Preconcentration of Trace Elements by Sorption

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In the determination of trace elements in complex matrices, enrichment and separation of the analytes is of special importance. A wide variety of methods have been proposed for preconcentration according to the nature of the samples, the types and concentrations of the analytes, and the methods to be used for measurement. Among them, the preconcentration techniques based on sorption seem to be convenient, rapid and capable of attaining a high concentration factor. Various efforts have been made to improve selectivity, rate and capacity of sorption, specially for heavy metals in natural waters. The use of silica gel as a support for loading or chemically immobilizing with complexing agents is a particular example. In this paper, the preparation and characterization of complex-forming adsorbents for the sorption of heavy metals will be critically reviewed, laying stress on the utilization of silica gel as a supporting material.

Keywords   Preconcentration, trace metal, natural water, complexing agent immobilized silica gel, complexing agent loaded silica gel, sorption behavior, analytical selectivity, transition metal

1   Introduction

In spite of recent advances in instrumental analysis, a direct determination of trace elements in complex matrices, such as environmental, biological, mineral, ore and high purity materials, seems still to be impossible because of insufficient sensitivity and selectivity of the methods.

A wide variety of methods have been proposed and used for preconcentration and separation of trace elements according to the nature of the samples, the types and concentrations of the analytes, and the methods to be used for measurement. Several comprehensive books[1-3] and special reviews[4-6] have been devoted to preconcentration in analytical chemistry. The methods for concentration of trace elements or components are briefly summarized in Table 1. Liquid-liquid extraction is the most extensively used method for the preconcentration and separation of trace metal ions prior to their measurement. However, this technique is impractical when dealing with a larger volume of sample, because there is an upper limit to the attainable concentration factor.

On the other hand, the preconcentration methods based on sorption are considered to be superior to the liquid-liquid extraction as regards simplicity, rapidity, and ability to attain a high concentration factor. The sorption phenomena utilized for preconcentration generally include adsorption, absorption, chemical adsorption and capillary condensation of gaseous compounds or dissolved substances on solid or liquid adsorbents. In practice, adsorption and chemisorption phenomena are useful for enrichment of trace metals from many kinds of samples. A number of adsorbents have been investigated for the separative concentration of trace metal species from aqueous solution. These include activated carbon, porous organic polymers, ion-exchange materials, complex-forming materials such as chelating resins, reagent-immobilized or -loaded silica adsorbents, and natural polymers such as celluloses, chitin and chitosan.

This review deals mainly preconcentration of trace inorganic elements in environmental samples by the use

Table 1   Method for preconcentration

Function	Method or agent
Evaporation	
Freezing	
Coprecipitation	coprecipitation with inorganic and organic precipitants
Flotation	ion flotation, carrier precipitation followed by flotation
Extraction	liquid-liquid extraction, extraction chromatography
Sorption	
Adsorption and chemisorption	activated carbon, porous polymer (styrene- or acrylate-based copolymer, poly(chlorotrifluoro-ethylene) resin), polyurethane foam, C_{18}-bond silica gel or glass beads
Ion exchange	inorganic ion exchanger, ion-exchange resin, ion-exchange membrane
Complex-forming sorption	chelating resin, silica gel- or glass beads-immobilized complexing agents, complexing agent-loaded silica gel or glass beads, complexing agent-loaded anion-exchange resin, cellulose, chitin, chitosan, DTC-chitin, DTC-chitosan, cellulose-immobilized complexing agents
Electrolysis	electrodeposition, stripping voltammetry

of complex-forming adsorbents.

2   Activated Carbon

Because the surface of activated carbon shows a strong hydrophobic property, this material has found extensive use in enrichment of trace organic compounds, sorption being mainly controlled by molecular interaction between sorbents and molecules to be adsorbed. In addition, chemical factors seem to be partly effective through formation of a compound on the surface of activated carbon which contains carboxylic and phenolic hydroxide groups.

A critical review on the use of activated carbon for concentration of inorganic substances has been published.[7] Although single metal ions such as Hg(II), methyl mercury and Fe(III) have been found to be adsorbed on activated carbon from hydrochloric acid medium, many kinds of trace metals are effectively retained in the presence of a complexing agent. Ethylxantogenate, diethyldithiocarbamate (DDTC), ammonium pyrrolidinecarbodithioate (APDC), dithizone, 8-quinolinol and Xylenol Orange have been successfully used for preconcentration of trace metals.

Preconcentration of trace metals is generally carried out as follows: 1) a sample solution with a suitable

complexing agent added is passed through a thin layer of activated carbon (50 – 150 mg) supported on a filter paper, or 2) after a sample solution with a certain amount of the adsorbent and complexing agent added is shaken, the solution is filtered off through a filter paper. The metal collected on the adsorbent is readily leached out by heating with nitric acid, followed by atomic adsorption- or inductively coupled plasma (ICP) emission spectrometry. Alternatively, the adsorbent loaded filter paper can be directly submitted to X-ray fluorescence method or neutron activation analysis.

Recently, complexing agent loaded activated carbon (AC), e.g., 8-quinolinol/AC^8 or 2,4,6-tri(2-pyridyl)-1,3,5-triazine/AC^9 has been reported for preconcentration uses. However, these loaded carbons reveal effective sorption ability only in batch experiments, but not column operations. The present author and coworkers[10] have examined adsorption behavior of Cu(II) with 2-mercaptobenzothiazole loaded activated carbon (MBT/AC) and silica gel (MBT/SG). The results are shown in Figs. 1 and 2. Although the sorption of Cu(II) ion by batch operation was almost the same for the two adsorbents, in column operation,
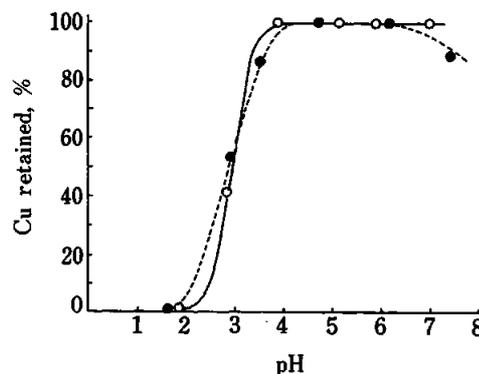

