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LIQUID-PHASE POLYMER-BASED RETENTION (LPR) - A NEW METHOD FOR SELECTIVE ION SEPARATION

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ABSTRACT

A new method based on the retention of ions by hydrophilic polymer reagents in a membrane filtration system, called Liquid-Phase Polymer-Based Retention, is described for selective ion separation. The principle and fundamentals of the method including the use of polychelatogens are explained and discussed.

The effect of several polychelatogens on ion separation is documented and described by numerous retention profiles. It is shown that LPR is a convenient and effective method for selective ion separation of metal ions and anions.

INTRODUCTION

Elemental analysis in geological, biological, environmental and industrial samples is increasingly important. Despite the application of modern instrumental methods of analysis, preliminary enrichment techniques are required to separate the components to be determined from the interfering constituents of the sample[1,2]. Liquid-liquid extraction. sorption, ion exchange, precipitation, and other methods, based on two-phase distribution, are used for the separation of ions contained in dissolved solid matrices, industrial fluids or natural waters[3-6].

Many such methods have been developed and successfully used, however, their application can cause problems connected with heterogeneous reactions and interphase transfer. In the case of preference of aqueous solutions for the subsequent procedure rather than organic solvents or solid concentrates, other problems can arise. In consequence, additional procedures are needed, e.g. back-extraction, desorption, dissolution of solid concentrates, etc. As a result, the analysis is complicated and eventually the sample is contaminated from the reagents added.

Separation methods based on membrane processes are appropriate to avoid two-phase systems. The use of chemically inert solid membranes makes it possible to achieve separation in homogeneous aqueous phase and these processes are easily handled and automated[7].

The high efficiency and selectivity of membrane separations have been applied on a preparative scale using water-soluble polymers in combination with membrane filtration[8-12]. To this end, different hydrophilic polymers with chelating groups have been prepared for use in the retention of metals in aqueous phase[8,11,12]. The main application of this method, based on separation of elements bound to the polymer from uncomplexed species, is the recovery of metals from diluted solutions. The technique can easily be applied to ion separation for analytical purposes.

Liquid-Phase Polymer-Based Retention is based on the application of a new class of polymeric reagents, called polychelatogens, and designed for selective ion separation in liquid phase in conjunction with membrane filtration.

PRINCIPLE AND FUNDAMENTALS OF LPR

The principle of the LPR method stems form the idea to recover metal ions from dilute solutions by using soluble polymers[8,9]. That procedure on a preparative scale was used for the preconcentration of elements from large volumes. In order to make this approach applicable to samples on an analytical scale, the sample is placed directly in the cell of the membrane filtration system and the ions are separated by elution with water[13-16]. A scheme to illustrate the principle is outlined in Figure 1.

The ion separation mechanism in LPR is a complex phenomenon and based on interactions of the ions with the polychelatogen in the form of complex formation, ion exchange, hydrophobic and other interactions. For the

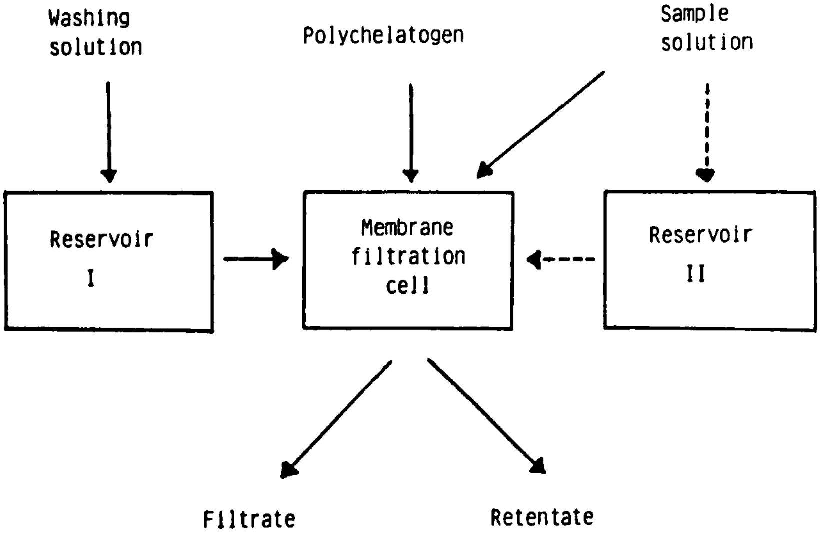


FIGURE 1
Principle of the LPR method: The sample solution is placed directly into the membrane filtration cell, which contains an aqueous solution of polychelatogen, or via the reservoir II for preconcentration. By adding the washing solution from reservoir I separation of ions is achieved by the selective retention of some of them in the retentate and the elution of the others in the filtrate.

separation of ions the ability of the polymeric reagents to retain the required ionic species in the course of one filtration run is important. As shown previously, the retention of any species, not bound to the polymer and therefore not rejected by the membrane, can be described by an exponential function[15]:

$$R = C_r \cdot C_o^{-1} = \exp(-V_f \cdot V_o^{-1})$$

where C_r is the species concentration in the retentate (cell solution after a filtrate volume of V_f has been passed), C_o is the initial species concentration in the cell, V_o is the volume of cell solution, and V_f is the volume of filtrate.

The retention of such species can be expressed as $\log R = -0.43\ Z$, where the filtration factor $Z = V_f \cdot V_o^{-1}$. According to this, the concentration of unrejected species in the cell can be made 10^3 times lower at Z=7 or more than 10^4 times lower at Z=11, and so on. Therefore, if ion A is completely retained in the cell ($R_A \rightarrow 1$), it can be separated from ion B with a maximum separation factor ($\beta = R_A \cdot R_B^{-1}$) expressed as $\log \beta = 0.43\ Z$. The conventional separation factor β, used in two-phase distribution methodology and expressed as a ratio of distribution coefficients for two species, is not applicable to distribution processes in homogeneous phase. Consequently, the separation factor in LPR is expressed as the ratio of retention values.

Some basis parameters are listed in Table I.

The basis of the elution diagrams, which show the metal ion concentration in the filtrate as a function of filtrate volume, are the filtrate analysis data from LPR studies (Figure 2).

If no metal ions can be detected in any filtrate fraction complete retention has been achieved. Complete retention of Cu^{2+} ions was achieved at pH 3.2, whereas the other four cations were washed out in the filtrate (Figure 2a). The dotted curve in Figure 2b is an approximation of elution curves which are obtained, when there is no retention. It is described by the exponential function:

$$C_f = C_o \cdot e^{-V_f/V_o} \quad \text{(see Table I)}$$

TABLE I.

Basis parameters used in LPR
and their definitions

Name	Symbol	Definition	Unit
Retention	R	$C_r \cdot C_o^{-1}$	%
Filtration factor	Z	$C_f \cdot V_o^{-1}$	-
Filtration quotient	F	$C_f \cdot C_o^{-1}$	-
Separation factor	β	$R_A \cdot R_B^{-1}$	-

C_o = Initial ion concentration
C_r = Ion concentration in the retentate
C_f = Ion concentration in the filtrate
V_o = Volume of retentate
V_f = Volume of filtrate

The elution profiles of the Ni^{2+}, Zn^{2+}, Cd^{2+} and Co^{2+} ions are similar to the theoretical curve in Figure 2b).

