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Naked-eye detection of trace arsenic(V) in aqueous media using molybdenum-loaded chelating resin having β-hydroxypropyl-di(β-hydroxyethyl)amino moiety

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Abstract

A naked-eye detection method for a trace amount of arsenic in aqueous samples has been newly developed. The proposed method is based on the formation of a hetero poly acid in a chelating resin phase. Molybdenum loaded on a chelating resin having β-hydroxypropyl-di(β-hydroxyethyl) amino moiety reacts with arsenic(V) to form the hetero poly acid, which makes the resin beads greenish blue in the presence of a reducing agent under acidic conditions. It was also found that the intensity of the color of the resin depends on the concentration of arsenic(V) in the sample solutions. Since the development of the color occurs in 20 min by heating of the mixture at 40 °C, this system can provide a simple, rapid and low-cost detection method of a trace amount of arsenic(V) in an aqueous media. The detection limit of this method is 1×10^{-6} mol dm^{-3}. A longer preconcentration time with the same resin gave the higher sensitivity of 1×10^{-7} mol dm^{-3} that is comparable with that of the instrumental analysis. The present method comprises both the concentration and detection step with the same solid material, and hence it gives higher sensitivity and easier handling than the ordinary colorimetric methods using a liquid medium.

Keywords: Naked-eye detection; Solid optical indicator; Trace arsenic; Molybdenum-loaded chelating resin; Molybdenum blue

1. Introduction

Arsenic is one of the most toxic elements whose concentration in both natural and waste water should be constantly controlled and monitored. The detection of 0.01 mg dm^{-3} (ppm) of arsenic is required in many countries including Japan in accordance with the regulations on environmental pollution control. The instrumental analysis such as atomic absorption spectrometry and inductively coupled plasma–atomic emission spectrometry is popularly used for the measurement of a low concentration of arsenic in aqueous solutions. However, it generally requires costly instrument, skilled techniques and a long operation time. The additional procedures of pretreatment including hydride formation process are sometimes necessary to remove interfering diverse ions and to increase the sensitivity. It is also very hard to carry out on-site measurement with such a large-sized instrument. Therefore, a simple, economic and rapid method for the detection of a trace amount of arsenic has been demanded for monitoring of waste or environmental water.

A lot of spectrophotometric methods for the determination of arsenic have been reported based on a molybdenum blue complex [1–3], a diethyldithiocarbamate complex [4–6] and a molybdate–rhodamine B complex [7]. Although the detection limits of these methods are low enough to measure 0.01 ppm of arsenic, they still need some tedious and complicated procedures, harmful reagents and medium-size instrumentation such as a spectrophotometer. Naked-eye detection is in the nature of the thing to give a simpler method than the ordinary spectrophotometry because any special

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instruments are not essential. When a simple method is more significant than precise measurements, the naked-eye detection must be one of the best solutions. Naked-eye detection methods of some anions except for arsenic have been so far reported [8–10]. Although these methods are simple to some extent, they are still based on a liquid sensing system. From a practical point of view, solid sensors are considered to give easier and simpler detection methods than the liquid systems.

It is well known that molybdenum forms so called hetero poly acids with arsenate to give an intense blue color under the reductive conditions. Since the development of this blue color is very stable and corresponds to the concentration of arsenate ion, it has been often used for the determination of arsenic [1–3]. Thus, we have tried to make the similar reaction to occur in the solid phase to fabricate solid optical sensors for arsenic detection. It is essentially required to prepare solid material containing molybdenum that is not in the poly acid structure for this purpose. It was expected that the chelating resins would meet this requirement due to the formation of the complex between molybdenum and the functional group of the resin. Several types of chelating resins which can adsorb molybdenum are known [11–13]. Among many types of adsorbent for molybdenum, the chelating resins having amino polyalcohol functional groups were considered to be most favorable because of their multidentate structure and strong affinity toward molybdenum [14]. In addition to the above, it has been also reported that some of the metal loaded chelating resins can adsorb arsenic from its aqueous solutions by the ligand substitution [14–16]. Based on these facts, we expected the reaction of molybdenum-loaded resin with arsenic in the solid phase. In this study, a molybdenum-loaded chelating resin having β-hydroxypropyl-di(β-hydroxyethyl) amino moiety has been newly prepared and proposed for the adsorption and detection of arsenic based on the formation of hetero poly acids in the resin phase.