Fig. 1   Effect of pH on retention of Cu(II) with MBT loaded silica gel and MBT loaded activated carbon.[10] (O) MBT/SG, (●) MBT/AC.
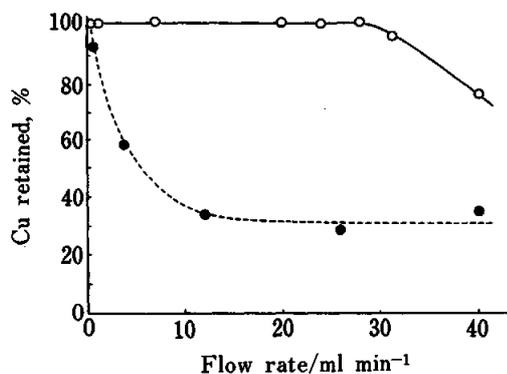

Fig. 2   Effect of flow rate on retention of Cu(II) with MBT loaded silica gel and MBT loaded activated carbon.[10] (O) MBT/SG, (●) MBT/AC.

the sorption efficiency with MBT/AC appreciably decreased with increase of flow rate, while that with MBT/SG was unaffected up to a flow rate of 30 ml min⁻¹. These facts suggest that hydrophobic nature of activated carbon may hinder a diffusion of metal ions towards the adsorbent, so that a rapid sorption is hard to attain under dynamic conditions.

Concerning the sorption mechanism of metal 8-quinolinolato complex on activated carbon, π-π interaction has been suggested between the aromatic ring on the surface of the carbon and the center of two aromatic rings of 8-quinolinol.[11] On the other hand, Hg(II), methyl mercury and Fe(III) seem to be adsorbed as their chloro-complex anions or oxyanions.[12-14]

3   Porous Polymers

3·1   Styrene- or metacrylate-based copolymers

Macroreticular polystyrene-divinylbenzene copolymers (PS-DVB) (Amberlite XAD-1, XAD-2 and XAD-4, Chromosorb 102, and Bio-Rad SM-2 and SM-4), and more hydrophobic methyl metacrylate-based copolymers (Amberlite XAD-7, XAD-8 and Bio-Rad SM-7) have been studied for the adsorption of organic substances in natural waters. It was reported that organic compounds of iron in natural waters were completely retained on XAD-2 resin, while no inorganic iron species was adsorbed at pH 3.[15] Thus, XAD-2 resin was used for speciation of Fe in seawater.[16] However, Mackey[17,18] emphasized that XAD-1 and XAD-2 resins are unsuitable for quantitative studies of trace metal speciation in natural waters since significant amounts of the simple cations of Cu(II), Fe(III) and Zn(II) are also adsorbed by the resins. The adsorption of inorganic cations was believed to occur at impurity sites on surface of the resins. He has examined how to eliminate these sites by methylation of the resin, but he could not do completely.

To saturate the cation-exchangeable sites, Hiraide et al.[19] prepared In(III)-treated XAD-2 resin by immersing the resin in an In(III) solution, and used it to collect humic colloids from river water.

XAD resins have been used extensively for concentration of trace metals as their complexes. Chromium-(VI) ion forms Cr(III)-diphenylcarbazone complex in aqueous solution and is effectively adsorbed on XAD-2 resin.[20] The complex retained on the resin can be eluted with methanol for spectrophotometric determination. A CHP20P resin (spherical macroreticular PS-DVB copolymer) column selectively adsorbed Cr(III) ions after complexation with 8-quinolinol.[21] The method was applied to determination of Cr(III) and Cr(VI) in seawater (10 l) by a graphite furnace AAS. XAD-4 resin was also utilized[22] as a collector of Ag(I), Bi(III), Co(II), Cu(II), Fe(III), Hg(II), Ni(II), Pb(II) and Zn(II) in seawater after complexation with bis(2-hydroxyethyl)dithiocarbamate.

On the other hand, these resins impregnated with liquid extractants, e.g., tributyl phosphate , or complexing agents, e.g., dithizone in chloroform are more extensively used for concentration of trace metals. The liquid-extractant-impregnated resins which are mainly used as column packing in extraction chromatography, however, have a fatal disadvantage that pre-equilibration is necessary for each sample solution with the same solvent.

3·2   Polyurethane foams

Braun and coworkers[23-26] have extensively investigated polyurethane (PU) foam sorbents as regards the preconcentration and separation of trace metals. Polyurethane foams are highly porous materials with open pores. Therefore, they have a large specific surface which can readily be saturated with complex-forming agents.

The foam column is prepared by placing a foam cylinder which can be made by cutting a block as one hopes, in a glass column, and applying gentle pressure with a glass rod. The column is then filled with water under vacuum. A sample solution is allowed to percolate through the foam column at different flow rates. A selective sorption by unloaded foams can be achieved by appropriate control of the composition of each aqueous solution.[25] In acidic aqueous thiocyanate media, sorption and separation of Fe(III), Co(II), Hg(II), In(III), Zn(II), Ir(III), Pd(II) and Rh(III) have successfully been performed.

Various kinds of reagents-loaded open-cell polyurethane foams have been prepared using dithizone, DDTC, 1-nitroso-2-naphthol, diethylammonium diethyl-dithiocarbamate, 1-(2-pyridylazo)-2-naphthol (PAN) and Alamine 336. These were used for preconcentration of traces of inorganic and organic Hg, Ag, Co, Sb, In, Au and radio-iodine under static and chromatographic conditions.[25]

The neutron-activation analysis showed that the original ether-type PU foam contained Sn (710–1110 ppm), Cl (96–178 ppm), Na (32–73 ppm), Mg (11–20 ppm), Al (1.3–3.1 ppm), I (1.8–4.3 ppm), Br (1.7–3.4 ppm), Mn (0.34–0.36 ppm) and lesser amounts of V, In, As, Sb and K as impurities.[26] The successive washing of the foam with 1 M nitric acid, double distilled water and acetone resulted in a reasonable decrease of alkali metals, halogens, Mn and V, but it did not affect the amount of Sn present.

