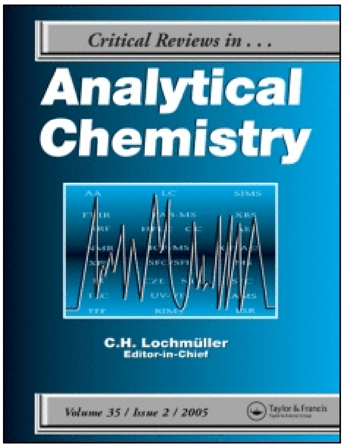

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Analysis of Trace Amounts of Metal Ions Using Silica-Based Chelating Resins: *A Green Analytical Method*

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ABSTRACT: This review is concerned mainly with the applications of chelating resins, based on silica gel, for the separation and preconcentration of trace metal ions from various substrates. General methods of preparations of silica-based resins have been discussed. A synthesis of various silica-based chelating resins and their applications in the extraction of trace amounts of metal ions have been reviewed critically and have also been reported in tabular form.

KEY WORDS: silica gel, chelating resin, separation, preconcentration, metal ions.

I. INTRODUCTION

An analysis of metal ions at trace levels poses unique problem to analysts, because it involves the rigorous requirements of versatility, specificity, sensitivity, and accuracy in the analysis. Trace amounts of metal ions present in various samples may be directly determined by various powerful instrumental methods. However, the results may be erroneous if the limitations of the devices go unheeded, because the metal ions may be present in these samples together with other elements and at low levels. Thus, to obtain the reliable results the best course is to separate and preconcentrate the metal ion from matrix constituents and determine them in the isolated state. The application of preconcentration results in the concentration of metal ion of interest, while its separation from the matrix constituents results in the simplification of sample matrix and immobilization of metal ion in a more stable chemical form. Various techniques have been employed for this purpose. The most widely used technique for the separation and preconcentration of metal ions with suitable complexing agent is liquid-liquid extraction. The extraction of metal ions that form complex with complexing agent at high temperature cannot be carried out by liquid-liquid extraction.[1–4] Moreover, the running cost using large amounts of solvent and complexing agent makes this technique economically unviable. This, however, also decreases the sensitivity of the system. Because the technique involves the use of large amounts of toxic chlorinated organic solvents and reagents, the method therefore is not eco-friendly. This technique is also inconvenient if emulsion forms between two phases on shaking. This difficulty can be overcome by extracting the metal complexes into molten extractants.[5–9] However, this method suffers from the disadvantage that this involves additional steps of filteration, and this reduces sensitivity and increases the time of extraction. Considering the drawbacks of conventional method of separation and preconcentration, a new method based on solid phase extraction of metal ions using chelating resins has been devel-

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oped.[10] The extraction of metal ions using chelating resin possesses many advantages over other methods of extraction. Some of these advantages are

1. Selective determination of metal ions is possible by using a chelating resin having a ligand possessing high selectivity to the targeted metal ion.
2. It is free from difficult phase separation, which is caused by mutual solubility between water and organic solvent layer: a difficulty commonly encountered in case of liquid-liquid extraction.
3. The extraction of metal ions using chelating resins is an economical method, since it uses only a small amounts of chelating resin and solvent for elution, and this also increases the sensitivity of the system.
4. Trace metal ions at as low as ppb level can be determined because the targeted ion is enriched on the solid phase.
5. The concentration of metal ions can be visibly estimated from the color intensity of the solid phase, if the metal complex formed possesses absorption in the visible wavelength region.
6. Particulate matter are suspended in aqueous sample, but they are not adsorbed on solid phase medium, and as a result solid phase extraction medium is free from interferences from suspended particle.
7. Above all, the use of carcinogenic organic solvents and other reagents is avoided and thus it is a green analytical method for the analysis of trace amounts of metal ions.

The chelating resins are preferred over conventional ion-exchange resins because of their high selectivity and capability of binding metals through multiple coordinating groups attached to the support.[11] The multiple coordination of metal ion on chelating resin makes it particularly suitable for the collection of polyvalent metal ions. The chelating resins are mainly prepared by immobilization of ligand on the resin matrix. The following properties are required for a selective chelating resin:

1. The complexing agent to be incorporated should yield a stable system with the support matrix.
2. It must be stable over a wide range of pH.
3. The solid support must have high chemical stability and a compact structure, so that during the synthesis of chelating resins the functional structure of chelating agents are not changed.
4. The structure of the chelating group should be compact, so that the formation of chelate ring with metal ions is not hindered with the resin matrix.

