acid and (para)formaldehyde under acidic condition. It is expected that the phosphomethylation (PM) rate can be controlled by the amounts of phosphonic acid and paraformaldehyde used for the phosphomethylation step. The solid-phase extraction behavior of trace elements with the chelating resin immobilizing phosphomethylated PEI (PM-PEI) seems to be governed by the PM rate, which means the ratio of the amount of the phosphonic acid group to that of the amino group in the PEI. However, to our knowledge, no report has focused on the relationship between the solid-phase extraction behavior and the PM rate until now.
In this work, we investigate the solid-phase extraction behavior of 37 kinds of trace elements, including REEs and 21 additional elements, with the chelating resin immobilizing the PM-PEI. A PEI having a molecular weight of approximately 600 is used because it is suitable for the preparation of the CM-PEI resin. The investigation is conducted regarding the preparation of PM-PEI resins with different PM rates. Using the obtained chelating resins, the effect of the PM rate on the solid-phase extraction of trace elements is investigated. The results of the fundamental investigation for application of the PM-PEI resin to the solid-phase extraction of REEs are also reported.

Experimental

Apparatus

The Beckman Coulter Multisizer 3 Coulter Counter and SA3100 Surface Area Analyzer were used for the characterization of a base resin. An Elementar vario MICRO cube was used for the elemental analysis of a resin immobilizing PEI. X-ray photoelectron spectroscopic (XPS) analyses of PM-PEI resins were conducted using the Thermo Scientific ESCALAB 250Xi. An Anton Paar Multiwave was used for the microwave digestion of PM-PEI resins and certified reference materials. The determination of P and trace elements was conducted using a PerkinElmer Optima 7300DV Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES); the operating conditions are summarized in Table S1 in the Supporting Information. The solution pH was adjusted using a Horiba D-24 pH meter.

Reagents

For preparing the base resin, glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDM), \(n\)-butyl acetate, 3-methyl-1-butanol, 2,2'-azobis(isobutyronitrile), and methylcellulose were purchased from the same suppliers as in the previous works. Polyethyleneimine 600 (PEI600, MW = ca. 600, Junsei Chemical), phosphonic acid (guaranteed reagent grade, Kanto Chemical), and paraformaldehyde (Tokyo Chemical Industries) were used to prepare a PM-PEI resin. Multi-element standard solutions R-I (Ce, La, Pr, Sc, Y, 100 mg L\(^{-1}\) each), R-II (Eu, Gd, Nd, Sm, Tb, 100 mg L\(^{-1}\) each), and R-III (Dy, Er, Ho, Lu, Tm, Yb, 100 mg L\(^{-1}\) each), which were used for the investigation of solid-phase extraction, were purchased from FUJIFILM Wako Pure Chemical. An ICP Multi-element Standard XVI (As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, 100 mg L\(^{-1}\) each, Merck) was also used to investigate solid-
phase extraction. Nitric acid (for poisonous metal analysis, Kanto Chemical) and ethylenediamine-
$N,N',N''$-tetraacetic acid, diammomium salt (EDTA, Dojindo) were used to elute the elements extracted on resin.
Lanthanum(III) oxide (99.99%, Nacalai Tesque) was used to prepare a La solution for investigating the
extraction capacity. The other reagents, which were of guaranteed or analytical reagent grades, were purchased
from FUJIFILM Wako Pure Chemical or Kanto Chemical.

**Preparation of PM-PEI resin**

A base resin, a copolymer of GMA and EGDM, was prepared by suspension copolymerization in
the same way reported previously. The obtained resin was classified using sieves; in this work, 53–90 µm
of resin was used. The average particle size, specific surface areas, pore volumes, and average pore diameters
of the resin are shown in Table S2 in the Supporting Information. The base resin (20 g) was added to a mixture
of 126.61 g of PEI, 30 mL of 2-propanol, and 120 mL of deionized water, and the solution was then stirred at
200 rpm for 20 h at 50˚C. After that, the resin, in which PEI was immobilized, was washed with deionized
water and then methanol. For the preparation of a PM-PEI resin (Fig. 1), 4 g of PEI resin was added to a
solution containing 40 mL of ethanol and 13 mL of concentrated hydrochloric acid. Phosphonic acid and
paraformaldehyde were added to the solution; the amounts added are summarized in Table 1. The solution
was stirred at 200 rpm for 12 h at 90˚C. The obtained PM-PEI resin was washed with deionized water and then
methanol.