3·3   Poly(chlorotrifluoroethylene) resins (PCTFE)

PCTFE resins have been widely used as a reversed phase chromatography column packing. The advantages of the resin are: stability to heat, indecomposability with mineral acids or inorganic chemicals, and no-swelling in organic solvents. The present authors[27] have found that PCTFE effectively adsorbed 8-quinolinole chelates of Cd(II), Cu(II), Fe(III), Mn(II) and Zn(II) in trace levels. A glass column is filled with a certain amount of the commercially available PCTFE, Neo-

flon® (60–80 mesh), slurried with ethanol. After washing the column with a sufficient amount of pure water, a sample solution containing 8-quinolinol, adjusted to desired pH, is passed through the column.

The 8-quinolinolates of Fe(III), Cu(II), Zn(II) and Cd(II) are quantitatively retained on the column at pH values above 3, 3.5, 5.7 and 6.2, respectively, while about 95% of Mn(II) is retained at pH above 6.7. The metals retained on resin can easily be eluted with 0.1 M hydrochloric acid or methanol.

Iron(II)-1,10-phenanthroline complex is also adsorbed, but Cu(II)-DDTC complex is not. Therefore, the sorption may be affected principally by molecular interaction caused by hydrophobicity of both adsorbent and complexes to be sorbed.

Copper(II)-8-quinolinol-5-sulfonate (Cu-SOx) and Cu-(II)-4-(2-pyridylazo)resorcinol (Cu-PAR) complex anions are not sorbed on PCTFE resin, while these are quantitatively retained on the resin in the presence of tetrabutylammonium ion (TBA⁺) as a counter ion at a high flow rate, e.g., 100 ml min⁻¹.[28] Moreover, adsorption efficiency increases with increase of TBA⁺ concentration, suggesting that ion-associated complexes are sorbed on the resin by a hydrophobic interaction. Cu-SOx retained on the resin is readily eluted with a small volume of ethanol containing TBA⁺ salt.

These results lead to applications of the method to rapid preconcentration of trace metals which form 8-quinolinolato complexes. River water samples were analyzed for copper contents using the proposed method.[28]

4 Complex-Forming Adsorbents

4·1 Chelating resins

A variety of chelating resins have been synthesized and utilized for preconcentration and separation of trace metals in natural waters. A Chelex-100 or Dowex A-1 resin in which the iminodiacetic acid functional group is incorporated to a styrene-DVB copolymer was first used by Riley and Taylor[29] for selective concentration of many transition metals from seawater. However, arguments about the quantitative preconcentration of trace metals with the resin from seawater have continued for years. Bruland et al.[30] found incomplete collection of Cu(II) from seawater at its natural pH. Recently, Pai et al.[31] made careful batch equilibration and breakthrough experiments and suggested that lower recoveries of heavy metals with Chelex-100 are caused by the complicated speciation of heavy metals in seawater medium and by the high concentration of Mg(II) and Ca(II) present, which act as competitors to heavy metal ions.

Recently, efforts have been made to improve selectivity, exchange velocity and capacity, and physico-chemical stability of chelating resins. A wide variety of complex-forming groups can be introduced into several kinds of polymers by chemical modification of the matrix or by the synthesis from monomeric ligands. Due to their physical and chemical stability, and capability of modification, PS-DVB copolymers have often been used as a support of the chelating resins. In general, the resin is chloromethylated prior to introduction of ligand groups. Typical examples of preparation of chelating resins reported by Suzuki and Yokoyama[32] are illustrated in Fig. 3.

The amounts of functional groups bound on the resins: I, II, III, IV and V were about 3.0, 1.7, 1.6, 2.0 and 1.8 mmol g⁻¹, respectively. Diethylenetriamine (DETA) resin (I) can sorb Cd, Co, Cu, Fe, Hg, Mn, Ni and Zn from aqueous solution at different pH values. DETA-bis(2-hydroxyethyl)amino (II) and DETA-bis-(phosphonomethyl)amino (III) resins were applied to
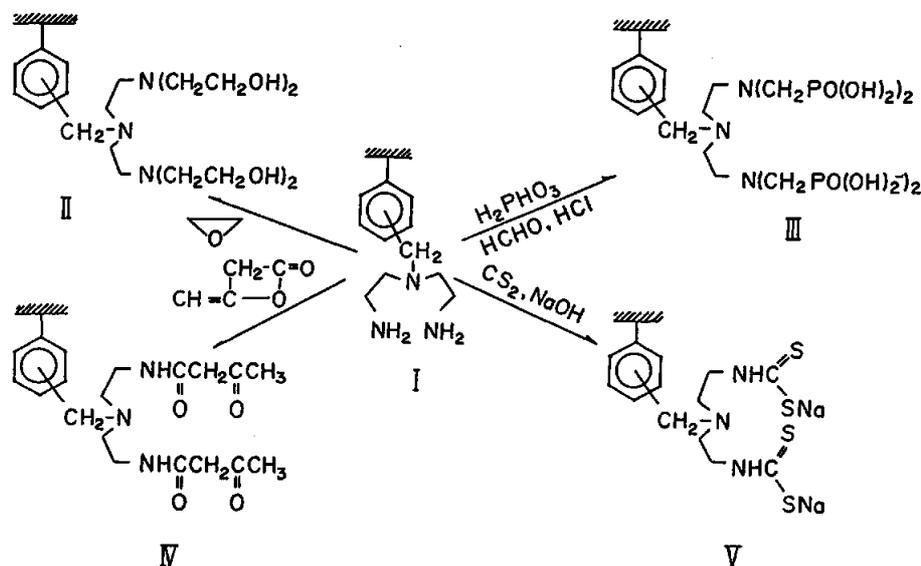

Fig. 3 Reaction scheme for the preparation of the chelating resins containing pendant multidentate ligands.[32]

