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## Preconcentration of Arsenic Species in Environmental Waters by Solid Phase Extraction Using Metal-loaded Chelating Resins

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The metal-loaded chelating resins were prepared with several elements such as lanthanum, cerium, iron and zirconium. The adsorption characteristics of As(III) and As(V) on the modified resins have been investigated. The pH dependence of the adsorption efficiencies of As(III) and As(V) on the Ce-, Fe-, Zr-, and La-loaded chelating resins have been tested. It was shown that both As(III) and As(V) were strongly adsorbed on the La-loaded resin in the pH range from 4 to 9. As(III) can be 90-95% collected by the Ce-, Fe- and Zr-loaded resin, while As(V) was moderately adsorbed on the Ce-, Fe-, and Zr-loaded resins. Arsenic species adsorbed on the La-loaded resin can be quantitatively determined by eluting with HCl concentrations from 2 to 6M following by hydride generation atomic absorption spectrometry (HG-AAS). Desorption of the arsenic species from the Ce-, Fe-, and Zr-loaded resins by either HCl or NaOH solution has only recoveries of 60-70%. Enrichment factors using the La-loaded chelating resin to adsorb arsenic species in solution are in the range 20-30 fold. The La-loaded chelating resin column could be applied to develop a simple, inexpensive and sensitive analytical method followed by HG-AAS for monitoring trace arsenic in environmental waters.

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Arsenic concentrations have been elevated in some natural waters due to oxidation weathering and dissolution of As-containing minerals. Also, arsenic is a common pollutant in groundwater and industrial wastewater. Although analytical instruments have been significantly improved, preconcentration methods for the determination of trace arsenic in natural water are usually required during the pretreatment of samples. The preconcentration methods include: solvent extraction<sup>1</sup>, coprecipitation with lanthanum or hafnium<sup>2,3</sup>, thorium or zirconium<sup>4</sup>, lead-pyrrolidinedithiocarbamate<sup>5</sup>, solid phase extraction<sup>6</sup>, or the extraction of arsenic (III) with a macroporous resin impregnated with bis(2-ethylhexyl)ammonium-bis(2-ethylhexyl)-dithiocarbamate<sup>7</sup>, thionalide loaded on silica gel<sup>8</sup>. Matsunaga *et al.*<sup>9</sup> have investigated the potential of using an iron-loaded chelating resin having a lysine-N<sup>α</sup>-N<sup>α</sup>-diacetic acid moiety for the removal of arsenic from aqueous solutions.

The chelating resin (Chelex-100 resin), which has iminodiacetic acid functional groups, was used in the iron form to preconcentrate the tellurium(VI) and selenium species in polluted water samples<sup>10</sup>. Muromac A-1(A1) resin resembles Chelex-100, both containing iminodiacetic acid[-CH<sub>2</sub>-N(CH<sub>2</sub>-COOH)<sub>2</sub>] functional groups but differs from chelating properties. The Muromac A-1 chelating resin is better purified and does not swell or shrink when converting its forms<sup>11</sup>. It has been used to preconcentrate Cu and Mo from seawater<sup>11</sup>, and separate copper or nickel ions when analyzing As in copper or nickel powders.<sup>12</sup>

In this study, we investigated the adsorption characteristics of As(III) and As(V) onto the solid phase extraction columns packed with metal-loaded Al chelating resins. The selected metals included Fe(III), Ce(III), La(III), and Zr(IV) which have been commonly used to coprecipitate arsenic species from solution. The pH dependence on the adsorption efficiency of As(III) and As(V) on the Ce-, Fe-, Zr-, and La-loaded chelating resins have been tested. Finally, the preconcentration of As(III) and As(V) in dilute solutions was performed using a solid phase extraction minicolumn packed with La-loaded Al chelating resin.

### Experimental

#### Apparatus

The concentration of As was determined by a two-channel Atomic Absorption/Flame Emission Spectrophotometer model AA-8500 MarkII equipped with a hydride generation HYD-10 system (Nippon Jarrell-Ash. Co). The pH was measured by a HORIBA digital pH/ion meter F-23. The mini-columns of 3 ml (Supelco Filtration Tubes) were purchased from Supelco, Inc., USA.