**Determination of nitrogen and phosphorus on the resin**

The amount of N on the PEI resin was determined by elemental analysis. For the amount of P on
PM-PEI resin, 5 mL of concentrated nitric acid and 1 mL of hydrogen peroxide were added into a
polytetrafluoroethylene (PTFE) tube containing 0.05 g of the resin ground by mortar. After the suspension was
allowed to stand for approximately 1 h at room temperature, microwave digestion was conducted under the
conditions shown in Table S3 in the Supporting Information. After digestion, the solution was diluted to 100
mL with deionized water; P in the solution was determined using ICP-AES.

**Capacity for La extraction**

A solution containing 1000 mg L$^{-1}$ of La was prepared by dissolving in a small amount of nitric acid
and then diluting with deionized water to investigate the extraction capacity for each resin. This solution was
diluted with deionized water, and the solution pH was then adjusted; approximately 60 mg L$^{-1}$ La solutions at pH 2 and 5 were obtained. PM-PEI or PEI resin (0.05 g) was added to a 50 mL centrifuge tube containing 20 mL of the La solution. The solution was shaken at 120 rpm for 12 h. The La in the solution was determined using ICP-AES after appropriate dilution.

**Solid-phase extraction of trace elements**

PM-PEI resin (0.25 g) was packed into a cartridge for solid-phase extraction (6 mL, GL Sciences). The resin was conditioned with 5 mL of methanol, 3 mol L$^{-1}$ nitric acid, 20 mL of deionized water, and 0.1 mol L$^{-1}$ ammonium acetate solution, in that order. A deionized water-based test solution (100 mL), containing 5 mmol L$^{-1}$ ammonium acetate and 10 µg of each element and adjusting the pH to 2–10 using nitric acid and aqueous ammonia, was passed through the cartridge at a flow rate of 3–11 mL min$^{-1}$. After washing the cartridge with 20 mL of deionized water, 3 mL of 3 mol L$^{-1}$ nitric acid or 0.2 mol L$^{-1}$ EDTA solution with the pH adjusted to 7 was added to the cartridge for elution of the elements extracted; the elements in the solution were determined using ICP-AES after dilution to 10 mL with deionized water. When the solid-phase extraction was conducted using the same cartridge, the cartridge was washed with 3 mL of 0.2 mol L$^{-1}$ EDTA solution for the elution of the nitric acid or 3 mol L$^{-1}$ nitric acid for that of the EDTA solution. The extraction percentage and the recovery were calculated based on the ratio of the extracted amount to the initial amount and the ratio of the amount in the solution after the elution to the initial amount, respectively, for each element.

To evaluate the applicability of solid-phase extraction using PM-PEI resin to the analysis of the sample solution containing large amounts of coexisting elements, an artificial seawater-based test solution was prepared in accordance with the literature$^{31,32}$; 5 mL of 0.1 mol L$^{-1}$ ammonium acetate and 10 µg of each element were added to 100 mL of the test solution, and the solution pH was adjusted to 2.0 using nitric acid. NIST SRM 1515 Apple Leaves were also used to evaluate the applicability of it to the analysis of the highly acidic sample solution. The SRM (200 mg) was digested under microwave irradiation with 3 mL of concentrated nitric acid and 1 mL of hydrogen peroxide; digestion conditions are summarized in Table S4 in the Supporting Information. In this study, the digestion was conducted using 6 of the digestion tubes at the same time; 6 of the solutions were mixed, and the solution was then diluted to 100 mL with deionized water. After the solution pH was adjusted to 2.0 using aqueous ammonia, solid-phase extraction was conducted at a flow rate of 4 mL min$^{-1}$. 
Results and Discussion