Table 2 Typical complex-forming groups introduced into chelating resins

| Functional groups	Metals	Matrices	Ref.	Functional groups	Metals	Matrices	Ref.
$-CH_2-N \big(-N(CH_2CO_2H)_2 \big)_2$	Cu, Co, Ni, Zn	sewage	34	$-CH_2OCCH_2SH$ (=O)	Ag, Au, Bi, Hg, Sb, Sn, Cd, Pb, U	NBS standard acidic brine soln.	46
$-CH_2-CH-$ $\overset{\parallel}{C}-OH$ $\overset{\parallel}{N}OH$	U	seawater	35, 36	$C_6H_5-CH_2-S-C \big\langle {}^{N-N-C_6H_5}_{N=N-C_6H_5} {}^{H} \big.$	Au, Os, Pd, Pt	acidic soln.	47
$-CH_2-CH-$ $\overset{}{C}-NH_2$ $\overset{}{N}OH$	Co, Cu, Mn, Ni, Zn	water	42	cyclic $[(CH_2)_5-COCH_2CO]_3$	U	carbonate soln.	48
$-C=CH-C \big\langle {}^{S}_{SH}$ $\overset{}{OH}$	Ag, Au, Hg, Pt	acid soln.	37	cyclic $[(CH_2)_6-C(CO_2H)_2]_3$	U	carbonate soln.	48
$-CH——CH-$ $H-N-C \quad C-N-H$ $\overset{}{OH} \overset{}{O} \quad \overset{}{O} \overset{}{OH}$	Cr, Cu, Fe	Cr plating bath	38	(macrocyclic structure)	U	carbonate soln.	48
$-CH——CH-$ $C_6H_5-N-C \quad C-N-C_6H_5$ $\overset{}{OH} \overset{}{O} \quad \overset{}{O} \overset{}{OH}$	Cu, Co, Ni, Fe	aq. soln.	39	$EtN-(CH_2)_9-N-(CH_2)_9-NEt$ (dithiocarbamate structure)	U	carbonate soln.	48
$CH——CH$ $\overset{\parallel}{N} \quad \overset{}{C}-CH_3$ $\overset{}{N}$ Polyorgs IV	Ag, Au, Ir, Os, Pd, Pt, Rh, Ru	ore products, sulfate soln.	40, 41	$-C=CH-C \big\langle {}^{S}_{SH}$ $\overset{}{OH}$	Ag, Au, Hg, Pt	water	49
$CH_3-C——CH-$ $\overset{\parallel}{N} \quad \overset{}{CH-}$ $\overset{}{NH}$ Polyorgs VI	Ag, Au, Ir, Os, Pd, Pt, Rh, Ru	ore products, sulfate soln.	40, 41	(macrocyclic COOR structure with (CH_2)_8)	U	seawater	50
$-CH_2-\overset{H}{\underset{COONa}{C}}-NH_2$	Cu, Hg	seawater	43				
$-CH_2-\overset{CH_3}{\underset{COCH_2CH-CH_2}{C}}-$ $\overset{}{O} \quad \overset{}{SH} \overset{}{SH}$	Ag, Au, Hg	water	44, 45	(crown thioether structure) $-CH_2O-$	Ag, Cu	water	51

enrichment of Mo(VI) and/or V(V) from aqueous solution.[33] An anologous resin functionalized with N,N,N',N'-tetraacetic acid (see Table 2) revealed the following selectivity sequence:

$$Fe(III) > In(III) > Ga(III) \approx Cu(II) > Zn(II) > Al(III),$$
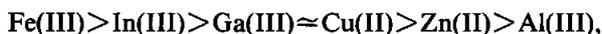
therefore, the selective recovery of In and/or Ga from Al was achieved using a column of the resin at pH 1.8.[34] Typical complex-forming groups introduced into chelating resins and their application to preconcentration of trace metals are shown in Table 2.[34-51]

4·2   Reagent-immobilized silica gel or glass beads

Leyden et al.[52-54] have prepared diamine-immobilized controlled pore glass beads (CPG) by treatment of CPG with N-β-aminoethyl-γ-aminopropylmethoxysilane (Dow-Corning Z-6020). This adsorbent was used for determination of trace amounts of AsO_4^{3-}, $Cr_2O_7^{2-}$, SeO_4^{2-}, MnO_4^-, WO_4^{2-} and VO_4^{3-}. By batch method 90% of MnO_4^- and SeO_4^{2-} were extracted in 2 min, $Cr_2O_7^{2-}$ in 4 min and AsO_4^{3-} in 8 min. By using a column of 100 mg of Z-6020/CPG, an average recovery of 103% was observed for SeO_4^{2-} at a flow rate of 50 ml min⁻¹. The three dithiocarbamates, N,N-dialkyldithiocarbamate (1) from Dow-Corning XZ-2024, N-alkyl (2), and bisdithiocarbamate (3) of Z-6020 diamine were synthesized by the same authors (see below). Among these

(1)

(2)

(3)
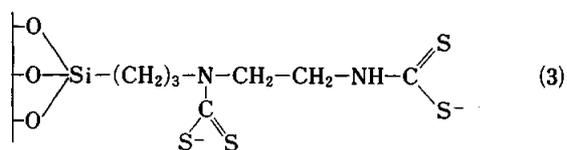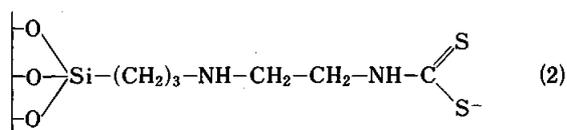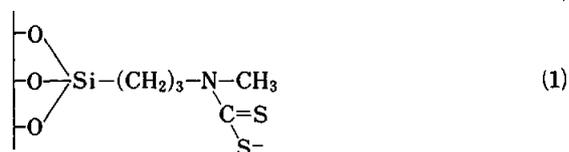
adsorbents, the first one seemed to be the most stable toward degradation due to release of carbon disulfide through the acid catalyzed breaking of the nitrogen-carbon bond. By the use of this, Ag, Cu and Hg are all over 90% removed at pH<2, Co, Fe, Ni, Pb and Zn are 90% removed at pH<6, while at pH 9.5 Mn reaches a 90% extraction level. At pH values between 6 and 8, most transition metal ions are quantitatively extracted.