Some retention values of bivalent cations are summarized in Table II by dependence of the pH. The ion retention is strongly influenced by the pH. For example, > 80% Cu^{2+} is retained at pH 2.1 with a filtration factor of 10, whereas the retention is complete at pH 3.2. In contrast, Mg and Na ions, which do not form stable complexes with this polychelatogen, are not retained at pH 5.3.

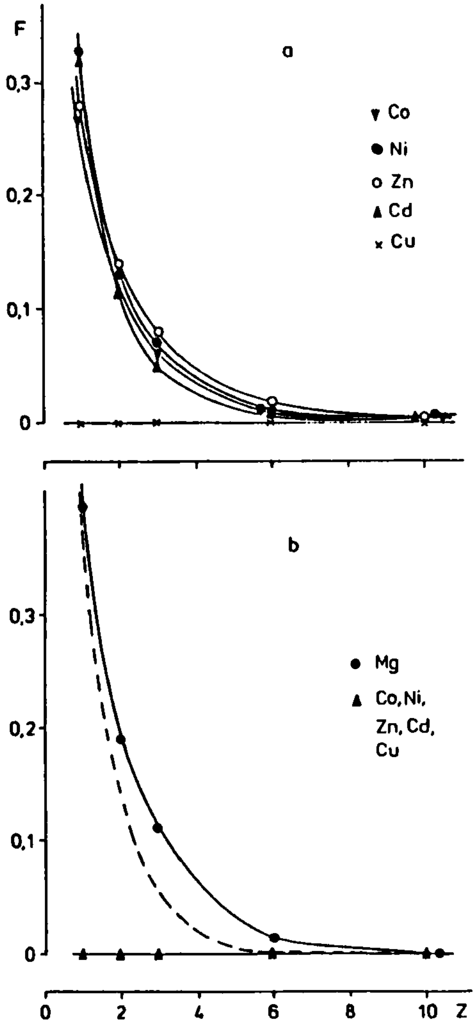


FIGURE 2

Elution diagrams for some bivalent metal ions separated by poly(ethyleneimine) using LPR[13]. Filtration quotient $F = C_f \cdot C_o^{-1}$ is plotted against the ratio $Z = V_f \cdot V_o^{-1}$ at pH 3.2 (a) and 5.3 (b); C_f, C_o and V_f, V_o are concentration and volume of filtrate and cell, respectively. Polymer concentration 1%, C_o = 10 mg·kg^{-1}. Dotted curve, elution of an arbitrary metal which is not retained in the cell.

TABLE II.

Retention of metal ions by poly(ethyleneimine) at different pH values using LPR[13]. Polymer concentration 1%, initial metal concentration 10 mg·kg^{-1}, filtration factor 10.

	Retention						
pH	Co^{2+}	Ni^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Mg^{2+}	Na^{+}
2.1	1.2	0.1	1.0	0.1	86.3	-	-
3.2	16.3	21.3	0.5	0.7	99.0	-	-
4.0	93.1	99.0	-	98.1	99.0	-	-
5.3	99.0	99.0	99.0	99.0	99.0	0.1	0.1

EQUIPMENT AND PROCEDURE

The equipment needed for Liquid-Phase Polymer-Based Retention consists mainly of a conventional membrane filtration system or, if a preconcentration step is required, a specially designed radial-flow membrane filtration system[15]. The main features are the membrane filtration cell, the membrane, the reservoir, the selector and regulator (Figure 3).

The membranes can be made of the usual materials, e.g. polysulfone, polyamide cellulose, etc.; also commercially available membranes are suitable for LPR (Amicon PM 10, Millipore PTGC, or equivalent). Essential parameters are the molecular mass exclusion rate, stability in wide pH ranges (pH 1-10), and an appropriate flow

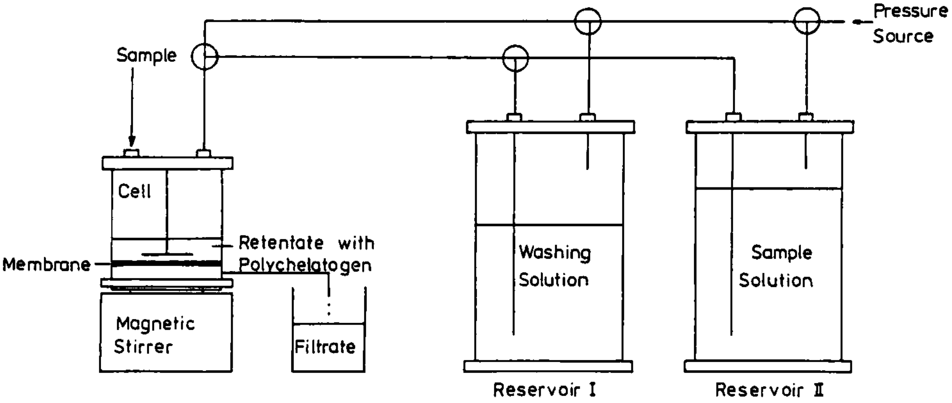


FIGURE 3
Scheme of the instrumental arrangement for Liquid-Phase Polymer-Based Retention.

rate (1-10 $ml \cdot min^{-1}$). The molecular mass exclusion rate depends mainly on the average molecular mass of the polychelatogen used, however, a nominal exclusion rate of 10000 $g \cdot mol^{-1}$ proved to be convenient for polychelatogens with a molecular mass between 30000 and 50000 $g \cdot mol^{-1}$.

Investigations of the influence of the polymer concentration on the flow rate are shown in Figure 4.

As(V) can be recovered up to 98% by 4% polychelatogen at pH 8.5 after a 7-fold enrichment. 2% polymer reagent retain 2% of the ion. A higher flow rate through the membrane can be attained by a lower concentration of the polymer. For example, with 2% of polychelatogen the flow rate is only 24% lower than with water. It is also dependent on the solution pH and salt concentration. The pH value has a stronger effect and the flow rate drops sharply at pH 11.

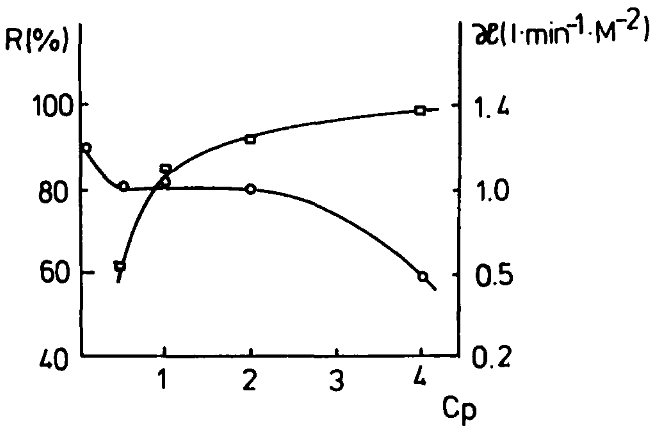


FIGURE 4
Dependence of the flow rate (ϰ) and retention (□) of arsenic(V) at pH 8.5 as a function of polymer concentration (c_p, PMP) for Z = 7[17].