Many materials, such as silica, cellulose,[12] Chelex-100,[13,14] Dionex,[15] Cyanex,[16,17] Amberlite,[18–20] Dowex,[21] etc., have been used as solid support for immobilizing the chelating agents. Among these, silica is most widely used as solid support. The silanol groups on the surface can be functionalized in various ways, which can then serve as point of attachment of chelating agent. Any unreacted silanol group can be easily capped by trimethylsilyl chloride and anhydrous conditions for this can be easily attained by flushing the appropriate solvent (this is an essential requirement for the automation of the process). Metal oxide, such as silica, offers a distinct advantage over organic polymers due to the following reasons:

1. Unlike organic polymers, which are flexible and can swell up to varying degree depending on the solvent, temperature, and pressure, metal oxides have rigid structures. So that during the synthesis of chelating resin the functional structure of chelating agents is not changed.
2. Metal oxides are less susceptible than organic polymers to chemical or thermal degradation, so the chelating resins based on metal oxides can be used over a wide range of temperature and under strongly acidic or alkaline conditions.
3. A stable structurally rigid support limits the number of surface attached ligand groups capable of binding to metal. Thus, it would be easier to control the degree of coordination of the metal center on a metal oxide

surface than in the pores of a flexible polymer matrix.

4. Although organic polymers can be stiffened by cross linking, they become increasingly brittle with increasing cross-linking and attrition of polymer particle becomes a difficult problem.
5. The metal complexed to the chelating resins have also been proposed to act as catalyst for various catalytic reactions. The structural rigidity is desirable in large-scale applications as catalyst because the size and porosity of catalyst bed should remain constant throughout the catalytic reaction.

II. METHODS OF PREPARATION OF CHELATING SILICA GEL

Chelating silica gel may be prepared by two methods:

1. By chemical immobilization of chelating agent on the surface of silica gel;
2. By adsorption of chelating agent on silica surface.

A. Chemical Immobilization of Chelating Agent on the Surface of Silica Gel

Chemical immobilization of a chelating agent on silica gel is generally carried out be two methods:

1. Method 1

This involves first functionalization of silica gel by reacting it with an appropriate silylating agent having appropriate functional group and then reacting this functionalized silica gel with the chelating agent, resulting in the immobilization of chelating agent on silica gel. This may be represented as follows:

$$\mathrm{SiOH+XSi{-}A} \longrightarrow \mathrm{Si{-}O{-}Si{-}A+HX}$$

$$\mathrm{Si{-}O{-}Si{-}A+L} \longrightarrow \mathrm{Si{-}O{-}Si{-}A{-}L}$$

where A = functional group on silylating agent;
L = Chelating ligand; X = Hydrolyzable group

Silane coupling agents; for example, XSi-A are attractive reagent for functionalizing surface -OH groups especially on silica. The reason for using silane as a coupling agent is the thermal and hydrolytic stability of the resulting Si-O linkage. This type of linkage is better than the surface Si-O-C bond attained by reaction of surface silanol with alcohol. Silane reagent also affords a more stable linkage than the Si-O-C or Si-NH-C bond achieved by surface chlorination with X_2SiCl_2 and subsequent reaction with alkylating agent or amine. For example, the immobilization of 3-hydroxy-2-methyl-1,4-naphthoquinone (HMNQ) on silica gel is carried out by this method (Figure 1).[50]

In this method silica gel is first reacted with 10% solution of 3-aminopropyltriethoxy silane in toluene resulting in the functionalization of silica gel-forming aminopropyl silica gel (APSG). In the next step, this APSG is then reacted with HMNQ resulting in the immobilization of HMNQ on silica gel.