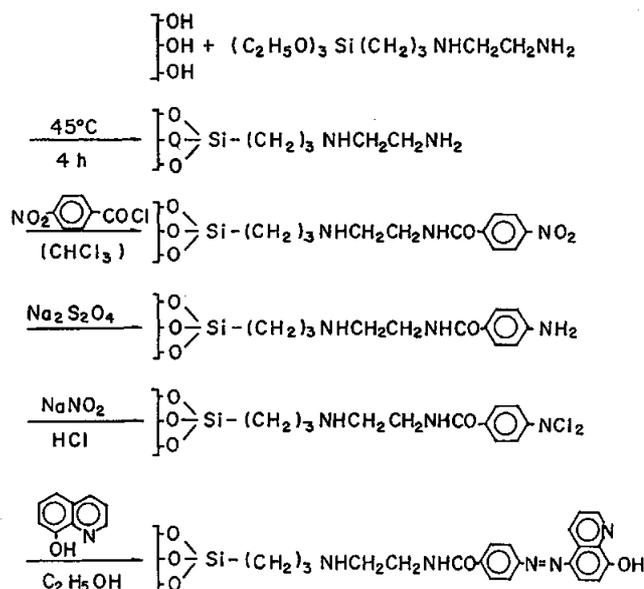Hill[55] has synthesized 8-hydroxyquinoline immobilized silica gel (8-OHSG) in the manner shown in

Fig. 4   Reaction scheme for the preparation of silica-immobilized 8-hydroxyquinoline.

Fig. 4. This new chelating adsorbent has been investigated for separation and preconcentration of trace levels of metal ions from dilute aqueous samples by a number of authors.

Sugawara et al.[56] also prepared CPG-8-hydroxyquinoline (CPG-8HOQ) via γ-aminopropyltriethoxysilane, and examined its extractability for Al, Co, Cu, Fe, Mo, Ni, Ti, V, W and Zr under various conditions. By applying the column method, the laboratory distilled-deionized water was analyzed for Cu (8 ppb) and Fe (<0.25 ppb) as ultratrace contaminants.

A material prepared from porous silica, Porasil-8OHQ, had a capacity of about 50 µeq g⁻¹, and behaved with an efficiency of about 0.2-0.5 mm/theoretical plate, it was capable of separating such similar metal ions as Co-Ni, Cd-Pb-Zn and La-Gd-Yb at trace levels employing both isocratic and continuous gradient elution.[57]

Recently, the extraction and back extraction behavior of SG-8HOQ for several metal ions has been studied by Honjo et al.[58] in order to ascertain the basic conditions for the separation of metals. The results are shown in Fig. 5. The disagreement of $pH_{1/2}$ (the pH of the half extraction) appearing between extraction and back extraction of Al, Co and Ni ions indicates that the extraction equilibrium was not reached.

SG-8HOQ adsorbents have been widely investigated for the preconcentration of Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn from natural waters prior to their determination by graphite furnace AAS or inductively coupled plasma mass spectrometry (ICP-MS).[59-62]

Some other modified silica gel with various kinds of complex-forming functional groups have been prepared and studied for their adsorption behavior and application to preconcentration of trace metals.[63-65]
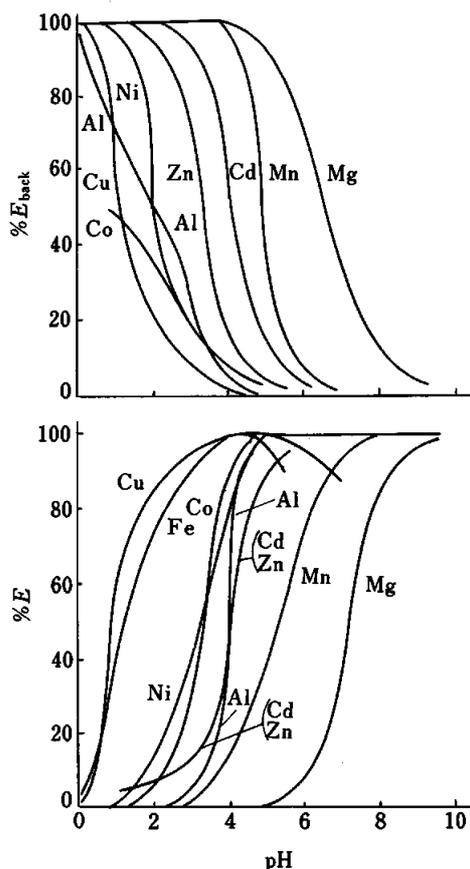
Fig. 5   Effect of pH on the solid-liquid extraction and back extraction of metals with silica gel-immobilized 8-hydroxy-quinoline.[58]

Seshadri *et al.*[64] reported that a β-diketone-immobilized silica gel shows complexing affinity for Cu(II), U(VI) and Fe(III); no significant affinity is observed for Ni, Co, Zn, Mg, Ca, La and Th.   Furthermore, 2,3-dihydroxybenzoyl and 3,4,5-trihydroxybenzoyl-amide functional groups immobilized silica exhibited significant affinity for Cu, U, Fe, Ce, Ti, V, Mo and Cr. The distribution coefficients in presence of 0.5 M NaCl showed large K_d values for U(VI) (5.3) at pH 6 and Cr(VI) (4.3) at pH 1, indicating their potential application as a preconcentration aid for U(VI) ion from seawater and natural waters.[64]

Ryan and Weber[65] have compared three types of chelating agents immobilized on glass with Chelex-100 for removing and preconcentrating trace Cu(II) ion from laboratory prepared solution.   Columns of immobilized N-propylethylenediamine (diamine), its bis(dithiocarbamate) (DTC) and 8-quinolinol (8-HQ) quantitatively removed Cu(II) (10 – 200 μg l⁻¹) from buffered solutions at pH 6.0. Chelex-100 gave the poorest results, removing only 62 and 75% of Cu(II) at the two levels tested.   The other immobilized reagents gave results that were strongly dependent on their contact time with the solution.   Longer columns and slower flow rates tended to improve results.

Of the chelating agents tested, 8-HQ seemed best suited for analytical preconcentration. By choice of the proper conditions, quantitative removal and recovery of Cu(II) could be obtained. DTC gave the best removal from solutions but did not readily release the bound Cu(II) from the sorbent.