The initial ion concentration in the cell solution or in reservoir II varies from 10^{-4}-10^{-7} mol·l^{-1}. Before starting, the pH of the cell and reservoir solutions is adjusted to the same value and the system is pressurized (300 kPa). Then the cell solution with the polychelatogen(1-4%) is stirred for 5 min and washed with the reservoir fluid at a flow rate of 4-6 ml·min^{-1} under stirring. The filtrate contains all the ions which are not retained as macromolecular interaction products by the polychelatogen.

Large volumes of very diluted samples are first enriched with respect to ions of interest by passing the solution form reservoir II to the much smaller volume of cell solution. Then, the additional separation process is performed by adding washing fluid from reservoir I to remove non-bound ions from the cell. The ion content of filtrate fractions and cell solution are analyzed by atomic absorption spectrometry, inductively-coupled plasma, radiometry, electrochemical methods, or others. The retention values were calculated from the measured concentrations of filtrate and retentate.

POLYCHELATOGENS

The salient feature of the LPR method is the use of soluble polymer reagents with chelating groups, called polychelatogens[13,15]. These hydrophilic, non-crosslinked polymers allow the application of membrane filtration by virtue of the great difference of their molecular mass compared to other interacting species. Thus, the retention of ions by a membrane which separates macromolecules from low-molecular compounds can be investigated and applied to ion separation.

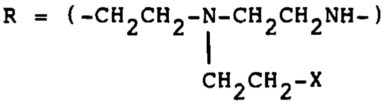
A polychelatogen is characterized by two main components, the polymer backbone, which provides the solubility and stability of the reagent, and the functional groups which are necessary for the selective reactivity of the polymer. Both ways, introducing different functional groups into the same polymer backbone, and varying the type of polymeric chain bearing the same functional group have been investigated. Some examples of the first approach are given in Table III for the water-soluble poly(ethyleneimine).

The structural formula of permethylated poly(ethyleneimine) (PMP) and poly(ethyleneimine) 8-hydroxy quinoline are depicted in Figure 5 and 6.

The interesting sulfur-containing ligand methyl thiourea was combined with three different hydrophilic

TABLE III.

Functional groups and abbreviations of some polychelatogens based on poly(ethyleneimine)



$$R = (-CH_2CH_2-\underset{\displaystyle CH_2CH_2-X}{\underset{|}{N}}-CH_2CH_2NH-)$$

Functional group X	Name	Symbol
$R-NH_2$	Amino	PEI
$R-NH-C(=S)-NH-CH_3$	Methyl thiourea	PTU
$R-N^+(CH_3)_3$	Trimethylammonium	PMP
$R-NH-SO_2$-oxine	8-Hydroxy quinoline	POX
$R-N(CH_2COOH)_2$	Imino diacetic acid	PDA

polymer backbones. This is an example of the second approach (Figure 7)[18].

In most cases the influence of the functional group is stronger than that of the repeating unit of the polymer chain[18].

Other basis polymers for polychelatogens are poly(vinylamine), poly(urethanes), poly(acrylic acid), poly(vinylalcohol), poly(oxyethylene), and poly(vinylpyrrolidone)[8-10,12].

The polychelatogen shows a different selectivity for inorganic ions which depends on both the reactivity of the functional group and the chemical nature of the

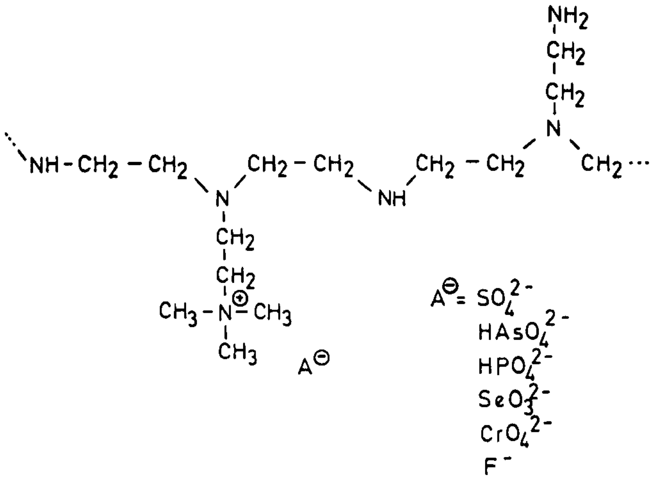


FIGURE 5
Structural formula of permethylated poly(ethyleneimine) (PMP) in conjunction with some anions.

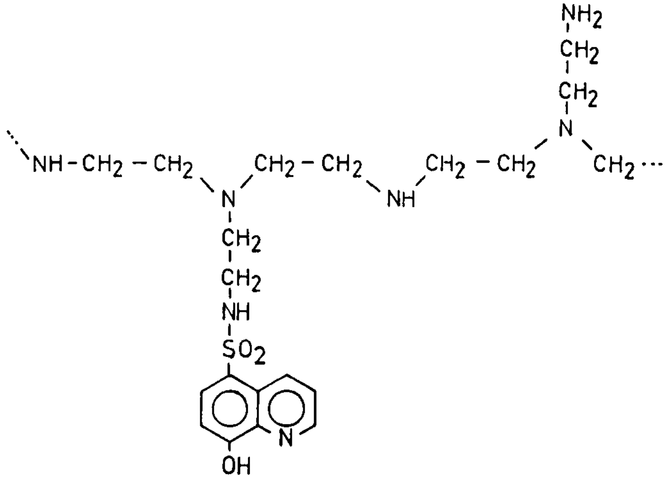


FIGURE 6
Structural formula of poly(ethyleneimine) oxine.

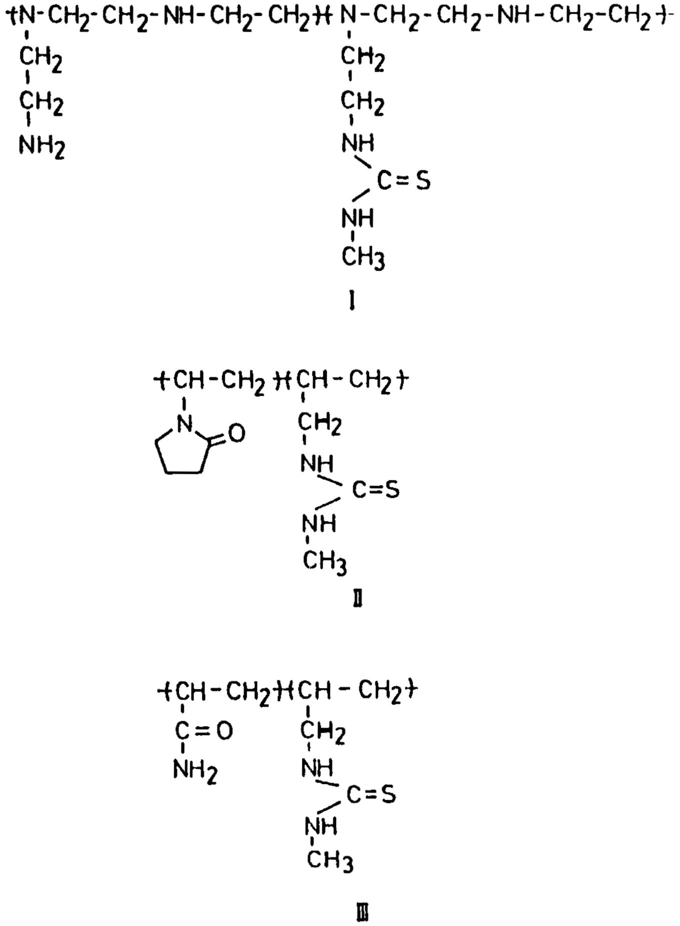


FIGURE 7
Methylthiourea-based polychelatogens with different polymer backbones: poly(ethyleneimine)(I), poly(vinylpyrrolidone)(II), poly(acrylamide)(III).