2. Experimental

2.1. Reagents and instruments

A chelating resin having β-hydroxypropyl-di(β-hydroxyethyl) amine (HDEA) was newly synthesized by the following procedure; diethanolamine (21 g) was dissolved into ethanol and cooled in an ice bath. To this solution was added ethanol solution (25 cm^3) of epichlorohydrin (18.5 g) drop wise in 30 min maintaining the bath temperature below 5 °C. After keeping the reaction mixture overnight at room temperature, the ethanol was removed by evaporation under the reduced pressure. To this solution was added chloroform (100 cm^3) and cross-linked polystyrene resin beads having aminomethyl moiety (AMR, 60–100 mesh, 15 g). The mixture was refluxed with stirring for 2 days. The resin was washed thoroughly with ethanol and dried.

A Stock solution of arsenic(V) (1×10^{-3} M, M = mol dm^{-3}) was prepared by dissolving 93 mg of Na_2HAsO_4 into 500 cm^3 of purified water. A stock solution of molybdenum (0.1 M) was prepared by dissolving 10.3 g of Na_2MoO_4 into 500 cm^3 of purified water. All other chemicals used were of analytical grade.

The concentration of metal ions in the stock solution was determined with a Seiko SPS-1500 Inductively Coupled Plasma Atomic Emission Spectrometer. Reflection spectra of the resins were measured with a Shimadzu UV-3150 UV-VIS-NIR spectrophotometer. A TOA-HM26S pH meter with a glass electrode was used for the measurement of pH. The valence state of molybdenum and arsenic in the resin phase was also checked with a ULVAC-PHI ESCA 5600 X-ray Photoelectron Spectrophotometer.

2.2. Preparation of molybdenum-loaded resins

Five grams of the HDEA resin beads were equilibrated with 200 cm^3 of 0.1 M sodium molybdate solution at pH 3 by shaking the mixture for 3 h. The pH of the solution was adjusted with a hydrochloric acid. The molybdenum-loaded resin was thoroughly washed with pure water and then dewatered between sheets of filter paper. The amount of molybdenum adsorbed on the resins was calculated by the difference of concentrations in the solution before and after adsorption procedure.

2.3. Adsorption of arsenic(V) on the molybdenum-loaded resins

An aliquot of the molybdenum-loaded resin was vigorously shaken with certain volumes of sodium arsenate solutions under various conditions with tightly capped glass bottles. The equilibrium adsorption was discussed with adsorption percentage calculated from the initial and equilibrated concentration of the arsenic(V) in the aqueous solutions. The formation of hetero poly acids (molybdenum blue) in the resin phase was discussed according to the XPS data and the reflection spectra of the resin.

2.4. Standard detection procedure of arsenic(V)

A 20 cm^3 portion of sample solution was taken into a glass bottle. The acidity of the solution was adjusted to 0.5 M H_2SO_4. To this solution was added 2 cm^3 of 0.1 M ascorbic acid. Then a 100 mg of molybdenum-loaded HDEA resin (Mo-HDEA) was added to the solution and the mixture was kept at 40 °C for 20 min in a hot water bath. The presence of arsenic in the sample solutions was detected by the sight of the color change of the resin from pale yellow to greenish blue. The concentration of the arsenic was determined also by comparing the color intensity of the target sample with that of the standard samples which can be prepared with the arsenic solutions of known concentration.

2.5. Detection of arsenic(V) with preconcentration

A 200 cm^3 portion of sample solution was taken into a glass bottle. To this solution was added 200 mg of Mo-HDEA and the pH of the solution was adjusted around 3 by hydrochloric acid. The resins were filtered and transferred to a test tube after the mixture was shaken for 180 min. To this test tube was added 2 cm^3 of 0.5 M H_2SO_4 containing 0.01 M ascorbic acid. The mixture was also kept at 40 °C for 20 min in a hot water bath. The detection of arsenic was carried out by the same method as described above.