Characterization of prepared resins

In the results of the elemental analysis, PEI resin contained 4.10% of N, corresponding to 2.93 mmol g\(^{-1}\) of N (Table 1). When we conducted XPS analyses of PM-PEI resins, which were prepared by phosphomethylating PEI on the resin using the amounts of phosphonic acid and paraformaldehyde shown in Table 1, the ratio of the peak area of P to that of N increased as the amounts of phosphonic acid and paraformaldehyde used for the phosphomethylation step were increased. The P contents on PM-PEI resins, which were determined using ICP-AES after microwave digestion, are also shown in Table 1. The amount of P also increased in the range from PM1-PEI to PM3-PEI resins as the amounts of phosphonic acid and paraformaldehyde increased; these results were consistent with those obtained by XPS analyses. The PM rates, defined as the ratios of the P content in PM-PEI resin to the N content in PEI resin, have also been appended in Table 1; the PM rate of the PM5-PEI resin was almost equal to that of the PM3-PEI resin. In the investigation of the extraction capacity of La, the capacity at pH 5 was larger than that at pH 2 (Table 1); both capacities increased as the PM rate increased. From these results, it can be seen that the PM rate of the PM-PEI resin could be controlled by using different amounts of phosphonic acid and paraformaldehyde in the phosphomethylation of PEI on the resin.

Solid-phase extraction behavior of trace elements

In the investigation of the solid-phase extraction behavior of trace elements using PEI resin and PM1-PEI–PM3-PEI resins, the PM5-PEI resin was not used because its PM rate was almost equal to that of the PM3-PEI resin (Table 1).

The extraction behavior was investigated first. The effects of pH on the extraction of trace elements are shown in Fig. 2 and Figs. S1–S3 in the Supporting Information. For REEs, low extraction percentages were obtained in the PEI resin. Extraction percentages were considerably improved by phosphomethylating the PEI on the resin. When the PM1-PEI resin was used, the extraction percentages of Yb and Lu were quantitative in a pH range of 2–9. The extraction percentages of the other REEs increased as the pH of the solution increased in a range of 2–4, and quantitative extraction was achieved at a pH above 4. The extraction percentages under acidic conditions increased as the PM rate increased. Quantitative extraction was achieved
for all REEs in a pH range of 2–9 when PM2-PEI and PM3-PEI resins were used. The phosphomethylation of PEI on the resin also improved the extraction of other elements. Quantitative extraction was obtained over a pH range of 2–9 for Be, Fe, and Ti. Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn were also extracted quantitatively at pH 4.5 and higher; the extraction percentages of these elements under acidic conditions slightly increased as the PM rate increased. This would be due to large stability constants of the complexes of these elements with aminophosphonic acid. Although the percentage of V under acidic conditions also increased compared with the percentage using PEI resin, that under alkaline conditions slightly decreased as the PM rate increased. Mg, Ca, and Sr were scarcely extracted over a wide pH range when PEI resin was used; however, these elements were quantitatively extracted at pH 4.5 and higher using all of the PM-PEI resins. Since the affinity of chelating resin immobilizing aminophosphonic acid group for the solid-phase extraction of the elements substantially follows the stability constant of the metal ion with the aminophosphonic acid as shown in Table S5 in the Supporting Information, the chelating resin generally shows high affinity for Ca and Mg. In PM-PEI resin, the extraction percentages of these elements under acidic conditions increased as the PM rate increased from 0.26 (PM2-PEI) to 0.29 (PM3-PEI). It is known that the acid dissociation constants of aminomethylphosphonic acid are as follows: pK_a1=1.45 and pK_a2=5.4 for the deprotonation of phosphonic acid group and pK_a3=11.0 for the deprotonation of amino group. It is also estimated that many of amino groups, which are not phosphomethylated, are present; these are protonated under the acidic conditions. It seems that the difference in the extraction percentages is due to the suppression by the protonated amino group in the PM-PEI. On the other hand, the increase of the PM rate worsened the extraction of As, Mo, and Se. These results indicate that the phosphomethylation of PEI on the resin is effective for the extraction of many elements, and excessive phosphomethylation is not suitable for some elements. The difference in base material between polymer resin and the other materials, such as silica gel and activated carbon, seems to be scarcely affected on the affinity. The affinity of silica gel immobilizing aminophosphonic acid for solid-phase extraction of elements is not significantly different from that of PM-PEI resin and the other resin immobilizing aminohosphonic acid. The activated carbon modified with aminohosphonic acid is useful for the extraction of Ce(III).