4·3   Reagent-loaded silica gel or glass beads

As can be seen from Fig. 2, silica gel seems to be the best supporting material for sorbent of trace metals; it is highly hydrophilic, while other materials such as activated carbon and PCTFE are more hydrophobic. The merits of silica gel include (1) porosity and broad surface, (2) resistance to acids, (3) hydrophilic property, (4) no swelling in various solvents, (5) resistance to heat and (6) mechanical strength. However, in preparation of reagent-immobilized silica gel, the silylation is essential prior to introduction of functional groups on silica gel. This treatment makes the surface of silica gel highly hydrophobic and thus hinders diffusion of metal ions toward the gel, so that fast retention of metal ions cannot be achieved. Further, the preparation of ligand-immobilized silica is complicated and time consuming, and the complexing agents which can bound to silica gel are few. Therefore, a wider variety of complex-forming sorbents which can be more simply prepared and can rapidly sorb traces of metals with high selectivity, has become needed.

Previously, in our laboratory, an excellent adsorbent for cesium-137, ammonium molybdophosphate loaded silica gel (AMP-SG), has been prepared and successfully applied to simple and rapid preconcentration of ¹³⁷Cs in seawater.[66] Silica gel (60 – 80 mesh) impregnated with a solution containing ammonium molybdate and ammonium monohydrogenphosphate (Mo:P= 12:1) was placed into a solution of ammonium nitrate in 3 M nitric acid, and the products were filtered and dried at 105°C. AMP-SG thus obtained has a sorption capacity of 10.8 mgCs g⁻¹ and is stable for a long period. By using a column packed with 10 g of AMP-SG (17 mm×80 mm), ¹³⁷Cs was quantitatively retained from 80 – 100 l of seawater at a flow rate of 5 – 8 l h⁻¹.

Most inorganic exchangers, such as AMP, appear to have been used preferentially for the preconcentration of alkali metals and some univalent metals such as Ag and Tl, but rarely for that of the transition metals.

In the author's laboratory, several exchange materials have been prepared by loading water-insoluble complexing precipitants on silica gel. These adsorbents show rapid and effective adsorbability for transition metals because most of them contain soft ligand atoms, S, and keep the hydrophilic property of the silica gel support as a whole.

Desirable properties for a reagent are: (1) water-insolubility, (2) high solubility in solvents of low boiling point, (3) stability in solutions of low pH and (4) rapid formation of insoluble complex with the metal ion of interest.

2-Mercaptobenzothiazole, 2-mercapto-N-2-naphthyl-

acetamide (thionalide), p-dimethylaminobenzylidenerhodanine, 1-nitroso-2-naphthol and 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I) are reagents which satisfy the above requirements.

These complexing agents have been used as precipitants for several metals to form sparingly soluble complexes in acidic to neutral solutions, and also as extractants for solvent extraction of these metals. These reagents are insoluble in water, but soluble in several organic solvents such as ethanol, dioxane and tetrahydrofuran.

2-Mercaptobenzothiazole loaded silica gel (MBT/SG), for example, is prepared as follows:[67] about 100 ml of tetrahydrofuran (THF) containing 10 g of MBT is slowly added from a separatory funnel to 60 g of a degassed silica gel which has been activated at 110°C for 20 h and then placed in a suction bottle. After remaining for 19 h in a refrigerator at 4°C, the impregnated gel is heated at 60°C under reduced pressure for 4 h to expel the solvent completely. The reagent-loaded gel is added to a certain volume of deionized water and the floated free reagent is removed by decantation. After this procedure is repeated three times, the gel is filtered with a glass filter, dried at 80°C for 20 h under reduced pressure, and stored in a polyethylene bottle standing in a desiccator.

The amount of MBT retained on silica gel was found to be 114 ± 6 mg g^{-1} (0.68 mmol g^{-1}), and the retention capacity for silver was 8.8 mg g^{-1} (81.5 μmol g^{-1}). This figure, however, indicates that 1 mol of Ag(I) ion reacts with 8.3 mol of MBT. It is known that Ag(I) forms a 1 : 1 metal-ligand complex with MBT[68], thus, the excess fraction of the reagent seems to have remained unreacted. This may be attributed to the porous structure of the silica gel surface and conglomerated crystallization of MBT on the silica gel which was revealed by a microscopic observation of freshly prepared gel. Most of the surface area of porous silica gel is within the pores, and access to some parts may be restricted by the ligand or silver complex.

The retention recoveries of various metal ions are shown in Fig. 6 as a function of pH and acid concentration.[67,69-71] Ag(I) is quantitatively retained on MBT/SG at pH$\geq$0, Hg(II) at pH$\geq$1, Cu(II), Hg(II) (from seawater) and ethyl mercury at pH$\geq$4, Cd(II), Pb(II) and methyl mercury at pH$\geq$5, and Zn(II) at pH$\geq$6.5, at flow rates of 10 ml min^{-1} for Pb to 23 ml min^{-1} for Hg by the use of column packed with 3-5 g of MBT/SG (10 mm i.d. and 50-70 mm bed height). The metals retained on the column are readily eluted with 1% thiourea in 0.1 M hydrochloric acid (Hg), 2% thiourea in 0.1 M nitric acid (Ag), (1+99) hydrochloric acid or nitric acid (Cd and Zn) and acetone-hydrochloric acid mixture (9+1) (Cu and Pb) for measurement by AAS. This method has been satisfactorily applied to analysis of seawater and natural waters for the above elements.