3. Results and discussion

3.1. Synthesis of HDEA resin

The chemical analysis of the HDEA resin showed that the nitrogen content was 6.5%, from which the content of the functional group was estimated to be 2.3 mmol g^{-1}. The chemical structure of the resin was confirmed by IR spectra which gave peaks at 3392, 1651, 1120 and 1073 cm^{-1} supporting the presence of OH, NH and CN bands. Fig. 1 shows an expected chemical structure of HDEA resin.

3.2. Adsorption of molybdenum

The effect of pH on the adsorption of molybdenum with HDEA resin was checked (Fig. 2). It was found that HDEA resin can adsorb molybdenum in the acidic range up to pH 6. The effect of shaking time on the adsorption of molybdenum was checked. The results were shown in Fig. 3. It takes more than 1 h to attain an equilibrium adsorption. Hence, the preparation of molybdenum-loaded resin (Mo-resin) was carried out by shaking the mixture of the resin and a molybdenum solution for 2 h. A maximum amount of molybdenum adsorbed on the HDEA resin was 1.9 mmol g^{-1}, which is roughly the same as the capacity of chelating moiety of the resin. Thus, it was considered that molybdenum was adsorbed to the resin to form 1:1 complex with the functional groups of the resin. The valence state of molybdenum in the resin phase was investigated with XPS. It was confirmed that the most of molybdenum was present as Mo(VI) in the resin phase since the XPS spectra showed peaks at 231.1 and 234.2 eV (Fig. 4(a)). Thus, a large part of molybdenum are considered

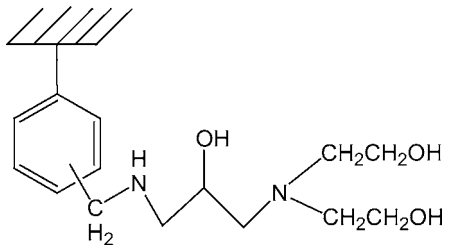

Fig. 1. An expected chemical structure of the HDEA resin.

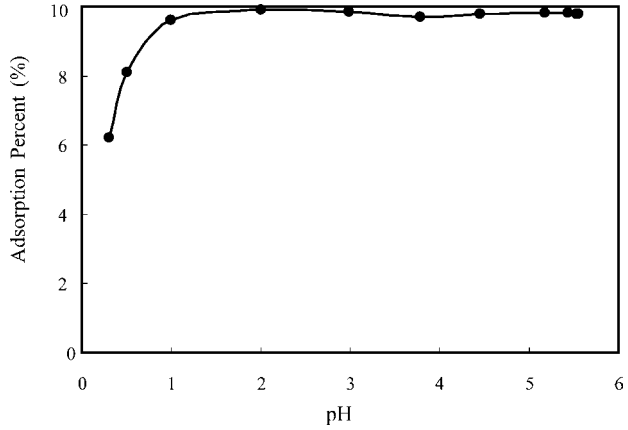

Fig. 2. The effect of pH on the adsorption of molybdenum with HDEA resin. [Mo] = 1.1 × 10^{-4} M.

to remain still as a monomeric species or in a low degree of condensation state in the resin phase and then the Mo-HDEA resin shows the same pale yellow as the color of the original resin. It was also confirmed that the resins of HDEA and Mo-HDEA are very stable and can be used for at least 3 months after preparation.