2. Method 2

This method involves first reacting the chelating agent with silane and then reacting this silylating agent with silica gel.

$$\mathrm{XSi{-}A+L} \longrightarrow \mathrm{XSi{-}A{-}L}$$

$$\mathrm{SiOH+XSi{-}A{-}L} \longrightarrow \mathrm{Si{-}O{-}Si{-}A{-}L+HX}$$

where A = functional group on silylating agent;
L = Chelating ligand; X = Hydrolyzable group

For example, for the immobilization of 2-thioaniline on silica gel, triethoxyvinylsilane is first reacted with 2-thioaniline in presence of 2,2-azobis(isobutyronitrile) (AIBN), and the resulting 2-[(2-triethoxysilyl)-ethyl]thioaniline is then reacted with silica gel in toluene (Figure 2).[35]

B. By Adsorption of Chelating Agent on Silica Surface

The loading of chelating agent on silica gel is generally carried out by soaking silica gel in the solution of the chelating agent, removing the supernatant after standing for some time and then

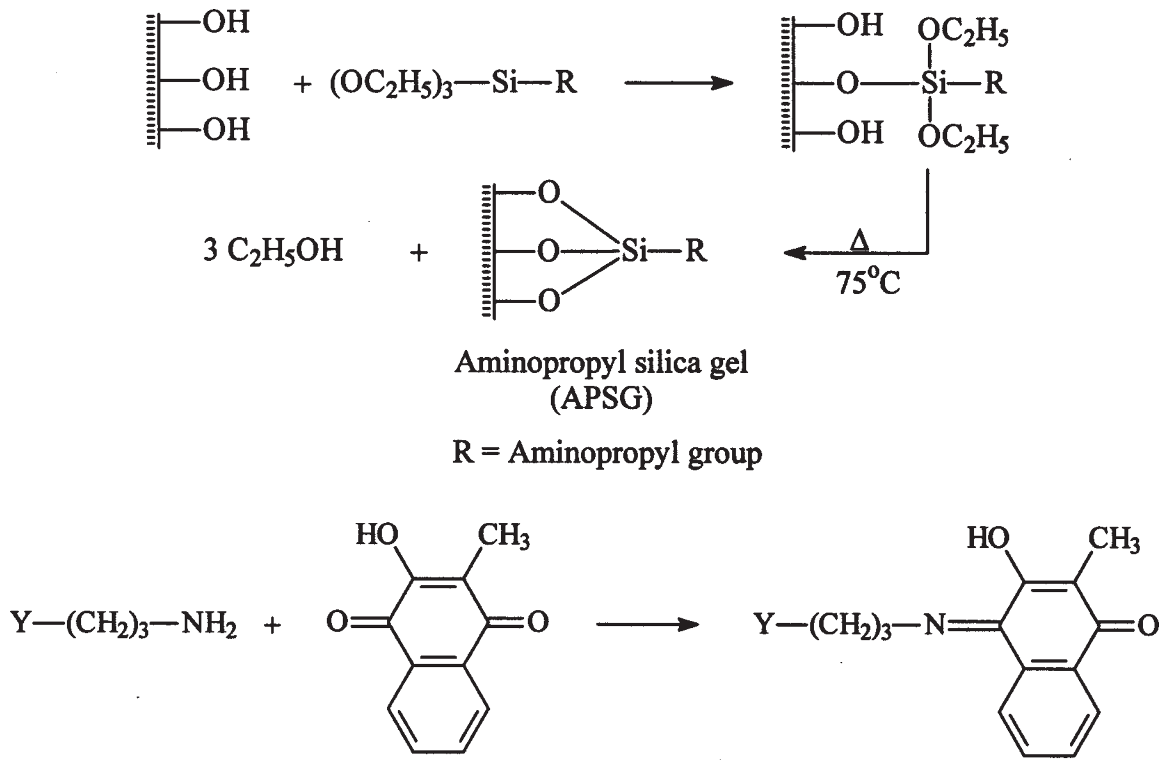


FIGURE 1. Immobilization of HMNQ on silica gel (Ref. 50).