TABLE IV.

Selectivity of polychelatogens for some metal ions[8,12].

Polychelatogen	Selectivity based on complex stability
PEI	$Au^{3+} > UO_2^{2+} \sim Cu^{2+} > Pt^{4+} > Ni^{2+} \sim Co^{2+}$
PTU	$Au^{3+} \sim Pt^{4+} \sim Cu^{2+} > Ni^{2+} \sim Co^{2+}$
PDA	$UO_2^{2+} > Pt^{4+} > Cu^{2+} \gg Au^{3+} \sim Ni^{2+} > Co^{2+}$
POX	$UO_2^{2+} > Cu^{2+} \sim Pt^{4+} > Ni^{2+} \sim Co^{2+} > Au^{3+}$

polymer backbone. To illustrate this phenomenon, selectivity series are summarized for some basis polychelatogens (Table IV).

Besides their primary effect due to their chemical structure polychelatogens show other influences during the LPR procedure based on their properties as polymeric compounds, e.g. solubility, stability and viscosity. A defined solubility and stability are a prerequisite for their use as polychelatogens. In contrast, the viscosity depends on the concentration. Therefore, retention has been studied as a function of the polymer concentration (Figure 8).

In general, it can be shown that the retention of anions decreases with increasing polymer concentration. For example, arsenic(V) and fluoride anions can be retained to an extent of 92% or 89%, respectively, when using polymer concentrations of 2% and a filtration fac-

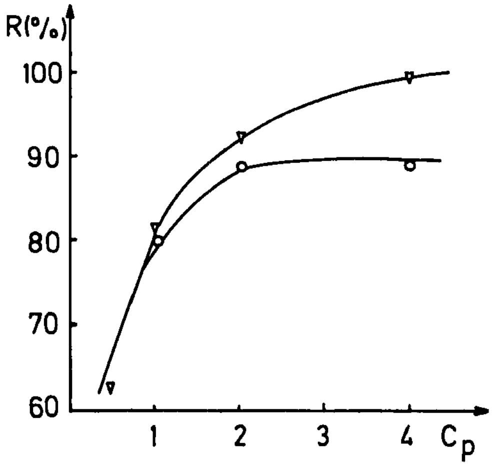


FIGURE 8
Retention (R) as a function of polymer concentration (c_p) for permethylated poly(ethyleneimine)(PMP), arsenic(V) (▿), fluoride (o) and a filtration factor Z = 7 at pH 8.5.

tor of 7[17]. Low polymer concentrations in the cell solution are not only advantageous in terms of a low consumption of polychelatogen but also a higher flow rate during membrane filtration. The latter fact is essential for the separation of species in very diluted samples.

SELECTIVE ION SEPARATION

Bivalent Cations

Among the different types of ions the bivalent cations represent a group of ions in connection with LPR of practical importance in terms of separation and enrichment. Bivalent metal ions can be separated using LPR in neutral solutions by poly(ethyleneimine) (PEI), a relatively weak polymeric complexing agent (Figure 9)[13,14]

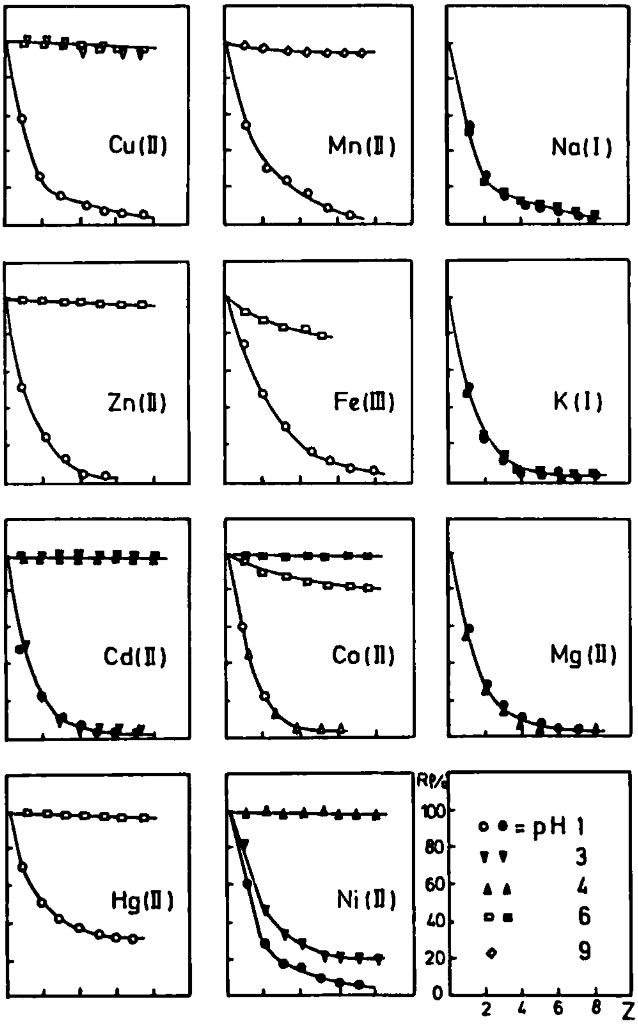


FIGURE 9
Retention of metal ions by 1% poly(ethyleneimine) (PEI) at different pH values in the absence (filled symbols) and presence of 0.15 M $NaNO_3$ (open symbols) as a function of the filtration factor Z.

At pH 6 several bivalent cations (Cu, Zn, Cd, Hg, Mn, Co, Ni) are quantitatively retained. Very interesting is that Mn^{2+} ions are also completely retained at pH 8 because extraction of this element from aqueous solution is a difficult problem for any separation method. Cu^{2+} ions form the most stable complexes with PEI and can be separated from other ions at lower pH values ($\geq$ 3). Alkali and alkaline earth ions are not retained at all at any pH value.

Bivalent cations such as Cu^{2+} (pH $\geq$ 3), Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} ($\geq$ 5), Co^{2+} ($\geq$ 7) are completely retained at relatively high pH values. This polychelatogen also separates Pb (5), Mn (8) and some other metals from alkali and alkaline earth ions under such conditions (Figure 10).

In the case of mixtures of bivalent and multivalent ions it is necessary to introduce a special functional group to achieve better separations because PEI is a less effective and selective reagent. To this end, 8-hydroxy quinoline groups have been introduced into poly(ethyleneimine) to yield a polychelatogen which forms stable metal oxinates. For example, Zr, Nb, W, Bi are quantitatively retained at pH 1 and can be separated from most other metal ions studied (Figure 11)[19].