3.3. Adsorption of arsenic(V)

The adsorption of arsenic on the original resin without molybdenum has been checked with respect to pH. Whereas the HDEA resin adsorbs arsenate ion above pH 3, the Mo-HDEA adsorbs it under more acidic conditions (Fig. 5). Thus the load of molybdenum on the resin gave better adsorbents for arsenic(V) than the original resin. In addition to these facts, no elution of molybdenum during the arsenic adsorption suggested that arsenate ion is adsorbed onto Mo-resin by the formation of ternary complexes with molybdenum in the resin phase. The valence state of molybdenum and arsenic in the resin with or without reduction was also checked with XPS. The XPS data showed peaks at 230.1 and 233.3 eV

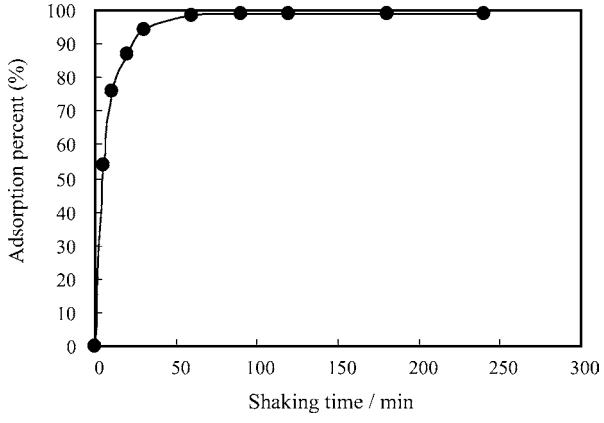

Fig. 3. The effect of shaking time on the adsorption of molybdenum with HDEA resin. Mo = 1.1 × 10^{-4} M, pH = 3.5.