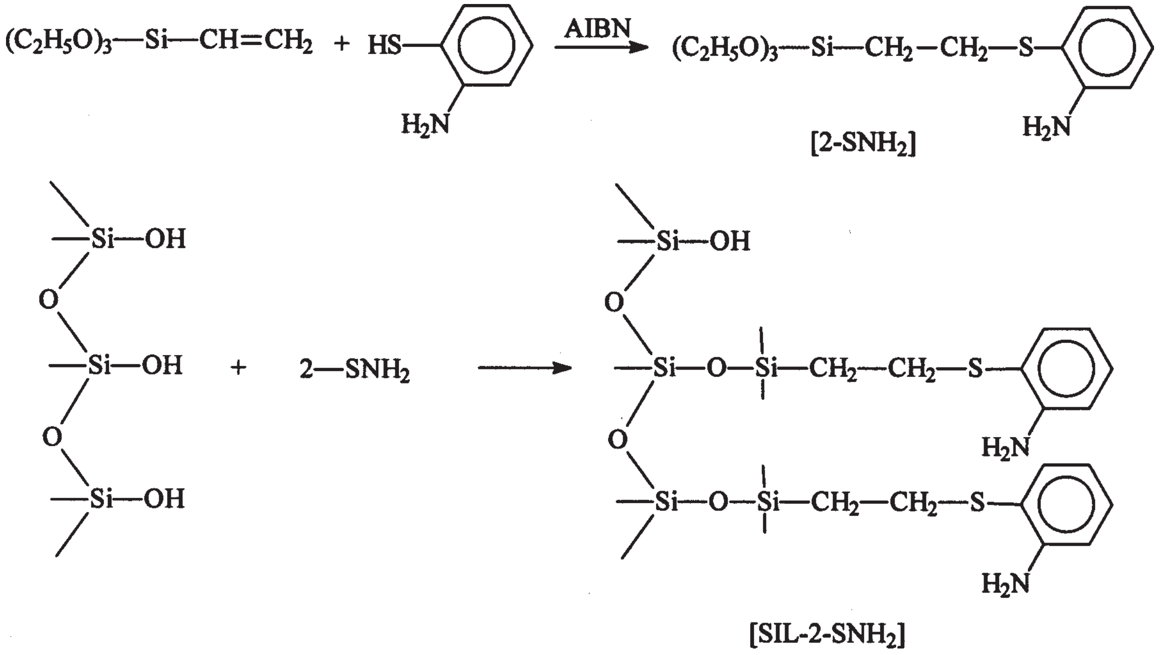


FIGURE 2. Synthetic route to silica immobilized 2-[(2-triethoxysilyl)-ethyl] thioaniline (Ref. 35).

finally evaporating the solvent at room temperature at reduced pressure.[23]

III. ANALYTICAL APPLICATIONS OF CHELATING SILICA GEL

Chelating agents that have been incorporated on silica support and used for the separation and preconcentration of trace amounts of metal ions have been discussed below and tabulated in Table 1.

1-Nitroso-2-naphthol immobilized on silica surface (Figure 3) was used by Gennaro et al. for the adsorption of Co^{2+}, Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, and Al^{3+} at pH 3.0 using the column method.[22]

Co^{2+} was always quantitatively retained from solutions with a concentration ranging between 1.00 to 25.00 ppm. Authors used various eluents such as, HCl, HNO_3, $HClO_4$, CH_3COOH, for the recovery of Co^{2+}, but none of these gave a recovery more than 5%. This observation can be explained on the basis of low solubility of complex of cobalt with 1-nitroso-2-naphthol and very high stability constant ($\log \beta = 46$) of the complex species with a ligand: metal molar ratio equal to 3. Of the other metal ions studied, Cu^{2+} and Hg^{2+} were quantitatively retained and recovered from the column. The retention of Cu^{2+} was in agreement with the high stability of the copper complex, whereas Hg^{2+} showed unexpected behavior because its complex with 1-nitroso-2-naphthol is not so stable. Because the resin showed high retention, but low recovery of adsorbed Co^{2+}, it cannot be used for the preconcentration of Co^{2+}. However, it was proposed to be useful for the removal of large amounts of Co^{2+} from liquid samples. This chelating agent loaded on silica gel was used by Terada and Nakamura for the selective preconcentration of Co^{2+} from natural water samples.[23] Cobalt was quantitatively retained on the column of chelating silica gel at pH > 3.0 and flow-rate of 1 l/h. Cobalt could be eluted from the column bed with glacial acetic acid or a 9:1 (v/v) mixture of acetone and hydrochloric acid and measured by atomic absorption spectrophotometry (AAS). Several metal species such as Fe^{3+}, Cu^{2+}, Ni^{2+}, UO_2^{2+} (in the concentration level 10 ng/ml to 200 ng/ml) were found not to interfere with the retention of trace amounts of cobalt. 1-Nitroso-2-naphthol noncovalently fixed on C_{16} hydrophobized silica gel has been used for preconcentration of Co^{2+}.[24] This method was also used for the determination of Ni^{2+} and simultaneous determination of $Ni^{2+}$and Co^{2+} in a sample.