Beryllium and barium remain partially in the retentate but other alkali and alkaline earth ions are eluted within the whole pH range. Thus, a convenient separation from other cations can be attained.

The separation profiles of a poly(vinylpyrrolidone)-based polychelatogen with functional thiourea groups for some bivalent cations are shown in Figure 12.

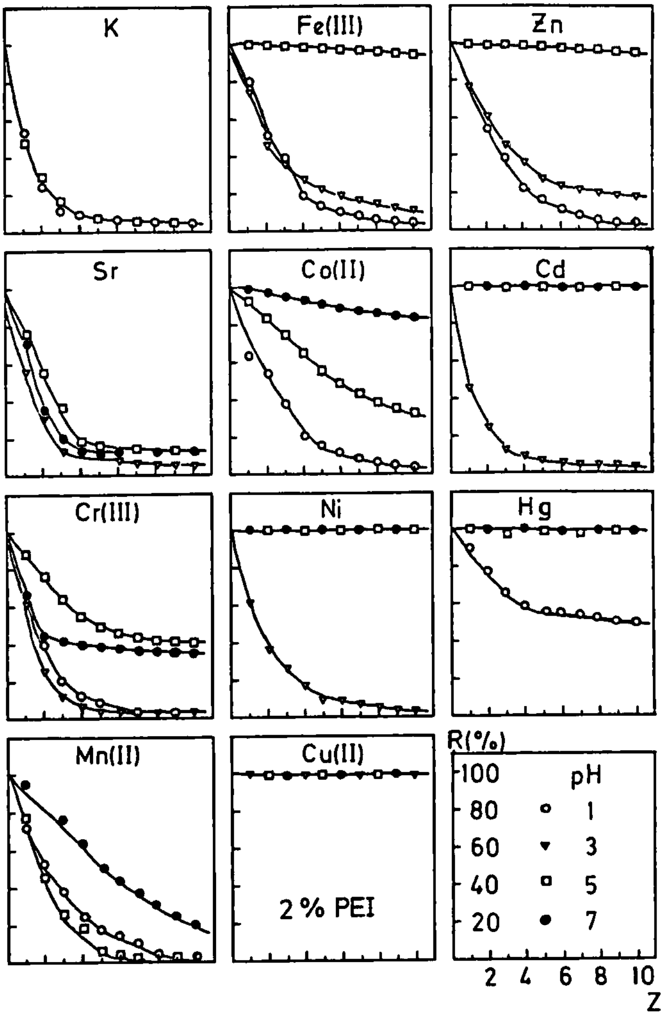


FIGURE 10
Retention of metal ions by poly(ethyleneimine) (2%) at different pH values in the presence of 0.15 M $NaNO_3$+HNO_3 as a function of the filtration factor Z.

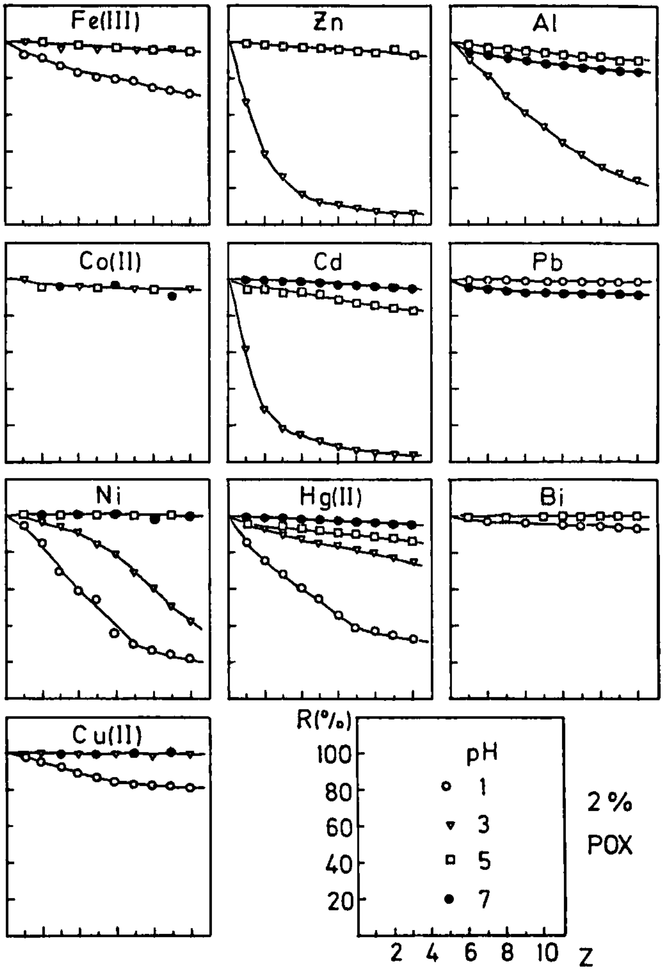


FIGURE 11
Effect of poly(ethyleneimine) oxine (POX) (2%) at different pH values in the presence of 0.15 M $NaNO_3$+HNO_3 as a function of the filtration factor Z.

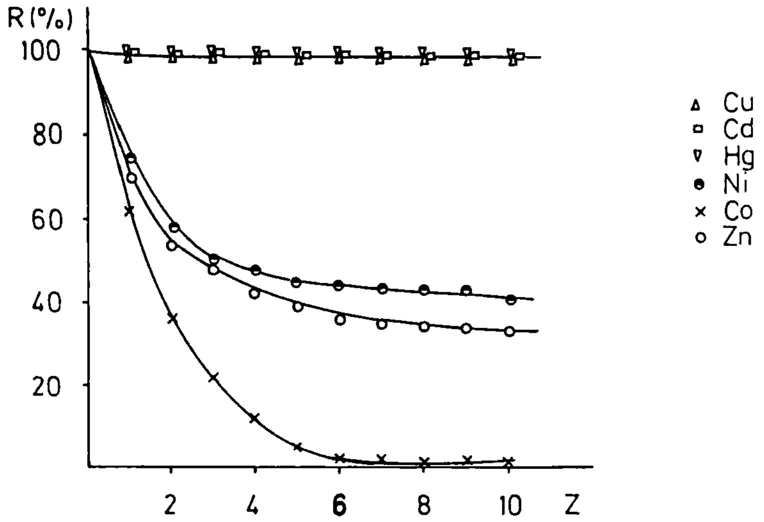


FIGURE 12
Effect of poly(1-vinyl-2-pyrrolidinone) allylmethyl thiourea on the retention of some metal ions at pH 5[18].

Whereas Cu, Cd and Hg ions are completely retained, Ni and Zn ions show only partial and cobalt no interaction with the polymer reagent. This indicates a dominating influence of the functional group over the polymeric backbone and is useful for the selective separation of the highly toxic cadmium and mercury ions.

Multivalent Elements

In contrast to bivalent ions, selective separation of ionic species of multivalent elements requires specially designed polychelatogens. For example sulfur-containing reagents are suitable for separating mercury and noble metals from other elements. An effective polychelatogen of this type is poly(ethyleneimine) methyl thiourea (PTU) which is synthetically accessible by a one-step reaction[8,18]. PTU quantitatively retains Hg^{2+}, Ag^{+}, Au^{3+}, Pd^{2+}, Pt^{4+} from chloride solutions at pH 1 and allows one to separate these elements not only from alkali cations but also from non-ferrous metals ions such as Co^{2+}, Zn^{2+}, Cd^{2+}, and In^{3+} (Figure 13).