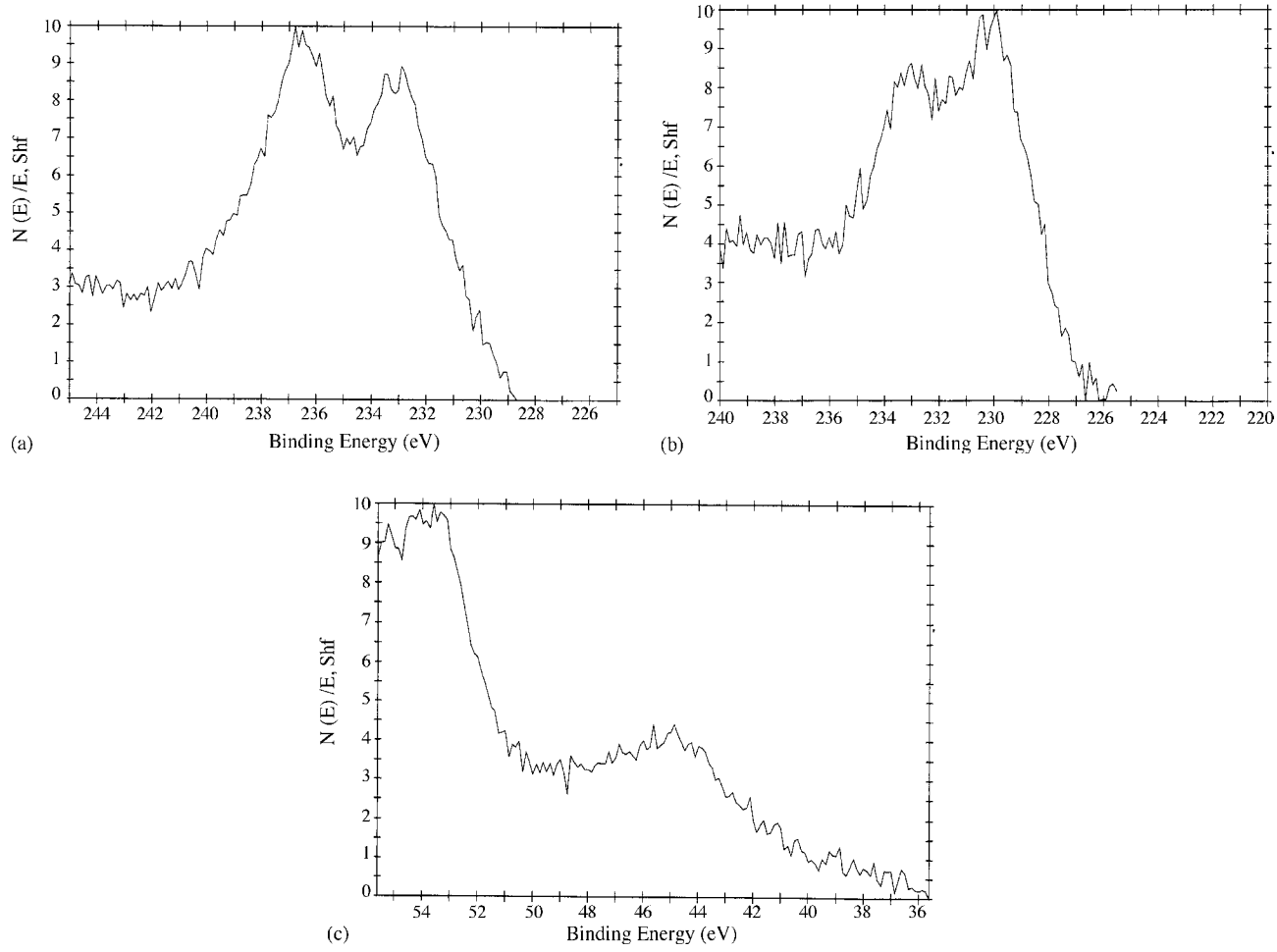

Fig. 4. The XPS spectra of the resin: (a) before adsorption of arsenic; (b) and (c) after adsorption of arsenic and reduction. X-ray source (Al Kα, 14 kV, 350 W).

(Fig. 4(b)), which are attributed to the presence of Mo(IV). Thus, a large extent of the molybdenum atoms in the resin were reduced to lower valence state such as Mo(IV) after the adsorption of arsenic and reduction. Some of the adsorbed arsenic was also found as its reduced form of As(III), showing the XPS spectra having a peak at 44.9 eV (Fig. 4(c)). It was suggested that the reduced hetero poly acids formed in the resin phase under the reductive conditions, and that the resin revealed the typical blue color by the formation of a molybdenum blue. The effect of shaking time on the adsorption of arsenic(V) was checked. The results were shown in Fig. 6. Although the adsorption reaction does not reach equilibrium

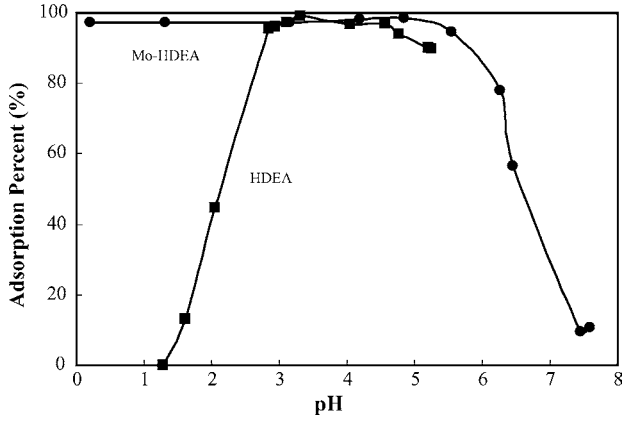

Fig. 5. The effect of pH on the adsorption of arsenic on HDEA resin with and without molybdenum. [As] = 1.3×10^{-5} M.

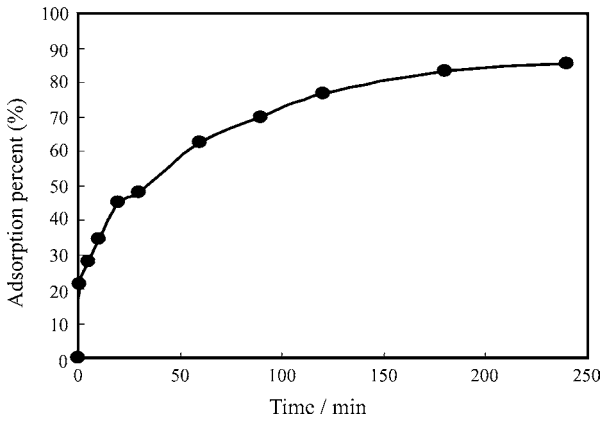

Fig. 6. The effect of the shaking time on the adsorption of arsenic(V) with Mo-HDEA resin. [As] = 1.3×10^{-5} M, pH = 1.