Kubota and Moreia prepared iminosalicyl-modified silica gel (ISSG) by reacting aminopropyl silica gel (APSG) with salicylaldehyde under anhydrous conditions.[25] The ISSG was used for the adsorption of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} from ethanol. The resin showed fast metal ion exchange kinetics, with about 7 min required for the quantitative adsorption of Cu^{2+} and Zn^{2+}, and for remaining metal ions the time required was about 10 min. The adsorption of metal ions was influenced by temperature, with the equilibrium constant being decreased as the temperature was lowered. The method was successfully employed for the preconcentration, and the recovery of these metal ions was almost 100%. The metal ions adsorbed on the column cannot be eluted with aqueous solution because the iminosalicyl group is sensitive to water, with which it can react and regenerate the APSG and liberate free salicylaldehyde to the solution. This disadvantage prevents its use for the adsorption of metal ions from the aqueous samples. However, the adsorbed metals can be eluted with citric acid-ethanol as eluent as the attached organofunctional groups were not lixiviated by this solution.

8-Hydroxyquinoline (HQN) immobilized on silica gel has been widely used by many workers for the preconcentration and separation of trace elements from various water samples. The choice of 8-hydroxyquinoline as chelating agent can be justified by the fact that it forms stable complexes with over 60 metal ions. Also because of the differences in the formation constants between the transition metal and alkali and alkaline earth elements, the former can be easily separated from lake water, high ionic strength samples, and sea waters. Silica immobilized 8-hydroxyquinoline has been used by Sturgeon et al. for the preconcentration of Cd^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, and Co^{2+} from sea water prior to their determination by graphite furnace atomic absorption spectrometry.[26] The resin is reported to be stable over a wide range of pH (pH = 0 to 9), is

TABLE 1
Analytical Application of Chelating Silica Gel for Separation and Preconcentration of Trace Amounts of Metal Ions

S. No.	Chelating agent immobilized	Metal ions separated/ preconcentrated	Reference
1.	1-Nitroso-2-naphthol	Co^{2+}, Hg^{2+}, Cu^{2+}	*(22)*
		Co^{2+}	*(23)*
		Co^{2+}, Ni^{2+}	*(24)*
2.	Iminosalicyl group	Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	*(25)*
3.	8-Hydroxyquinoline	Cd^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}	*(26)*
		Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}	*(27)*
		Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}	*(28)*
		Cu^{2+}, Ni^{2+}, Cd^{2+}	*(29)*
4.	Mercapto group	Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}	*(30)*
		Arsenite	*(31)*
		Cu^{2+}, Cd^{2+}	*(32)*
		Cu^{2+}, Ag^{+}, Au^{3+}	*(33)*
		Co^{2+}, Ni^{2+}	*(34)*
5.	2-Thioaniline	Pd^{2+}	*(35)*
6.	Eriochrome black-T	Zn^{2+}, Mg^{2+}, Ca^{2+}.	*(36)*
7.	Formylsalicylic acid	Fe^{3+}	*(37)*
8.	Adogen 464	Cu^{2+}, Co^{2+}, Cr^{6+}	*(38)*
9.	2-Pyridinecarboxaldehyde phenylhydrazone	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}	*(39)*
		Mn^{2+}, Fe^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}	*(40)*
10.	1-(2-Pyridylazo)-2-naphthol (PAN)	Pr^{3+}, Nd^{3+}, Sm^{3+}, Y^{3+}	*(41)*

inert to chloroform, benzene, acetic acid and acetone, and can be used in saline media. The resin was found to permit large enrichment factor of 500, while providing rapid processing of large volume samples, quantitative recovery of these elements, and a matrix-free concentrate suitable for instrumental analysis. However, the relatively low exchange capacity exhibited by this material

TABLE 1 (Continued)
Analytical Application of Chelating Silica Gel for Separation and Preconcentration of Trace Amounts of Metal Ions