The results of a comparative study between selenium(IV), arsenic(V) and some bivalent elements are illustrated in Figure 14.

The reagent permethylated poly(ethyleneimine) (PMP) retains As(V) and Se(IV) in the form of oxo anions as well as bivalent cations such as Cu, Cd, Zn, and Co[17]. This represents a mixed ion interaction mechanism involving ion exchange of the anionic species by the quarternary ammonium groups and complex formation of the cationic species by the imino groups of the polymer backbone. Although the selectivity to anions is reduced it opens the possibility to retain various other ions from aqueous solutions simultaneously.

It is also possible to separate two different valence forms of an element. For example, arsenic(III) and arsenic(V) can be separated at pH 8.5 (Figure 15).

At this pH about 98% of arsenic(V) remains in the retentate whereas only 6% of arsenic (III) is retained under such conditions. These values are referred to a filtration factor of 7 and if it is increased, complete separation can be achieved.

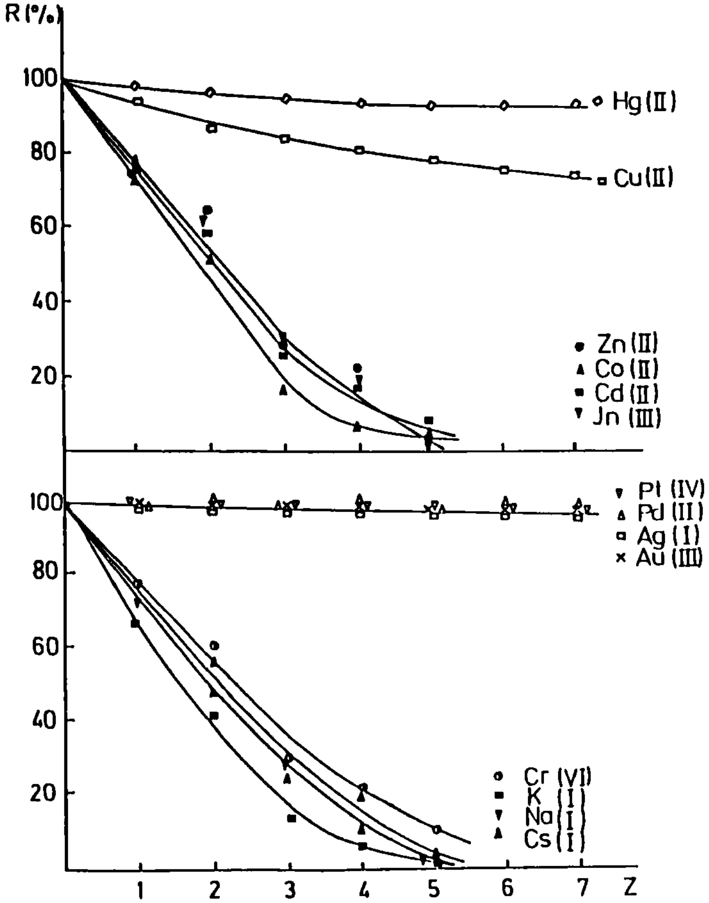


FIGURE 13
Effect of poly(ethyleneimine) methyl thiourea (PTU) (3% solution) on the retention of metal ions from 0.15 M NaCl at pH 1 as function of the filtration factor Z.

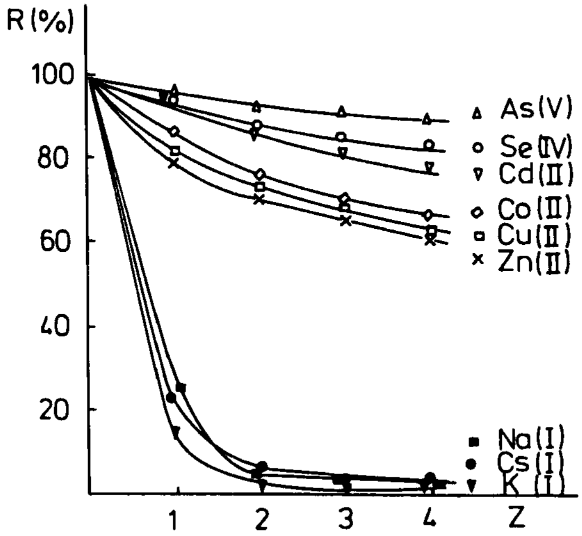


FIGURE 14
Retention of elements by a 4% solution of permethylated poly(ethyleneimine) (PMP) from 0.01 M NaCl at pH 8.5.

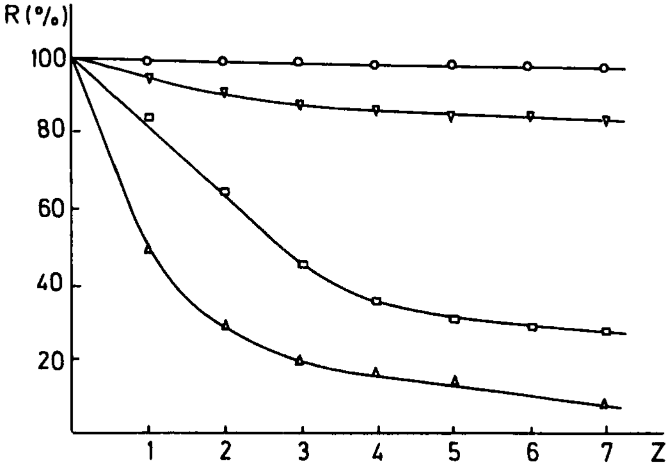


FIGURE 15
Separation of arsenic(V) (o,▽) and arsenic(III) (□,△) by permethylated poly(ethyleneimine) (PMP) (4%) at pH 8.5 (o,△) and 11 (▽,□); retention is plotted versus the filtration factor.

Actinide Ions

The separation of actinide ions is not only interesting theoretically, but also of practical importance for radionuclide analysis. Higher charged ions require special functional groups of the polychelatogen for selective separation. For the actinide series of elements the oxine derivative of poly(ethyleneimine) (POX) proved to be an effective reagent for LPR[19,20]. Figure 16 shows the retention profiles of U(VI), Pu(IV), Am(III), Cf(III), and Cm(III) by POX at different pH values as a funtion of the filtration factor.

It can be shown that practically all elements remain in the retentate at pH 6. Quantitative separation (95% for $Z = 10$) was observed for Pu(IV) at pH $\geq$ 2, U(VI) at pH 4 - 7, and for transplutonium elements at pH 6. Comparative studies proved the dominating effect of the oxine groups and only a slight activity of the polymeric backbone of the basis polychelatogen.

From a practical point of view it is essential not only to be able to preconcentrate and separate the actinide ions but also to regenerate the polychelatogen. The first step is carried out by direct separation of the ions in the retentate and adding reservoir solution to the ion mixture. Regeneration of the polymer is performed by placing the ion mixture in the cell and carrying out the separation by changing the pH of the feed solution. Figure 17 illustrates that process for the separation of plutonium, uranium, and americium.