#### Reagents

Sodium tetrahydroborate was of laboratory reagent grade (Wako Pure Chemical Industries, Japan). It was dissolved in sodium hydroxide solution just before use. Hydrochloric acid, ascorbic acid, sodium hydroxide, lanthanum chloride heptahydrate, ferric

sulfate n-hydrate, cerium (III) chloride n-hydrate and potassium iodide were of analytical grade (Wako Pure Chemical Industries, Japan). Zirconium (IV) chloride was of reagent grade (Aldrich Chem.Co.). A 1000mg/L As (V) solution was prepared by dissolving extra pure reagent potassium dihydrogenarsenate ( $\text{KH}_2\text{AsO}_4$  Nakarai Chemicals, Ltd., Japan). The 1000 mg/L As (III) standard solution was from Wako Pure Chemical Industries, Japan.

Muromac A1 in  $\text{Na}^+$  form, 50-100mesh (Muromachi Kagaku Kogyo Kaisha, Ltd., Japan) was used through all the experiments. Doubly deionized water ( $>18\Omega\text{cm}$ ) from the Millipore  $\alpha$  Hi-grade Pure Water System Milli-RX 12 was used throughout this study.

#### Preparation of metal-loaded chelating resin columns

The Muromac A1 chelating resin  $\text{Na}^+$  form (A1) was washed with 2M NaOH and 2M HCl solutions and then deionized water to remove any trace impurities. The cleaned resin was loaded into the columns and polyethylene frits were fixed on both ends of the columns. An excessive amount of metal ion solutions of La(III), Ce(III), Fe(III) or Zr(IV) was fed with a flow rate of 1.0 -1.2 ml/min. The La and Ce solutions were adjusted to pH 4 using sodium acetate buffer. The pH of the Fe and Zr solutions were from 1 to 2. After the metals were loaded, the columns in the metal forms (A1-M) were well washed with 30 ml deionized water to remove any trace metal ions in the resin beds. Fifty ml of  $\text{NH}_3$  or NaOH solutions (3mM) was passed through the column at a flow rate of 1.5-2.0 ml/min. and then 5 ml of deionized water was added to wash the NaOH or  $\text{NH}_3$  residue in the resin bed. The metal-loaded chelating resin column in the A1-M-OH form is now ready to adsorb the As species from solution.

#### Analytical procedure

An appropriate volume of an aqueous solution containing  $1.0\mu\text{g}$  of As(III), As(V) or a mixture of these species was prepared to studied pH and percolated through the column at a flow rate from 0.8 to 1.0 ml/min. The effluent was collected and retained for the arsenic determination in order to monitor the efficiency of the As adsorption process. The column was then eluted with 5ml of 2M NaOH or 2M HCl solutions at a flow rate from 0.5-0.8 ml/min. The entire effluent was used for the arsenic determination by HG-AAS to calculate the recovery of arsenic from the elution process. The arsenic determination was performed as follows: 5ml of As solution was added to 5M HCl, 1 ml of the mixture solution of reductant agent (5% ascorbic acid and 10% potassium iodide w/v) and deionized water to reach a final HCl concentration of 2M in 10 ml. The solution was allowed to stand for 45 min. to convert any As(V) to the As(III) form, and the As concentration was then measured by HG-AAS.

## Results and Discussion

#### Prereduction of Arsenic(V) to Arsenic(III)

It is well-known that at room temperature and at low pH (pH<1), the As(V) oxidation state is reduced relatively slowly by sodium tetrahydroborate ( $\text{NaBH}_4$ ) whereas As(III) is instantaneously converted to arsine when reacted with  $\text{NaBH}_4$ . The arsine atomic absorption peaks are usually decreased by one-fourth to one-third for As (V) when compared to As(III)<sup>14</sup>. This may explain the phenomenon in the preliminary experiments when the arsenic(III) experiments were carried out, and the arsenic recovery was about 50%. There may be part of the As(III) being converted to As(V) during the adsorption and/or desorption process. In order to speed up the reaction and to increase the sensitivity of the method, all As(V) should be converted to the As (III) form before reacting with sodium

tetrahydroborate. Various prereducing agents<sup>13</sup> have been used to convert As (V) to As (III) depending on the hydride generation systems and arsenic detector equipment. We have tested with several reducing agents such as: potassium iodide in HCl acid concentration, sodium sulfite, thiourea, L-cystine or mixture of potassium iodide with ascorbic acid or sodium sulfite. As reported by Brindle<sup>15</sup>, potassium iodide alone must be reacted with As(V) in high concentration of HCl and take a long time (4-5h) at room temperature. L-cystine can reduce As(V) to As(III) and also increase the sensitivity in the determination of arsenic<sup>15</sup>. However, we have found that it was very difficult to distinguish signals between arsine and the L-cystine residue in solution. A mixture of potassium iodide and sodium sulfite which liberated hydrogen sulfide caused overlapping peaks when measuring As. Ascorbic acid used in combination with potassium iodide can prevent the oxidation of iodide to triiodide by air or with an oxidant like  $\text{Fe}^{3+}$ . Among the solutions tested, the solution mixture of 10% KI and 5% ascorbic acid in 2M HCl was found to be most suitable for the quantitative reduction of As(V) to As(III) at room temperature.