S. No.	Chelating agent immobilized	Metal ions separated/ preconcentrated	Reference
11.	Dimethylglyoxime (DMG)	Ni^{2+}	*(42)*
12.	1-(2-Thiasolylazo)-2-naphthol	Cu^{2+}, Zn^{2+}	*(43)*
13.	Dithizone and zinc dithizone	Ag^{+}, Pb^{2+}, Hg^{2+}	*(44)*
14.	Benzimidazole	Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}	*(45)*
15.	Didecylaminoethyl-β-tridecyl-ammonium iodide (DDATA)	Co^{2+}, Cu^{2+}, Zn^{2+}	*(46)*
16.	1,10-Phenanthroline	Fe^{2+}, Cu^{2+}, Ag^{+}	*(47)*
17.	Sodium diethyldithiocarbamate	Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}	*(48)*
18.	Ammonium hexamethylene dithiocarbamate	Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}	*(48)*
19.	Aminomethylphosphonic acid	Alkaline earths, Cu^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Ni^{3+}, Pb^{2+}, Cd^{2+}	*(49)*
20.	3-Hydroxy-2-methyl-1,4-naphthoquinone	Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}	*(50)*
21.	*o*-Vanillin	Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}	*(54)*
22.	2-Mercaptobenzothiazole (MBT)	Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}	*(55)*
		Hg^{2+}, CH_3Hg^{+}, $C_2H_5Hg^{+}$	*(56)*
23.	*p*-Dimethylaminobenzilidene-rhodanine	Ag^{+}, Au^{3+}, Pd^{2+}	*(57)*
24.	Crown ether carboxylic acid	Na^{+}, K^{+}, Rb^{+}, Cs^{+}	*(59)*

limits its use to separations involving trace level concentration. The exchange capacity for Cu^{2+} was found to be 0.061 mmol g^{-1}, which reduced to 0.040 mmol g^{-1} for used material, because the extended operation of the column at high pH results in the hydrolysis of the silica substrate and cleavage of the bound phase, thereby reducing exchange capacity. They have also used the reverse phase liquid chromatographic technique (RPLC) based on a combination of multielement chelation by 8-hydroxyquinoline with subsequent adsorption on C_{18}-bonded silica gel for the concentration of Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Fe^{3+} from sea water.[27] The stationary phase (in this case the C_{18} silica gel) is less polar than the mobile phase (sea water). Its effectiveness as

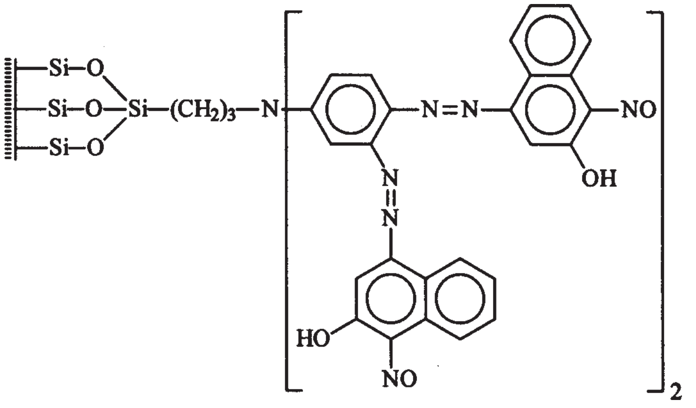


FIGURE 3. 1-Nitroso-2-naphthol immobilized on silica gel (Ref. 22).

a trace element enrichment method in this case lies in the fact that manipulation of secondary chemical equilibria in the aqueous mobile phase (formation of metal chelates) permits the concentration of these hydrophobic, less polar complexes at the head of the column. Furthermore, the weak surface attraction energies of the nonpolar stationary phase promote the rapid mobile phase equilibration on the column during sample enrichment and elution as well as gradient regeneration. In the present case as well, the authors have taken the advantage of the nonspecific reactivity of HQN to complex simultaneously a number of metals present in seawater. With a suitable adjustment of pH and HQN concentration, chelation of matrix elements (Ca^{2+} and Mg^{2+}) were minimized relative to the transition elements leading to an enrichment factor of 50 to 100. The elution of adsorbed metal ions was carried out with methanol and subsequently analyzed by graphite furnace atomic absorption spectrometry. The precision of the analysis was about 10% and the application of *t*-test (at 95% confidence level) showed no significant difference between the results obtained by C_{18} adsorption procedure and the accepted values.

8-hydroxyquinoline immobilized on silica has also been used for sorption of Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, and Hg^{2+}.[28] The metal uptake capacities were in the range from 0.2 to 0.7 mmol g^{-1}, and the distribution ratios in the range from 1×10^3 to more than 9×10^4.

Silica immobilized 8-quinolinol was synthesized and characterized by Lan and Yang.[29] They developed a one-step Mannich reaction for immobilization of 8-quinolinol on aminopropyl silica gel. They studied the pH effect on the extraction of Cu^{2+}, Ni^{2+}, and Cd^{2+} by this resin. Retention capacity of 466 μmol g^{-1} was found for Cu^{2+} using silica immobilized 8-quinolinol.