The elution of the elements extracted on the PM-PEI resin was then investigated. The results for the PM2-PEI resin have been appended in Fig. 2. When the elution of REEs was attempted using 3 mol L^-1 nitric acid, which is used as the eluent for CM-PEI resin, Yb and Lu were not eluted, and the elution of the
other REEs was not quantitative. It is known that the stability constant of REE with aminophosphonic acid tends to increase as the atomic number of REEs increases, as shown in Table S5 and Fig. S4 in the Supporting Information. This seems to be related to the difficulty of the elution. Elution was improved considerably by using EDTA solution as the eluent. For the elution using the 0.01 mol L\(^{-1}\) EDTA solution, the recoveries of REEs were 37–81%. Recovery increased as the concentration of EDTA increased, and the quantitative elution of REEs, except for Sc, was observed using a 0.2 mol L\(^{-1}\) EDTA solution (Fig. 2). Although the recovery of heavy REEs, such as Yb and Lu, varied, this problem got better when the pH of the EDTA solution (pH approximately 4.5) was adjusted to 7. On the other hand, the recovery of REEs also tended to vary as the PM rate increased. For the other elements, the extracted elements, except for Fe, Mo, and Ti, were quantitatively eluted using 3 mol L\(^{-1}\) nitric acid, although recoveries were insufficient using a 0.2 mol L\(^{-1}\) EDTA solution. The recovery of V varied and was poor, and Fe, Mo, and Ti were scarcely eluted when 3 mol L\(^{-1}\) nitric acid was used. The use of 0.2 mol L\(^{-1}\) EDTA solution was effective for the elution of these elements; however, the recoveries were not quantitative. Sb, which was extracted at less than 70%, could not be eluted using both eluents.

From these results, it can be seen that the PM-PEI resin is highly capable of extracting REEs, Fe, Mo, Sb, and Ti as compared with PEI and CM-PEI resin. For the solid-phase extraction of trace elements, it seems that PM2-PEI resin is preferable because of its high extraction ability and easy elution; the resin is useful for separating and preconcentrating REEs using a 0.2 mol L\(^{-1}\) EDTA solution as the eluent and Be using 3 mol L\(^{-1}\) nitric acid. Alkaline earth elements, such as Ca, were hardly extracted at pH 2; the separation of many elements in solutions containing these elements seems to be achieved at this pH. However, it is possible that the Fe, Mo, Sb, Ti, and V contained in the sample solution affect the extraction of trace elements when the resin is reused because of their incomplete elution.