It is clearly shown that a pH gradient of the feed solution allows a complete separation of plutonium and uranium from trivalent transplutonium elements in con-

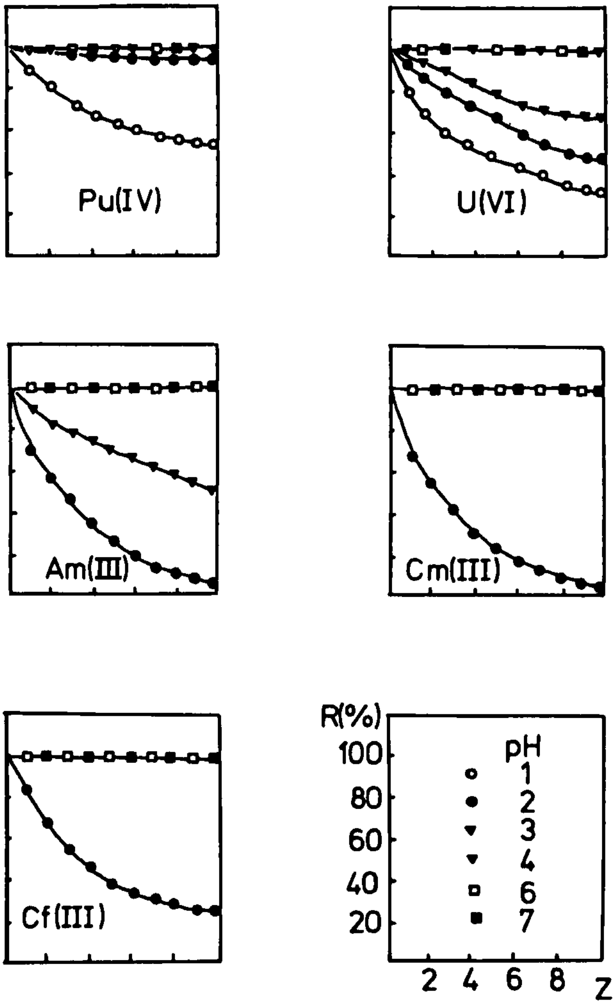


FIGURE 16
Retenion of actinide ions by poly(ethyleneimine) oxine (POX) (2% solution) at different pH values as a function of the ratio of filtrate volume to retentate volume (Z).

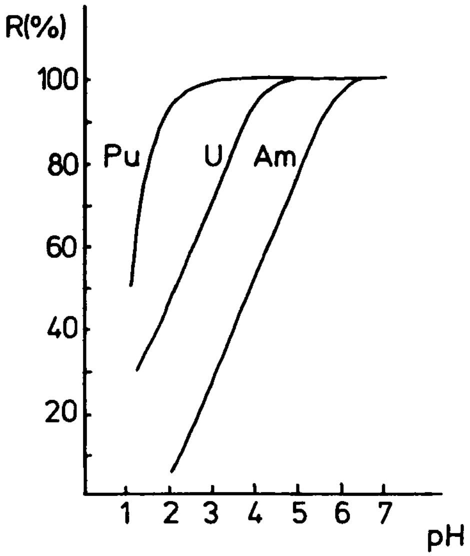


FIGURE 17
Separation of Pu(IV), U(VI) and Am(III) by a 2% solution of poly(ethyleneimine) oxine (POX) for a filtration factor of 10 in dependence of the pH.

junction with an additional competetive complexing agent[20].

Anions

Due to the basic structure of many polychelatogens retention of cations is possible without further modification procedures. However, for anion separation it is a prerequisite to introduce positively charged functional groups to provide ion exchange properties. Quarternizing poly(ethyleneimine) by alkylating reagents is an easy access to quarternary ammonium groups on a hydrophilic polymer. Permethylated poly(ethyleneimine) (PMP), for example, is an appropriate polymeric reagent for

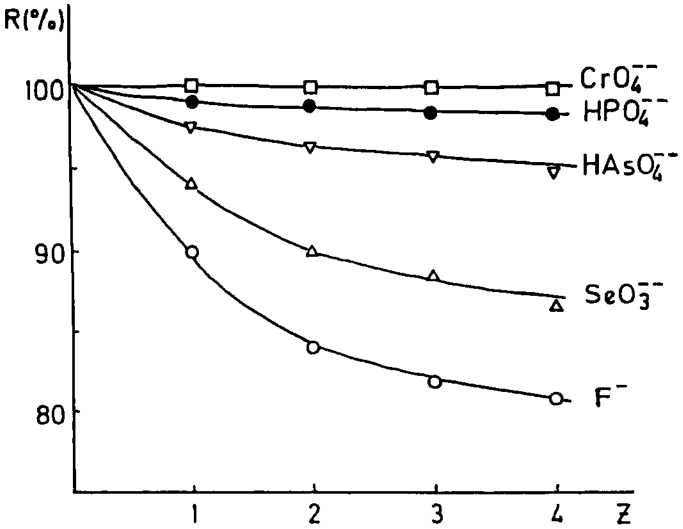


FIGURE 18
Anion retention by a 4% solution of permethylated poly(ethyleneimine)(PMP) from 0.01 M sodium salts at pH 8.5.

anion retention[21]. The influence of this polychelatogen on the retention of some anionic species is shown in Figure 18.

Evidently, the anions studied are retained by PMP. For example, chromate and phosphate anions show a retention of 98% or higher at pH 8.5 and fluoride of 82% under these conditions. Important parameters are the type of the exchange reaction and the corresponding exchange anion ($HAsO_4^{2-}$, HPO_4^{2-}, SeO_3^{2-}, CrO_4^{2-}, F^-), the pH of the solution, the concentration of cations, and the selected polychelatogen. Anions which interact with the polymer exhibit an increased retention. Cations which are strongly bound to retained anions show the same effect.

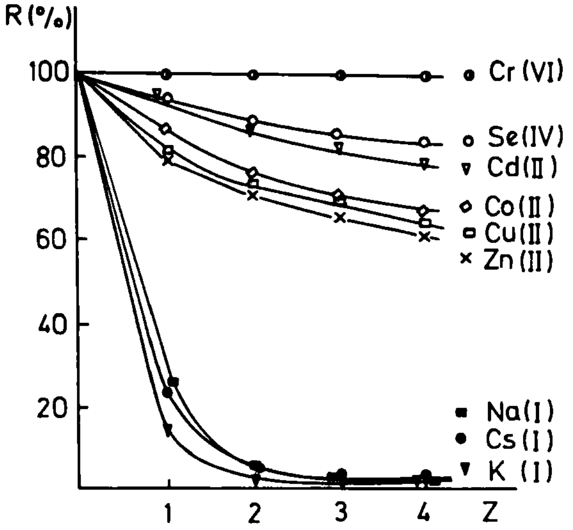


FIGURE 19
Effect of permethylated poly(ethyleneimine) (PMP) (4% solution) on the retention of metals ions and oxo anions from 0.01 M NaCl at pH 8.5.