Thionalide loaded silica gel (thionalide/SG) is prepared like MBT/SG was. The loaded gel retains ca. 54 mg of the reagent per gram. Retention capacity of the loaded gel for As(III), Bi(III), Pd(II) and Sb(III) were found to be 5.6, 2.1, 7.5 and 4.6 μmol g^{-1}, respectively.[72-75]

The effects of acid concentration and pH on retention of some elements are shown in Fig. 7.[72-75] Palladium(II) ion is quantitatively retained on thionalide/SG from 5 M hydrochloric acid solution, whereas untreated silica gel retains only 20% of the element from aqueous solution at pH>4.[72] Palladium retained on the gel column is eluted with 0.1 M hydrochloric acid containing 0.2 M thiourea. Antimony(III) is retained from aqueous solution of 2 M hydrochloric acid to pH 3, while Bi(III) is at pH$\geq$1.0, and both elements retained on the gel column are readily eluted with 6 M hydrochloric acid followed by hydride generation AAS measurement.[73,74]

In the case of arsenic, As(III) is adsorbed at pH$\geq$6.5, but As(V) and organic arsenic compounds are not retained at all. Hence, the differential preconcentration of both arsenic species is attainable. After enrichment
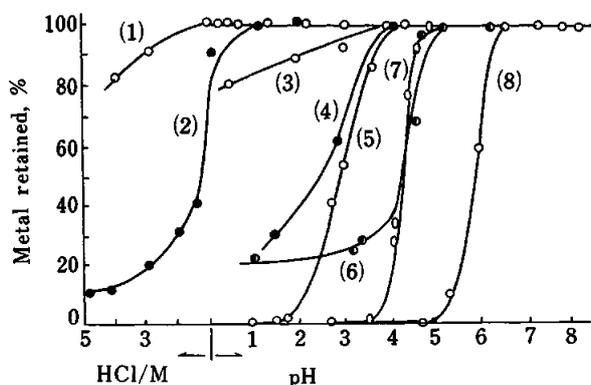

Fig. 6 Effect of pH and acid concentration on retention of metal ions with MBT loaded silica gel.[5] (1) Ag(I), (2) Hg(II), (3) Hg(II) (seawater), (4) ethyl mercury, (5) Cu(II), (6) methyl mercury, (7) Pb(II) and Cd(II), (8) Zn(II).
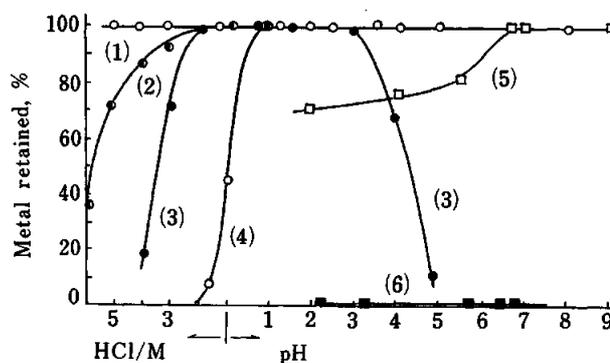
Fig. 7 Effect of pH and acid concentration on retention of metal ions with thionalide loaded silica gel.[5] (1) Pd(II), (2) Bi(III) (HNO₃), (3) Sb(III), (4) Bi(III) (HCl), (5) As(III), (6) As(V).
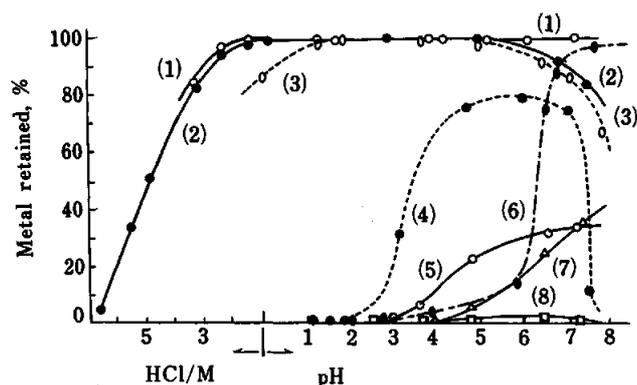
Fig. 8 Effect of pH and acid concentration on retention of metal ions with DMABR loaded silica gel.[5] (1) Ag(I), (2) Au(III), (3) Pd(II), (4) Fe(III), (5) Cu(II), (6) Pb(II), (7) Cd(II), (8) Zn(II).

of As(III) on the gel column, As(V) in the remaining sample solution can be subsequently concentrated after reduction to As(III).[75]

p-Dimethylaminobenzylidenerhodanine-loaded silica gel (DMABR/SG) can also be prepared in a similar way to that described above. The sorption behavior of several metal ions is illustrated in Fig. 8 as function of acid concentration and pH.[76] In batch experiments, Ag(I) is quantitatively retained on the DMABR/SG at acidities ranging from 1.7 M to pH 7, and Au from 1 M to pH 5; equilibrium is achieved within 1 min for both elements. From seawater, Ag(I) ion is completely retained at pH 1.0-6.5 and Au(III) ion at pH 1.0-3.5. In the case of Pd(II), shaking for about 20 min is required for quantitative retention at pH 1.0-5.0. The chelating capacity for the DMABR/SG is 23 μmol Ag, 11 μmol Au and 11 μmol Pd per g. Quantitative recovery of Ag and Au on the gel columns from seawater is achieved at higher flow rates (1-21 h⁻¹ and 2-31 h⁻¹, respectively) than with other chelating resins, e.g., Chelex-100; palladium requires slower flow rate (150 ml h⁻¹). The above three elements retained on the column are quantitatively eluted with 20 ml of 0.1% thiourea in 0.1 M hydrochloric acid.

On the other hand, Cd(II), Cu(II), Fe(III), Pb(II) and Zn(II) are retained at higher pH. Hence, Ag(I), Au(III) and Pd(II) ions can be selectively concentrated on DMABR/SG column and separated from the above metals.

2,5-Dimercapto-1,3,4-thiadiazole loaded silica gel (DMT/SG) quantitatively retains trace amounts of Bi(III) from 0.2-0.5 M nitric acid solution.[77] The complexing capacity of the DMT/SG for bismuth is 17 μmol g⁻¹ at 0.2 M nitric acid. Bismuth retained on the gel column is completely eluted with 10 ml of 0.05 M EDTA solution, and determined by hydride-generation AAS or iodide-complexes spectrophotometry. Halogenide ions strongly hindered the retention of Bi(III), due to a competitive reaction for the element with DMT. The method is useful for preconcentrating trace amounts of Bi(III) from water samples containing less than 2 g l⁻¹ of chloride ion.

Cobalt(II) ion is selectively retained on a column of 1-nitroso-2-naphthol loaded silica gel at pH>3.0 and flow rate 17 ml min⁻¹.[78] The cobalt is eluted from the column bed with glacial acetic acid or with a mixture of acetone and hydrochloric acid (9:1 v/v) and is measured by AAS.