Therefore, the reusability of the PM2-PEI resin was investigated. Extraction was conducted using 100 mL of a solution containing 10 \(\mu\)g of each REE and 21 elements at pH 2.0 at a flow rate of 4 mL min\(^{-1}\). The extracted elements were eluted using 3 mL of 0.2 mol L\(^{-1}\) EDTA solution or 3 mol L\(^{-1}\) nitric acid; the resin was reused after washing with 3 mol L\(^{-1}\) nitric acid or 0.2 mol L\(^{-1}\) EDTA solution, respectively, and then deionized water. The results obtained for REEs are shown in Fig. 3. When the EDTA solution was used as the eluent, the quantitative extraction and elution of REEs, except for Sc, Yb, and Lu, could be achieved at least 10 times without any influence from the coexisting elements. The recoveries varied slightly when the solid-
phase extraction was repeated, although the extraction was still quantitative. For Yb and Lu, the extraction percentages were almost 100%; however, the recoveries varied considerably in the series of experiments. For Sc, the extraction as well as the elution was insufficient. Extraction and elution using 3 mol L\(^{-1}\) nitric acid for Be were quantitative at least 10 times. The extraction of Mo, Ti, and V was quantitative even when extraction and elution were conducted 15 times; high extraction percentages with relatively high variation were obtained for Cu and Fe. However, the quantitative and precise elution of these elements was difficult.

These results indicate that PM2-PEI resin is reusable at least 10 times for the solid-phase extraction of REEs, except for Sc, and Be. It can also be seen that some elements, which are quantitatively or considerably extracted, cannot be eluted completely using 0.2 mol L\(^{-1}\) EDTA solution and 3 mol L\(^{-1}\) nitric acid; this means that these elements are accumulated on the resin when the resin is reused. However, the coexistence of these elements did not seriously affect the solid-phase extraction of REEs and Be for at least 10 times.

The ability for the extraction of REEs and Be using PM-PEI resin are excellent in comparison with CM-PEI resin,\(^{24,29}\) which are prepared using a similar procedure to PM-PEI resin. The REEs and some elements, such as Fe, Mo, V, and Ti, extracted on PM-PEI resin were scarcely eluted using nitric acid, although the quantitative elution was achieved for CM-PEI resins. For Cd, Co, Cu, Ni, Pb, and Zn, however, CM-PEI resin are superior, or nearly equal, to PM-PEI resin. These seem to be because of the difference in the affinity between aminophosphonic acid group and aminocarboxylic acid group.\(^{33,34}\)

**Applicability of PM-PEI resin for separating and preconcentrating REEs**

As described above, PM2-PEI resin seems to be useful for separating and preconcentrating REEs. Therefore, the solid-phase extraction of REEs in artificial seawater spiked with REEs and certified reference materials was attempted using this resin to evaluate its applicability.

Before the application, the effect of the flow rate on the recoveries of REEs was investigated. As shown in Fig. 4, quantitative recoveries, except for Sc, were obtained over a flow rate range of 1–9 mL min\(^{-1}\). However, the recoveries of heavy REEs, especially Yb and Lu, decreased at a flow rate of 10 mL min\(^{-1}\). In further investigations, solid-phase extraction was conducted at 4 mL min\(^{-1}\).

The results for the recovery tests using artificial seawater-based test solution spiked with 10 µg of each REE are shown in Table 2. High recoveries of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er were obtained with 1–9% of the relative standard deviations (RSDs). However, recoveries of Tm, Yb, and Lu were less than 80%, and only 28% of Sc was recovered. The major elements, namely Na, K, Mg, and Ca, were
barely recovered; more than 99% of the elements were removed. From these results, PM2-PEI resin seems to have application for the separation and preconcentration of REEs, except for Sc and some heavy REEs. In general, environmental water is stored under acidic conditions after filtration. PM2-PEI resin would be useful for separating and preconcentrating REEs in such a sample solution because only a small amount of alkali solution is needed to adjust the solution pH to 2.0.

NIST Standard Reference Material 1515 Apple Leaves was adopted as a certified reference material because the information value from NIST and/or the values reported in the literature\textsuperscript{40,41} were obtained. The results are summarized in Table 3; Sc was not investigated because of its low recovery from the artificial seawater-based test solution. The obtained results for many REEs were nearly equal to the information values and/or the values reported in the literature; however, low values were obtained for Yb, and the contents of Tm and Lu were less than 0.1 mg kg\textsuperscript{-1}. These results indicate that solid-phase extraction using PM2-PEI resin should be applied to separating light rare earth elements in such a sample. Since the solution after acid digestion contains a large amount of acid, appropriate dilution and neutralization of the solution are generally needed before solid-phase extraction. PM2-PEI resin would also be useful for separating the elements in a solution after acid digestion.