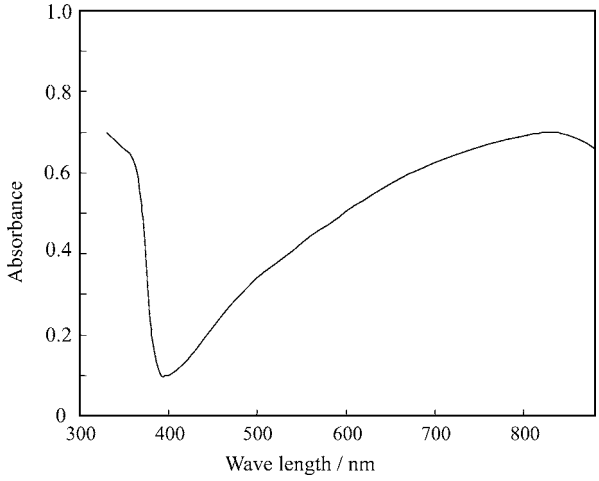

Fig. 7. The reflection spectra of the resin after the color developing reaction with arsenic(V).

even after shaking for 4 h at room temperature, the heating of the mixture helps color development due to the formation of a hetero poly acid. The color change by heating is large enough to detect arsenic in a short time.

3.4. Color development reaction of the resins

It is well known that molybdenum oxides forms a hetero poly acid with silicate, phosphate and arsenate. Since such a hetero poly acid gives blue color under the reductive conditions, the reaction has been utilized for the determination of the corresponding anions [1–3,17,18]. The authors found that the reaction forming molybdenum blue happens also in the resin phase under the similar conditions to that in the homogeneous system. The reflection spectra of the resin after the color developing reaction with arsenic were measured (Fig. 7). It shows the spectra having a peak at 830 nm which can be attributed to the formation of a hetero poly acid [19]. Fig. 8 shows the effect of acid concentration on the formation of molybdenum blue in the resin phase. It was found that 1 M HCl was adequate for the reaction. As was described above,

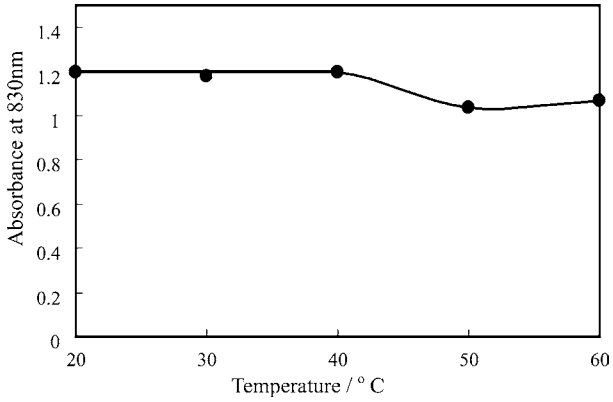

Fig. 9. The effect of the heating time on the formation of molybdenum blue.

although the adsorption of arsenic is not so rapid, it can be accelerated by heating the mixture. The effect of the temperature on the reaction is shown in Fig. 9. It was found that the temperature over 50 °C affects the reaction. Since the color intensity detectable by naked-eye was obtained by shaking for more than 20 min at 40 °C, these conditions were chosen for the standard procedure.

It was found ascorbic acid and hydrazine sulfates were effective as a reducing agent similar to the corresponding aqueous system. The effect of the concentration of ascorbic acid on the formation of molybdenum blue in the solid system was checked (Fig. 10). The excess amount of ascorbic acid did not affect the color reaction in contrast to the corresponding aqueous reaction in which the blue color diminishes at higher concentration of ascorbic acid. It was also found that the color reaction can be attained with more than 0.005 mol dm^{-3} of the ascorbic acid. Under these conditions, developed color is very stable and did not change during the detection procedure.