#### Effect of resin bed volume.

The columns were packed with the A1 metal-loaded chelating resin in various volumes from 0.25 to 2.5 ml resin bed. Obviously, the adsorption capacity of the arsenic compounds increases when increasing the resin bed volume. However, this may require a large volume of eluting agent. Therefore, the volume of a 1 ml resins bed is suitable for the adsorption of arsenic from dilute solution.

#### Effect of pH on the adsorption of arsenic species

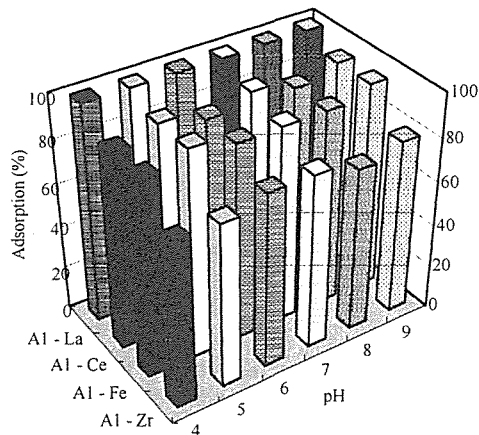


Fig. 1 Effect of pH to the adsorption of As (III)

The effect of pH on the adsorption of arsenic(III) and arsenic(V) on the A1 metal-loaded resin column was examined. The arsenic solution containing  $1.0\mu\text{g}$  As was passed through the column and the effluent collected and As determined by HG-AAS in order to calculate the arsenic adsorption efficiency on the column. The pH of the arsenic solutions was adjusted using  $5.10^{-2}$  M NaOH or  $\text{NH}_3$  solution to the studied pH (from pH 2.0 to pH11.0). At pH values below 4.0, the adsorption efficiency of arsenic (percentage) decreased. This may be caused by dissolving a part of the metals loaded on the resin at low pH, especially lanthanum and cerium. At pH values higher than 9.0, the adsorption efficiency is also gradually decreased with increasing  $\text{OH}^-$  concentration. When the pH of the arsenic solution is 12 or more, arsenic was not adsorbed on the resin.

Wakui<sup>7</sup> and Matsunaga *et al.*<sup>9</sup> have used 0.1 M NaOH solution to remove the arsenic compounds from the column. Therefore, the adsorption of arsenic on the column at pH 10 or more is ineffective. The effects of the pH on adsorption efficiency of arsenic (III) and arsenic (V) on each metal-loaded column in the pH range from 4.0 to 9.0 are shown in Figure 1 and Figure 2, respectively. At these pHs, both arsenic (III) and arsenic(V) were strongly adsorbed at 98-100% on the La-loaded resin column. Arsenic(III) can be collected at 90-95% by the Ce-, the Fe-loaded Al resins. The arsenic(V) was moderately adsorbed on the Ce-, Fe-, and Zr-loaded Al resins. These metals have been employed by several authors to coprecipitate As and other trace metals from solution. In this study, after the adsorption of metal ions onto the Al resin, the metal-loaded Al resin (Al-M) was converted to the Al-M-OH form by alkali solution as described in the experimental section.

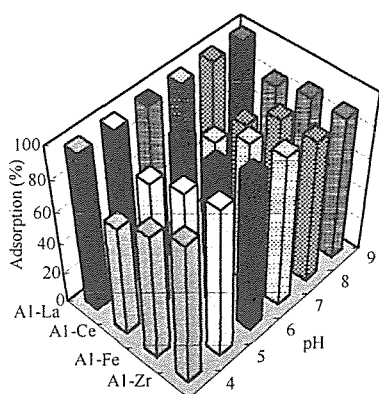


Fig. 2 Effect of pH to the adsorption of As (V)

However, the adsorption mechanism of arsenic species onto the modified resins is not totally a coprecipitation mechanism. Our experimental results on the behavior of the As (III) and As (V) adsorption on the Al, Al-M and Al-M-OH or on the cation exchange resin may lead to the supposition that a ligand substitution mechanism may be involved. In addition, the nitrogen atom in the iminodiacetic acid functional groups may have some contributions to the arsenic absorption process. The mechanism could be a mixture of several mechanisms and will be investigated and discussed in our future studies. However, in this procedure, the coprecipitation process is considered to be the major mechanism for the adsorption of arsenic species by Al metal-loaded chelating resins.