Samara and Kouimtzis have described utilization of 2,2′-dipyridyl-3-[(4-amino-5-mercapto)-1,2,4-triazolyl]hydrazone loaded silica gel (DPTH/SG) regarding preconcentration of traces of Cu(II), Co(II), Cd(II), Ni(II), Pb(II) and Zn(II) from tap, lake and seawater[79], and Ag(I), Au(III) and Pd(II) from water samples.[80] DPTH/SG has been prepared using dimethylformamide containing DPTH in the same manner as reported by the present author and co-workers.[72]

Recently, Tong et al.[81,82] have prepared 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone loaded silica gel (C₁₈/SG) for preconcentration of Cu(II), Co(II) and Ni(II) as well as In(III) prior to AAS measurement. The former three metals are quantitatively retained on the adsorbent above pH 4, and the latter is retained at pH>2.8. By using a column packed with 1.0 g of C₁₈/SG, Cu, Co and Ni are completely retained at a flow rate of slower than 5 ml min⁻¹ while In even at 16 ml min⁻¹. The metals are readily eluted from the column with 1 M hydrochloric acid, and adsorption-elution cycle can be repeated ten times with no observable decline in the efficiency of the adsorbent. The method has been applied to samples of sodium chloride solution and tap water.

5 Natural Complex-Forming Polymers

5·1 Chitin and chitosan

As a natural polymer, chitosan, which is readily obtained by deacetylation of chitin, has been employed as an adsorbent for the collection of metal ions by Muzzarelli et al.[83-85] Thus this polymer has received attention in connection with the removal of toxic heavy metals or radionuclides, as well as the recovery of useful metals from industrial sewage. Chitosan itself can sorb many kinds of metal ions by chelate-formation with an amino group containing aminosaccharide ring of chitosan. This adsorption, however, occurs at neutral pH region and therefore is not selective. Recently, Muzzarelli et al.[86] studied the introduction of the dithiocarbamate function into a natural aminosaccharide chain of chitosan and demonstrated its adsorbability for several metal ions in the range of pH 1-12.

However, the dithiocarbamate-chitosan (DTC-chitosan) synthesized by their method has a tendency to gelatinize in an acidic media and can hardly be used for column operation. The present authors[87] has prepared dithiocarbamate-chitin (DTC-chitin) by mixing chitin powder with carbon disulfide, 2-propanol and tetramethylammonium hydroxide in benzene. The DTC-
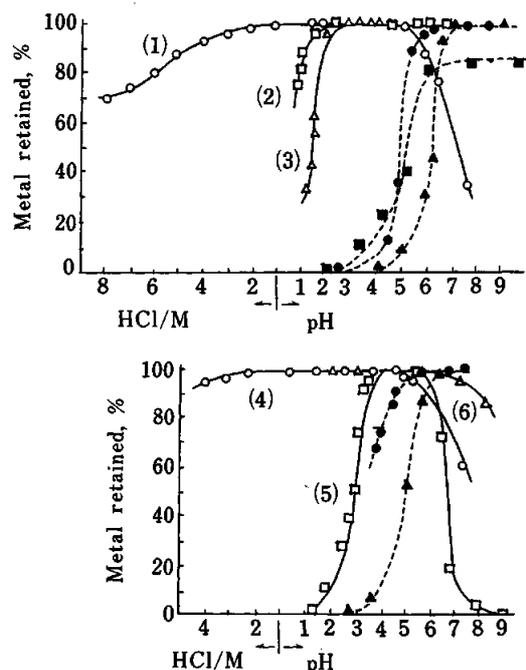
Fig. 9 Effect of pH and acid concentration on retention of metal ions with dithiocarbamate-chitin and untreated chitin.[87]
(1) Cu(II), (2) Ni(II), (3) Co(II), (4) Ag(I), (5) Fe(III), (6) Cd(II).
—O— DTC-chitin, --●-- untreated chitin.

6 Conclusion

In analytical chemistry of trace elements in a wide variety of samples, concentration and separation of analytes from complex matrices are important prior to their determination. The present review shows that a number of functional adsorbents have been synthesized and characterized in order to improve the selectivity and rapidity of quantitative preconcentration of trace elements. Each adsorbent presented to date, however, seems to have merits and demerits. In analytical preconcentration, it is quite desirable to develop a number of adsorbents which make possible the speciation of trace elements. This should help to solve many important problems included in studies of nuclear technology, electronics, metallurgy, mining, medicine, agriculture, fisheries and environment.

chitin obtained does not gelatinize even in 6 M nitric acid, and shows effective adsorbability for transition metal ions from an acidic solution.

The amount of sulfur combined with chitin is found to be 0.71%, which corresponds to only 2.3% of that calculated by expecting that a CS_2 group can be bound to each unit ring of chitin. This facts suggests that a small portion of the acetamide group in the chitin chain might convert to amino group (chitosan) during treatment with tetramethylammonium hydroxide, and that the amino group is linked by CS_2.

The retention behavior of several traces of metal ions is shown in Fig. 9. Cobalt(II) and Ni(II) are quantitatively retained at pH above 2.5, while Ag(I) and Cu(II) are at pH below 5.0, even from 1 M nitric acid. Cadmium(II) is also retained at lower pH, but Fe(III) is only retained in the narrow pH range: 4.0–6.5. On the other hand, these metal ions are also retained on untreated chitin at pH above 7.0, suggesting retention of metal hydroxides. The sorption capacities of DTC-chitin are 37 μmol g^{-1} (Ag), 4.4 μmol g^{-1} (Cd), 9.2 μmol g^{-1} (Co), 49 μmol g^{-1} (Cu), 16.5 μmol g^{-1} (Fe) and 7.2 μmol g^{-1} (Ni). Silver(I), Cu(II) and Co(II) are quantitatively retained on DTC-chitin column at a high flow rate (15 ml min^{-1}). Silver retained on the column is eluted with 0.1 M nitric acid containing 2% thiourea, Cu and Ni are eluted with 1 M nitric acid containing 3% thiourea, and Co can be eluted with 2 M nitric acid containing 3% hydrogen peroxide.

The method was successfully applied to river water samples for determination of Ag and Cu.[87]

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