In this study, the blank value was less than the limit of detection for each element in ICP-AES, which defined as 3 times the standard deviation for the blanks (n = 8, 10 mL of the solutions containing 3 mL of 0.2 mol/L EDTA solution).

**Conclusions**

In this work, the effect of the PM rate on the solid-phase extraction behavior of trace elements using PM-PEI resin was investigated. It can be seen that the PM rate depends on the amounts of phosphonic acid and paraformaldehyde used in the phosphomethylation of PEI immobilized on the resin. The extraction ability of PM-PEI resin for many elements increases as the PM rate increases. REEs and Be, Fe, Mo, Ti, and V can be quantitatively extracted even at pH 2; however, Mg and Ca were scarcely extracted at this pH. Such ability seems to be attractive when the elements in an acidic sample solution, including acidified environmental water and solution after acid digestion, are separated and preconcentrated. On the other hand, it can be found that the increase of the PM rate causes elution difficulty; therefore, use of a PM-PEI resin that has an adequate PM rate
is important. When PM2-PEI resin (with a PM rate of 0.26) is used, REEs and Be can be completely eluted using 0.2 mol L\(^{-1}\) EDTA solution and 3 mol L\(^{-1}\) nitric acid, respectively. Although the quantitative elution of some elements is not achieved, the resin can be reused at least 10 times without any influence from the elements. Solid-phase extraction using PM2-PEI resin seems to be applicable to the separation and preconcentration of REEs, except for Tm, Yb, and Lu, in artificial seawater and NIST SRM 1515 Apple Leaves; further study regarding the improvement of the solid-phase extraction of Tm, Yb, and Lu is needed. Since solid-phase extraction is useful for on-site or on-line separation and preconcentration,\(^{12,14,42-48}\) such attempt is also important for PM-PEI resin.

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Supporting Information

Additional information and data, including operating conditions for ICP-AES and microwave apparatus, characteristics of base resin, effect of pH on the extraction of REEs and the other 21 elements using PEI and PM-PEI resins, and stability constant of the complex of some elements with aminophosphonic acid, are given as Supporting Information. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.
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Table 1  Characteristics of PEI and PM-PEI resins prepared in this work

| ID      | N content a / mmol g⁻¹ | Phosphomethylation | P content b / mmol g⁻¹ | PM rate | Extraction capacity for La / mmol g⁻¹ | pH 2 | pH 5 |
|---------|------------------------|--------------------|------------------------|---------|-------------------------------------|------|------|
| PEI resin | 2.93                   | -                  | -                      | -       | < 0.001                             | 0.008 |
| PM1-PEI resin | 9.60                | 3.52               | 0.47                   | 0.16    | 0.005                              | 0.060 |
| PM2-PEI resin | 19.21                | 7.04               | 0.77                   | 0.26    | 0.049                              | 0.13 |
| PM3-PEI resin | 28.81                | 10.56              | 0.84                   | 0.29    | 0.049                              | 0.13 |
| PM5-PEI resin | 48.02                | 17.60              | 0.85                   | 0.29    | 0.044                              | 0.14 |

a: Determined by elemental analysis.  
b: Determined by ICP-AES with microwave digestion.
Table 2  Recoveries of REEs in an artificial seawater-based test solution

| Element | Recovery a, % |
|---------|---------------|
| Sc      | 28 ± 12       |
| Y       | 87 ± 1        |
| La      | 82 ± 1        |
| Ce      | 93 ± 1        |
| Pr      | 94 ± 1        |
| Nd      | 91 ± 1        |
| Sm      | 97 ± 1        |
| Eu      | 92 ± 1        |
| Gd      | 96 ± 1        |
| Tb      | 95 ± 1        |
| Dy      | 88 ± 1        |
| Ho      | 87 ± 1        |
| Er      | 86 ± 1        |
| Tm      | 79 ± 3        |
| Yb      | 70 ± 6        |
| Lu      | 62 ± 9        |