#### Desorption of arsenic species from column.

Arsenic species retained on the column can be eluted by a number of eluting agents<sup>6,7</sup>, however sodium hydroxide and hydrochloric acid are commonly used when arsenic species determine by the HG-AAS method. Various NaOH solutions, from 0.1M to 4M were tested. At a NaOH concentration below 2.0, the arsenic desorption was inefficient. With a NaOH concentration of 2M or more, about 60-70% arsenic can be removed from the column in the first elution fraction of 5 ml. The subsequent elution fractions had very low recoveries. The results of using 2M NaOH solution to elute arsenic from metal-loaded resin columns are shown in Figure 3. It is recognized that

a solution of 2M NaOH can remove arsenic from the column but a large volume of NaOH solution is required. This will decrease the detection limit of the method.

On the other hand, the elution of arsenic species from column using 0.1, 0.5, 1, 2, 3, 4, and 5M HCl were performed. With low HCl concentration, 0.1M to 1.5M, the elution of the arsenic retained on column is incomplete. The results of the elution process using 5 ml HCl from 2-5M are shown in fig. 4.

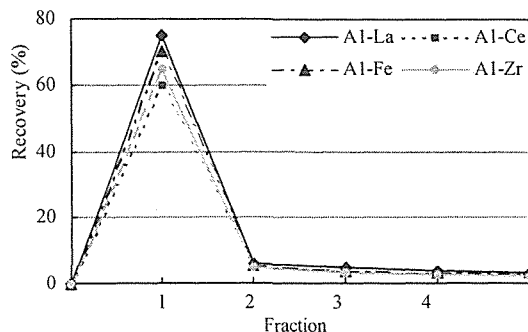


Fig. 3 Desorption of As by NaOH solution

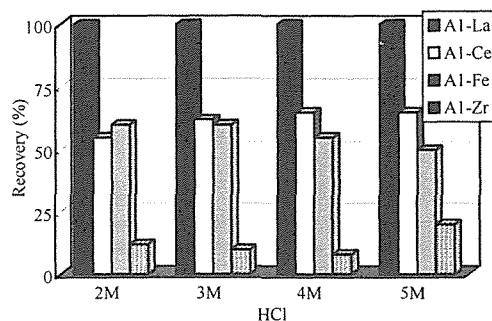


Fig. 4 Desorption of As by HCl solutions

It is recognized that arsenic on the La-loaded resin can be completely eluted using just 5 ml. Therefore, a 2M HCl solution has been used in the following experiments carried out using the Al La-loaded resin column. The arsenic on the Ce-, Fe- and Zr-loaded chelating resins was very difficult to remove from the column, especially the column packed with the Zr-loaded resin. The reason may be that arsenic species are strongly bounded to these modified resins, so both NaOH and HCl could not completely elute arsenic. In addition, Zr and Fe liberated from resin can interfere with the process of arsenic determination by HG-AAS. To overcome these problems, other eluting agents or complex agents to mask the Fe, Ce, and Zr ions should be examined and will be reported in future work.

#### Preconcentration of As by La-loaded Al resin column

As mention above, all the metal-loaded chelating resins can quantitatively adsorb arsenic (III) and arsenic (V) on a relative basis. However, a comparison of these metal-loaded resin showed that the Ce-loaded resin could easily prepare column but the results of the As recovery were quite variable. The Fe and Zr-loaded resin are very difficult to prepare columns because these ions are easily hydrolysed leading to the column becoming blocked. Moreover, arsenic recovery by eluting HCl or NaOH solution which are convenient for the determination of As by HG-AAS technique was low. Therefore, the La-loaded chelating

resin is the most suitable solid phase extraction material for the preconcentration of arsenic species from water samples. The solid phase extraction column packed with La-loaded resin, which is simple and inexpensive, provided an enhanced sensitivity for the As determination by HG-AAS. Preliminary experiments for the preconcentration of arsenic species from solution by the La-loaded Al chelating resin were performed. The concentration of arsenic (III), Arsenic(V) or the mixture of As(III)+As(V) from 0.5ppb to 20 ppb and for a volume from 50 to 300ml was passed through the column and the arsenic determination was carried out as described above. The enrichment factors calculated for this method are in the range of 20 to 30 fold based on the initial concentration. It is suggested that this method should be used for the preconcentration of trace arsenic species in environmental waters.

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