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V. M. Shkinev[a]; G. A. Vorob'eva[a]; B. Ya. Spivakov[a]; K. E. Geckeler[b]; E. Bayer[b]
[a] VERNADSKY INSTITUTE OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY ACADEMY OF SCIENCES, MOSCOW, USSR [b] INSTITUTE OF ORGANIC CHEMISTRY UNIVERSITY OF TÜBINGEN, TÜBINGEN, FEDERAL REPUBLIC OF GERMANY

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Enrichment of Arsenic and Its Separation from Other Elements by Liquid-Phase Polymer-Based Retention

V. M. SHKINEV, G. A. VOROB'EVA, and B. YA. SPIVAKOV
VERNADSKY INSTITUTE OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY
ACADEMY OF SCIENCES
MOSCOW 117975, USSR

K. E. GECKELER and E. BAYER
INSTITUTE OF ORGANIC CHEMISTRY
UNIVERSITY OF TÜBINGEN
D-7400 TÜBINGEN, FEDERAL REPUBLIC OF GERMANY

Abstract

Preconcentration and recovery of arsenic from diluted aqueous solutions by soluble polymeric reagents in combination with membrane filtration were investigated. Quaternized poly(ethyleneimine) was found to be an efficient reagent for removal of arsenic and for separation of As(III), As(V), and divalent metal cations such as Cu, Cd, Zn, and Co. Using a 4% solution of the polymer reagnet, 98% of arsenic(V) was retained at pH 8.5, which could be stripped off by addition of a 0.15 *M* solution of a sodium salt solution at the same pH. A practical application was demonstrated by the removal of more than 95% of As(V) from actual concentrations of arsenic in wastewater.

Arsenic is one of most toxic elements present in wastewaters and various industrial fluids (*1*) which must be decontaminated to provide allowable arsenic levels. Complete extraction of arsenic from aqueous solution, particularly from very dilute solutions, is a difficult problem for arsenate precipitation methods, mainly used for the purpose, as well as for other known techniques. Yet, most analytical methods for determining arsenic require that they be preconcentrated from test solutions or preseparated from major constituents of dissolved solid matrices (*2*). That is why development of new methods of arsenic separation is important, including methods of separating arsenic(III) and arsenic(V) which possess quite different chemical properties and toxicity.

Membrane processes are among the most promising techniques for enrichment of various species from dilute solutions (*3*). Better retention of inorganic ions and higher selectivity of membrane separations can be achieved by using water-soluble polymeric reagents in combination with membrane filtration (*4*). A variety of water-soluble polymers with strong complexing properties have been synthesized and used to retain metal ions in the homogeneous aqueous phase (*5*, *6*). Separation of inorganic ions with water-soluble polymeric reagents is based on the retention of certain ions by a membrane which separates low molecular mass compounds from macromolecular complexes of the ions. We call this method liquid-phase polymer-based retention (LPR) (*7*), which is probably the most adequate term for the technique.

Most publications on the LPR method have been devoted to metal cation retention although some attempts have been made to separate chromate ions (*8*, *9*) and anionic complexes of some noble metals (*5*). No information about arsenic separation by the technique appears to be available.

This report describes our results on the retention of arsenic(V) from aqueous solutions, and its separation from arsenic(III) and other elements using permethylated poly(ethyleneimine) (P) as reagent.

EXPERIMENTAL

Reagents and Radionuclides

The salt solutions as well as hydrogen chloride and sodium hydroxide solutions were prepared from analytical-grade chemicals. Permethylated poly(ethyleneimine) (molecular mass = 30,000–40,000 g/mol) was synthesized by alkylation with dimethyl sulfate and membrane filtrated prior to use.

The radionuclide of ^{76}As, used for retention studies, was obtained by irradiation of elemental arsenic in a nuclear reactor with a neutron flux of 10^{13} neutron/s for 20 h. The sample was then dissolved in concentrated HNO_3 containing several drops of $HClO_4$, evaporated, and dissolved in 0.005 *M* NaOH to obtain arsenic in the form of Na_3AsO_4. Extraction of ^{76}As from an iodide-sulfate solution into benzene followed by stripping into water was used to obtain the radionuclide in the form of arsenic(III). In order to study the distribution of other elements between the cell solution and the filtrate, the following radionuclides were used: ^{24}Na, ^{39}K, ^{134}Cs, ^{64}Cu, ^{69m}Zn, ^{115}Cd, ^{75}Se, ^{60}Co. They were obtained by irradiation of a mixture of the elements under the same conditions as arsenic. The sample was treated with concentrated HNO_3, evaporated, and dissolved in 0.1 *M* HCl. The concentrations of elements in the experiments were varied from 10^{-4} to 10^{-7} mol/L (10–0.01 mg/L).