a: Mean ± standard deviation (n = 3).
Table 3  Results for determining REEs in NIST SRM 1515 Apple Leaves

| Element | Found * mg kg\(^{-1}\) | Information value / mg kg\(^{-1}\) | Literature value / mg kg\(^{-1}\) |
|---------|-------------------------|------------------------------------|----------------------------------|
|         |                         |                                    | Ref. 40                         | Ref. 41 |
| Y       | 9.3 ± 0.1               |                                    | 9.710                           |         |
| La      | 18 ± 1                  | 20                                 | 19.2                            | 17.990  |
| Ce      | 2.5 ± 0.01              | 3                                  | 2.8                             | 2.410   |
| Pr      | 3.7 ± 0.01              | 3                                  | 3.8                             | 2.390   |
| Nd      | 15 ± 1                  | 17                                 | 14.3                            | 15.060  |
| Sm      | 3.3 ± 0.03              | 3                                  | 2.3                             | 2.630   |
| Eu      | 0.2 ± 0.01              | 0.2                                | 0.25                            | 0.231   |
| Gd      | 2.8 ± 0.03              | 3                                  | 2.8                             | 2.890   |
| Tb      | 0.3 ± 0.04              | 0.4                                | 0.39                            | 0.317   |
| Dy      | 1.5 ± 0.01              |                                    | 1.7                             | 1.700   |
| Ho      | 0.2 ± 0.02              |                                    | 0.29                            | 0.227   |
| Er      | 0.6 ± 0.1               |                                    | 1.3                             | 0.582   |
| Tm      | < 0.1                   |                                    | 0.04                            |         |
| Yb      | 0.1 ± 0.02              | 0.3                                | 0.18                            | 0.200   |
| Lu      | < 0.1                   |                                    | 0.02                            | 0.0170  |

* Mean ± standard deviation (n = 3).
Figure captions

Fig. 1 Estimated structure of PM-PEI resin.

Fig. 2 Effect of pH on the extraction (■) or recovery (○,●) of REEs (a) and other elements (b) using PM2-PEI resin.
Extraction: Solution volume, 100 mL; REEs or the other 21 elements, 10 μg each; flow rate, 4 mL min⁻¹.
Elution: 3 mol L⁻¹ nitric acid (○) or 0.2 mol L⁻¹ EDTA (●), 3 mL; final volume, 10 mL.

Fig. 3 Reusability of PM2-PEI resin for the extraction (■) or recovery (○,●) of REEs.
Extraction: Solution volume, 100 mL; REEs and the other 21 elements, 10 μg each; pH, 2.0; flow rate, 4 mL min⁻¹.
Elution: 3 mol L⁻¹ nitric acid (○) or 0.2 mol L⁻¹ EDTA (●), 3 mL; final volume, 10 mL.

Fig. 4 Effect of flow rate on the recovery of REEs using PM2-PEI resin.
Extraction: Solution volume, 100 mL; REEs, 10 μg each; pH, 2.0.
Elution: 0.2 mol L⁻¹ EDTA, 3 mL; final volume, 10 mL.
Fig. 1  Estimated structure of PM-PEI resin.
Fig. 2  Effect of pH on the extraction (■) or recovery (○, ◦) of REEs (a) and other elements (b) using PM2-PEI resin.

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**Fig. 3** Reusability of PM2-PEI resin for the extraction (■) or recovery (○, ◊) of REEs.

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Graphical Index

[Diagram showing the structure of PM-PEI resin and PEI resin, with arrows indicating phosphomethylation.]

[Graphs showing the extraction of La and Ca at different pH values.]