The effect of diverse ions of anions and cations were checked. Common anions like sulfate, nitrate, chloride, bromide and fluoride up to 1×10^{-2} M did not affect the detection of 1×10^{-5} M of arsenic(V). Sodium, potassium, magnesium and calcium up to 1×10^{-2} M did not affect either. Interference by cobalt, nickel, cupper, antimony

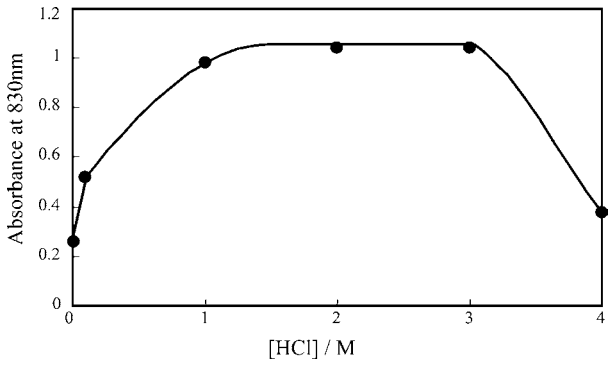

Fig. 8. The effect of the acid concentration on the formation of molybdenum blue in the resin phase.

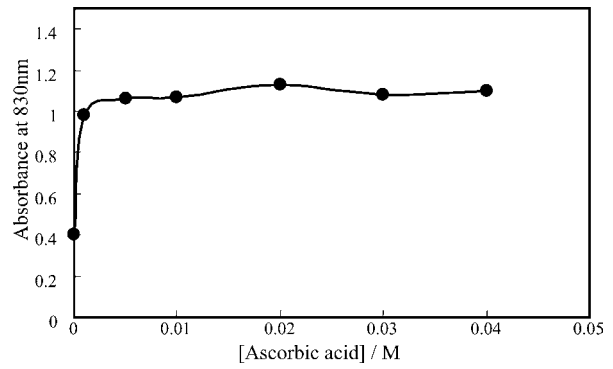

Fig. 10. The effect of the concentration of ascorbic acid on the formation of molybdenum blue in the solid system.

and selenium up to 1×10^{-2} M was not recognized. The influence of 5×10^{-3} M iron was observed but it was successfully masked by the addition of 1×10^{-2} M EDTA. Phosphate up to 1×10^{-5} M or silicate up to 1×10^{-4} M did not interfere with the color change reaction of 1×10^{-5} M of arsenic(V). No significant effect of organic compounds such as acetic acid and EDTA having little redox properties was observed. Although the disturbances by the other organic chemicals especially having some color are expected because the system is based on the color change of the resin, they can be assessed in each specific case.

3.5. Detection of arsenic(V)

Standard arsenic(V) solutions of 1×10^{-6} to 1×10^{-4} M together with a blank solution were measured by this method. The color of the resin changed from pale yellow to deep greenish blue (Fig. 11). A practical sample of hot-spring water in Akiu of Japan was measured by this method. The color of the sample showed 1.5 ppm according to the color scale obtained from the standard solutions. The ICP–AES measurement of the same sample is summarized in Table 1. The present naked-eye detection gave good agreement with the result of ICP–AES.

3.6. Preconcentration and detection of arsenic(V)

The effect of pH on the adsorption of arsenic with Mo-HDEA resin indicated the preconcentration can be attained preferably at pH 3 than strongly acidic conditions which is adequate for the detection procedures. Thus, the detection of a low concentration of arsenic was performed by two steps, preconcentration at pH 3 in the first step and formation of a hetero poly acid by reduction in the second step. An arsenic(V) solution of 1×10^{-7} M was successfully detected by this method, since the color of the resin changed to slightly greenish blue which is detectable by naked-eye (Fig. 12).