Equipment

Membrane filtration studies were performed with a unit consisting of a cell with an Amicon PM 10 membrane (exclusion rate 10,000), a reservoir, a selector, and a regulator. The presence of nitrogen was kept constant (300 kPa), the solution in the cell being stirred during membrane filtration. Radiometric measurements of arsenic concentration in the cell solution and in the filtrate (permeate) were performed with an NRG-603 automatic γ-counter (Tesla). Simultaneous measurements of γ-activities of other elements were made with a Ge(Li) detector connected with a multichannel LP-4900 Nokia analyzer. The γ-spectra were computer processed using a program developed by V. P. Kolotov and V. V. Atrashkevich at the Vernadsky Institute.

Procedure

To study the retention of arsenic and other elements, an aqueous solution of the elements was placed into the filtration cell containing a P solution to make a total constant volume of 2 or 4 mL. The system was pressurized and the cell washed with a reservoir solution (Procedure I). This procedure is convenient for analytical preseparation of retained elements to be determined from interfering sample constituents which do not form macromolecular complexes.

To show the possibility of decontamination of diluted solutions, enrichment was performed by passing a large volume of arsenic solution from the reservoir through the polymer-containing cell solution (Procedure II). Our studies have shown that both procedures give approximately the same retention of arsenic or any other element if pH and foreign salt concentration in the cell and reservoir have been adjusted to the same value and equal volumes of fluid are passed through the cell.

The filtrate fractions were collected and subjected to radiometric measurements as well as cell solution before and after each membrane filtration run. The retention percentage values (R) were calculated and plotted as a function of the ratio $Z = V_f/V_0$, where V_f and V_0 are the volumes of the filtrate and the cell solution, respectively.

RESULTS AND DISCUSSION

In neutral and slightly alkaline solutions, e.g., in waste industrial waters with pH = 5–11 (*1*), arsenic(V) exists in the form of metal orthoarsenates and arsenic(III) in the form of arsenious acid. That is why we used an anion-exchange reagent, P, to retain arsenic(V) in the filtration cell solution.

The retention of arsenic(V) as well as arsenic(III), placed into the cell (Procedure I), by a 4% P solution has been studied as a function of the water volume passed through the cell (Fig. 1). About 98% of arsenic(V) remains in the cell even if 28 mL of water with pH 8.5 is passed into the cell containing 4 mL of polymer solution (Z = 7) having the same pH. Only 6% of arsenic(III) remains in the cell under such conditions. Further

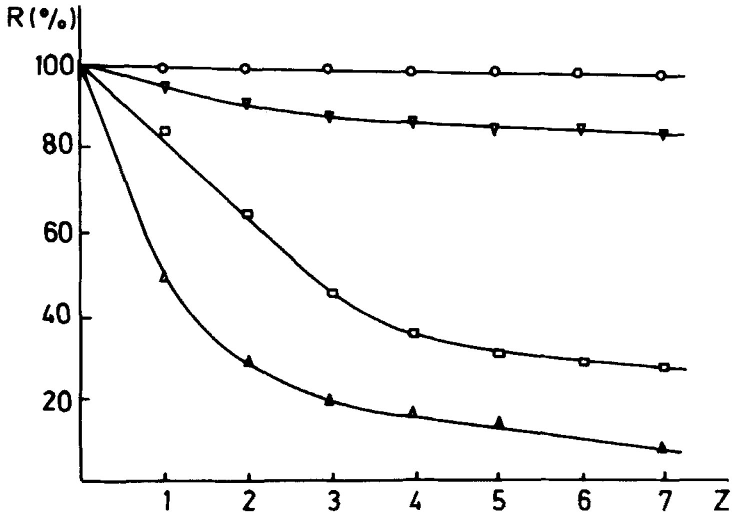

FIG. 1. Retention of arsenic(V) (○, ▽) and arsenic(III) (□, △) by 4% P solution at pH 8.5 (○, △) and 11 (▽, □) as a function of the ratio of filtrate volume to cell solution volume (Z).

washing the cell results in complete removal of arsenic(III) from the cell, arsenic(V) being retained and then determined in the cell solution. Such a good separation of arsenic(V) and arsenic(III) cannot be achieved at pH 11 (Fig. 1, Curves 2 and 3). In this case, 28% of arsenic(III) is retained due to better dissociation of arsenious acid to give free oxo anions at high pH values. On the other hand, retention of arsenic(V) decreases from pH 8.5 to pH 11, and that also worsens the separation.