The cleavage of the anionic species from the polymer and the regeneration of the polychelatogen is easily possible with higher concentrated salt solutions. Arsenate and other anions, for example, can be stripped off up to 99% using a 0.15 M sodium salt solution. Regeneration of the polymer is then performed with 0.1 M hydrochloric acid.

LPR separation is also suitable for mixtures of different anionic and cationic species. For example, chromate ions are readily separated by PMP from bivalent cations at pH 9.5 (Figure 19)[15].

Under the same conditions, selenium(IV) is also retained, probably as selenite. Partial retention is ob-

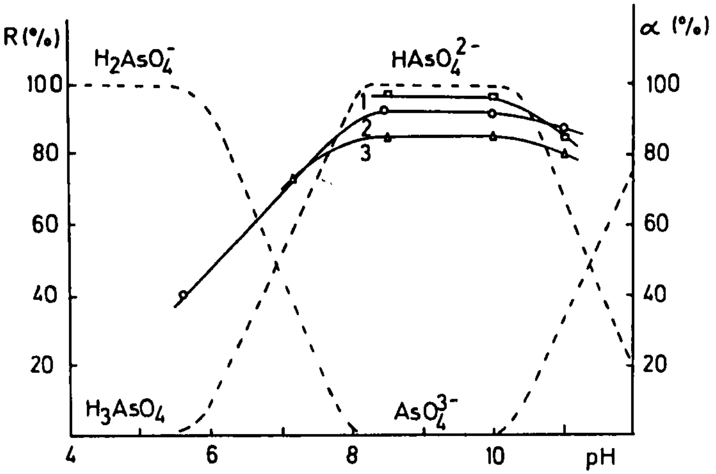


FIGURE 20
Separation of different arsenate anions in dependence of pH by a solution of permethylated poly(ethyleneimine) (PMP) (solid lines). Arsenate protonation (dashed lines); retention by 4% PMP from water (1), 2% PMP from water (2), 4% PMP from 0.01 M NaCl (3).

served for the ions Cd^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+}. Thus, bifunctional reagents allow the simultaneous retention of various elements.

An example or the separation of several different ionic species of the same element is given in Figure 20.

It shows the retention of arsenic(V) as a function of pH together with the formation curves of different arsenate forms in solution.

Best retention is achieved within a pH range of 8-10 where arsenic(V) mainly exists in the form of the $HAsO_4^{2-}$ anion. Lower retention at higher pH value can be attributed to the formation of AsO_4^{3-} anions. The

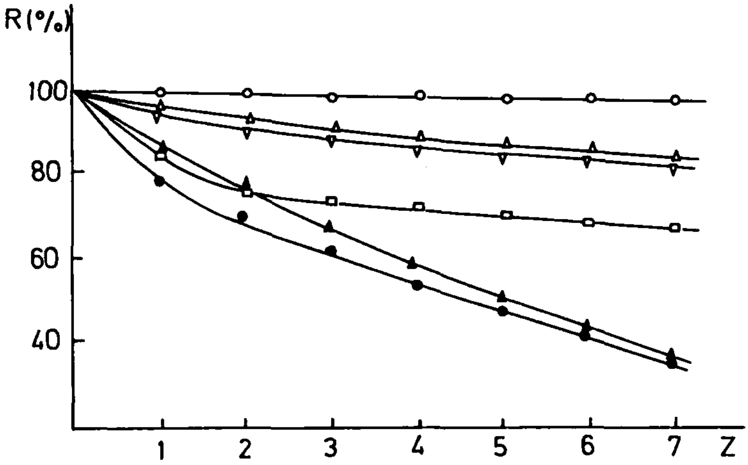


FIGURE 21
Dependence of the arsenic(V) retention on the presence of sodium salts at pH 8.5 (4% PMP): (o) water, (□) 0.01 M Na_2CO_3, (△) 0.01 M NaCl, (▲) 0.5 M NaCl, (▽) 0.01 M $NaNO_3$, (●) 0.01 M Na_2SO_4.

protolysis equilibrium shifts at lower pH values to $H_2AsO_4^-$ and then to non-retained H_3AsO_4. In addition, anions of the acid added to adjust the appropriate pH can be competitive for the polymeric reagent.

Another study shows that anions present in solution rather strongly influence the retention. Figure 21 illustrates the effect of sodium salts in the feed solution on the retention of As(V) at pH 8.5[17]. Retention decreases in the following order: Cl^-, $NO_3^- > CO_3^{2-} > SO_4^{2-}$. By reason of their higher electrostatic affinity to positively charged polymer sites, bicharged anions must be stronger competitors for the reagent than chloride and nitrate. However, both monovalent anions do not influ-

TABLE V.

Determination of some bivalent metal ions in waters by the LPR-flame AAS technique. 2% polymer, concentration (c) in $\mu g \cdot L^{-1}$; s_r = relative standard deviation. Preconcentration 250 fold; n = 11 for PEI, n = 3 for PTU.

		Drinking water (Tuebingen)		River water (Neckar)
Element		PEI	PTU	PEI
Cu	c	10.0	9.8	8.0
	s_r	0.1	0.15	0.1
Zn	c	120	-	160
	s_r	0.06	-	0.1
Ni	c	0.6	0.8	3.0
	s_r	0.2	0.25	0.2
Cd	c	0.004	0.004	0.004
	s_r	-	-	-

ence retention at pH 11. This can be explained by the dominating influence of OH^- ions.

COMBINED METHODS

For practical applications it is interesting to combine the LPR method with instrumental techniques of analysis, especially in the presence of interfering components. More convenient and less expensive is a combination of modern standard equipment with such a preconcentration and separation method. For example, flame atomic absorption determination of metals in conjunction with LPR proved to be very advantageous for the analysis of drinking and river waters[17,22]. Some results of these investigations are summarized in Table V.

A decrease of the atomic absorption signal is not observed. Because PEI retains Cu, Ni, Hg, and Cd quantitatively, these elements can be determined from low concentrations using filtration factors between 20 and 250. The determination of heavy metals using the combination method is characterized by detection limits ($\mu g \cdot L^{-1}$) as low as 0.008 for Cu, 0.016 for Zn, 0.04 for Ni, 0.008 for Cd, and 0.0001 for Hg (cold vapor technique). Thus, the LPR-flame AAS combination also offers the possibility of analyzing of very pure waters.

CONCLUSION

Liquid-Phase Polymer-Based Retention (LPR) represents a new method for selective ion separation and enrichment in homogeneous phase. By application of polychelatogns soluble polymeric ion associates are formed and separated from other ionic species and low-molecular compounds by membrane filtration. Thus, inorganic ions not bound to the polymer can be removed with the membrane filtrate whereas the water-soluble macromolecules are retained over the membrane. This method allows the selective enrichment and separation of varius ions in the presence of large excess quantities of other species which could otherwise interfere with subsequent analysis.

In addition, Liquid-Phase Polymer-Based Retention offers a new method for anion exchange extraction and enrichment in aqueous phase. The method is applicable not only for inorganic cations and anions but also for all ionic forms of organic compounds and complexes of metal ions with high hydration energies. Finally, the combination of LPR with other determination methods, e.g. AAS, ICP-AES, stripping voltammetry, and others, can be successfully used to improve the sensitivity of the determination methods.

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