Table 1
The ICP measurement of the practical sample from the hot spring (Akiu, Japan)

Elements	Concentration (M)
Na	0.35
K	0.015
Mg	6×10^{-6}
Ca	1×10^{-5}
Se	2×10^{-6}
Si	6.4×10^{-4}
P	1×10^{-5}
As	2.3×10^{-5}

3.7. Regeneration of the resin

Since the HDEA resin can hardly adsorb molybdenum and arsenic in alkaline conditions (Fig. 5), it was expected that the used resin can be regenerated by a sodium hydroxide solution. It was found that the elution of molybdenum and arsenic was successfully carried out by the treatment of the colored resin with 1 M NaOH solution. It was also confirmed that the regenerated resins can be used as the detection material again by the adsorption of molybdenum.

Fig. 11. A color change of the resin with the different concentrations of arsenic(V). The real colors of the resins can be seen in the electronic version of this paper. [As(V)] = 0, 1×10^{-6}, 1×10^{-5}, 2×10^{-5}, 1×10^{-4}, 2×10^{-4} M, from left to right.

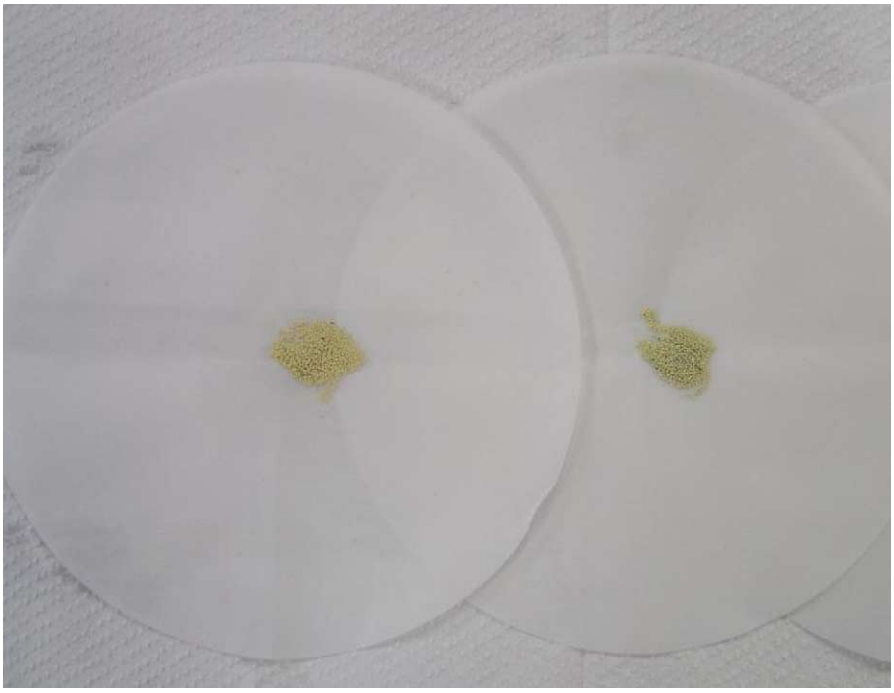

Fig. 12. A color change of the resin via concentration step. The real colors of the resins can be seen in the electronic version of this paper. [As(V)] = 0 (left), 1×10^{-7} M (right).

4. Conclusion

It was found that the molybdenum in the chelating resin reacts with arsenic(V) to give a greenish blue color in the presence of a reducing agent under the acidic conditions. The mechanisms of the color change are considered to be due to the formation of hetero poly acid in a chelating resin phase. Based on this phenomenon, a trace amount of arsenic(V) of 1×10^{-6} M can be detected by naked-eye observation with a molybdenum-loaded chelating resin having β-hydroxypropyl-di(β-hydroxyethyl) amino moiety. This detection limit can be lowered to at least 1×10^{-7} M by preconcentration with the same resin before the color development procedures.

Complicated procedures or costly instruments have been so far required for the determination of this level of arsenic(V) concentration. The new system using a solid indicator must lead to simple, rapid and low-cost detection method of trace amount of arsenic(V) in aqueous media.

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