Figure 2 illustrates the dependence of arsenic(V) retention on pH together with the formation curves for different arsenate forms in aqueous solution. Comparison of the graphs in this figure shows that the best retention is achieved within a pH range of 8–10 where arsenic(V) mainly exists in the form of discharged anions $HAsO_4^{2-}$. Two factors can be responsible for the lower retention at higher pH values: formation of AsO_4^{3-} anions and competition of OH^- ions for the reagent. At lower pH values the protolysis equilibrium shifts to $H_2AsO_4^-$ and then to non-retained H_3AsO_4. Besides, competition for the polymeric anion exchanger can occur from anions of the acid added to acidify the solution.

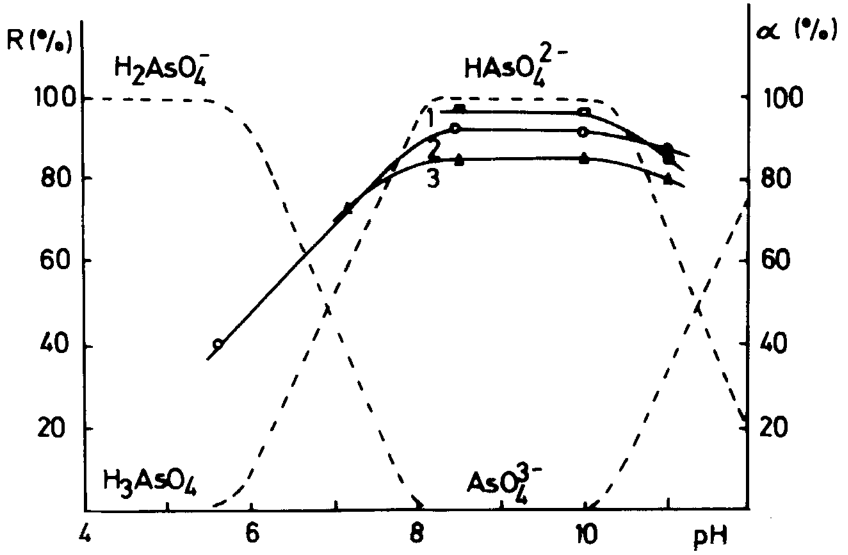

FIG. 2. pH dependence of arsenic(V) retention by polymer P solution (solid lines) and of arsenate protonation (dashed lines); retention by 4% P from water (1), 2% P from water (2), 4% P from 0.01 *M* NaCl (3).

Metal salts rather strongly influence the retention of arsenic(V). Figure 3 shows the dependence of arsenic retention at pH 8.5 by 4% P on the volume of 0.01 *M* sodium salt solution passed from the reservoir. The retention decreases in the order: NaCl, $NaNO_3 > Na_2CO_3 > Na_2SO_4$. Discharged anions must be stronger competitors for the reagent than chloride and nitrate because of their higher electrostatic affinity to positively charged polymer sites. Yet, different salts can have different effects on the conformation of polymer molecules (*10*), resulting in different activities of the reagent functional groups. It is also worth noting that chloride and nitrate at pH 11 do not have a practical effect on the retention, probably due to the dominating influence of OH^- ions.

A comparative study has been made of the behavior of several elements of different natures under conditions for arsenic(V) retention. Figure 4 shows the retention of nine elements by 4% P at pH 8.5 in the presence of 0.01 *M* NaCl. P retains As(V) and Se(IV) in the form of oxo anions as well as divalent metal cations (Cu, Cd, Zn, Co) which can interact with the base polymer imino groups left after their partial quaternization. This worsens the reagent selectivity to anionic forms of the elements but makes it possible to retain a number of various ions from aqueous solution similtaneously. Alkali metal cations, as well as

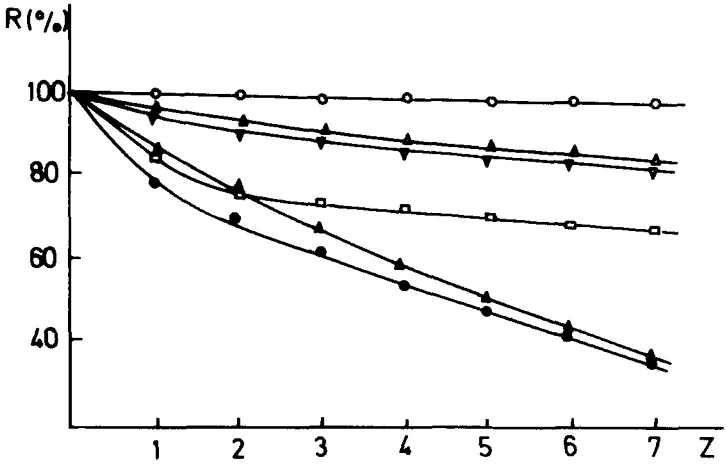

FIG. 3. Influence of sodium salts on the arsenic(V) retention by 4% P at pH 8.5: (○) water, (□) 0.01 *M* Na_2CO_3, (△) 0.01 *M* NaCl, (▲) 0.5 *M* NaCl, (▽) 0.01 *M* $NaNO_3$, (●) 0.01 *M* Na_2SO_4.

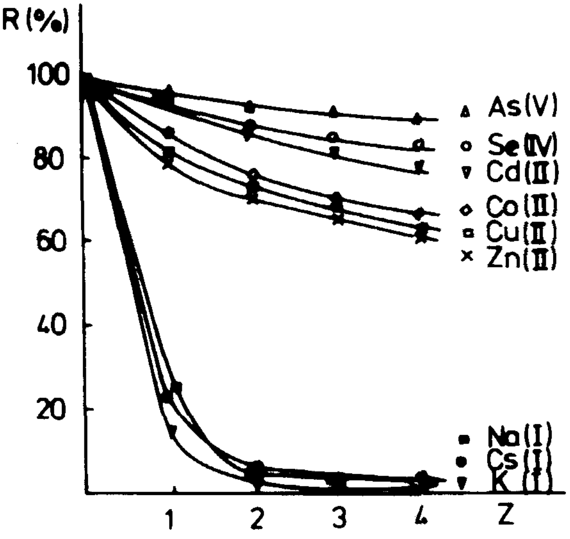

FIG. 4. Retention of elements by 4% P from 0.01 *M* NaCl at pH 8.5.

other ions which do not react with any reagent groupings, are completely washed into the filtrate (Fig. 4).

The data obtained show that arsenic(V) can be enriched by passing a large volume of diluted arsenic solution through a filtration cell containing a small volume of P solution (Procedure II). Thus 98% of arsenic was retained by the cell solution if 28 mL of arsenic solution was diafiltrated from the reservoir through 4 mL of 4% P at pH 8.5 (sevenfold enrichment). Arsenic(V) can also be recovered by a less concentrated reagent solution. For example, 92% of arsenic was retained by 2% P at $Z = 7$ (Fig. 5).

A lower concentration of the polymer provides a higher flow rate through the membrane. Thus, with 2% P the flow rate is only 24% lower than with water. The flow rate is also dependent on the solution pH and foreign salt concentration; the pH value has the stronger effect. The flow rate drops sharply at pH 11.

As seen from data on the influence of metal salt and acid concentration on arsenic retention, its cleavage from the polymer is no problem. With a 0.15 *M* solution of any sodium salt tested, 99% of arsenic can be stripped from the cell at pH 8.5 and $Z = 5$. Stripping of enriched arsenic and, therefore, recovery of the polymeric reagent can also be easily performed by 0.1 *M* HCl.

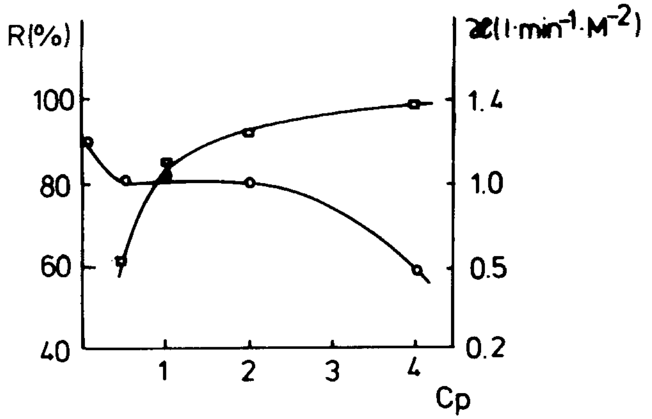

FIG. 5. Retention of arsenic(V) (□) and flow rate æ (O) at pH 8.5 as a function of P concentration (C_p).

By studies on the arsenic concentration dependence it was shown that more than 95% of As(V) and 90% of As(V) are retained at a arsenic concentration in the reservoir of $\leqslant 1$ and 10 mg/L, respectively. These data are based on $Z = 20$, a polymer concentration of 4%, and pH 8.5. Therefore, a two-step retention is sufficient to provide allowable levels of arsenic in the filtrate (0.05 mg/L) for a initial concentration of 10 mg/L.

In conclusion, it is worth noting that, using the polymer reagent P and the LPR method, wastewaters can be decontaminated from both arsenic(V) and arsenic(III) because the latter is readily oxidized even by air at relatively high pH values.

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