Mercapto-modified silica gel has been used by many workers for the preconcentration of some trace metal ions. Volkan et al. used this resin for preconcentration of trace amounts of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} from aqueous solution.[30] The resin showed the uptake of trace metal ions over a wide pH range and from highly saline solution. Authors used various eluting agents, such as $Hg(NO_3)_2$ in HCl, which gave 97% recovery of Pb^{2+} and Cu^{2+}, while EDTA was effective for elution of Pb^{2+} and was partially effective for Zn^{2+}. However, the recoveries of these metal ions were quantitative (>95%) using 3 N nitric acid, as the oxidative character of nitric acid contributed to the elution of the metal ions from modified silica. The preconcentration experiments were carried out on both spiked and untreated sea water using both batch and column experiment. Both the experiments gave excellent recoveries (~100%), with a concentration factor of 8 for column procedure and 40 by batch procedure at pH 7.0. Although both methods were effective for preconcentration, still batch procedure was proposed to have significant advantage in terms of sample turnover and suitability for the analysis of unstable samples. They also used this resin for the selective preconcentration of arsenite from natural waters.[31] The sorbent selectively removes arsenite, monomethyl arsenate, and dimetyl arsenate. Arsenite was quantitatively retained over the pH range 1.5 to 8.5. Because a number of potentially suitable acidic and basic eluting agents were all ineffective in removing arsenic from the mercapto-modified silica gel, authors oxidized arsenite to arsenate by eluting with 2.0 g l^{-1} potassium iodate solution in 0.5 *M* hydrochloric acid.

The thiol-modified silica gel has also been used by Suleyman et al. for the preconcentration and determination of trace amounts of Cu^{2+} and Cd^{2+} by flame atomic absorption spectrometry.[32] These metals were quantitatively retained on the adsorbent in acidic media, and the adsorbed metal ions were recovered with 2 *M* HCl. The Cu^{2+} was found to be about 0.022 mmol Cu/g silica. Koklu et al. has used this adsorbent for adsorption of Cu^{2+}, Ag^{+} and Au^{3+}.[33] The equilibrium constants for mercapto-modified silica were found to be 10.19 (pH 2.74 to 3.50) and 9.48 (pH 1.95 to 2.77) for Ag^{+} and Au^{3+}, respectively. They also used this resin for the separation and preconcentration of Co^{2+} and Ni^{2+} prior to their determination by graphite furnace atomic absorption spectrometry.[34]

2-Thioaniline (2-SNH_2) immobilized on silica (SIL-2-SNH_2) has been synthesized and characterized by Seshadri and Haupt.[35] The solid phase was colorless but reacts with platinum group metals and gold to produce different colors in the pH range 0.5 to 3.0. The SIL-2-SNH_2 resin showed high capacity for Pd^{2+} (0.46 mmol g^{-1}), which may be explained by the fact that silica-ligand-Pd^{2+} complex has a stoichiometry of 1:1 as both thioether sulfur and primary amine nitrogen atoms are available for complex formation. This fact was confirmed by the authors by isolating and characterizing silane ligand {2-[(2-(triethoxysilyl)-ethyl)thio]aniline}complex of Pd^{2+}, which indicated the complex to be a *cis*-square planer monomer with ligand silane binding through both amino nitrogen and thioether sulfur (Figure 4). The silica-bound thioaniline shows a dynamic exchange capacity of 0.64 mmol g^{-1} for Pd^{2+}. Exchange studies indicated that Pd^{2+} could be quantitatively extracted within 1 min, whereas the extraction of Ir^{3+} and Rh^{3+} were found to be negligible. The modified silica may be used as a selective sorbent for the separation and preconcentration of Pd^{2+} from large quantities of base metals, Rh^{3+} and Ir^{3+}.

Silica gel immobilized with Eriochrome black-T indicator (silica-ERT) (Figure 5) has been used by Mahmoud as the solid phase extractor for Zn^{2+}, Mg^{2+}, and Ca^{2+}.[36] The stability of silica-ERT phase was carried out (in pH range 1 to 10) by overnight equilibration of the solid phase with the selected buffer solution. The stability studies indicated that maximum degree of phase hydrolysis occurs at lower pH values (pH 1 to 3), whereas the hydrolysis was negligible in pH range 4 to 7. The order of metal ion capacity values of the tested metal ions was found to be $Zn^{2+} > Mg^{2+} > Ca^{2+}$, which are in good agreement with the order of formation constant values of these metal ions with Eriochrome black-T. The selective extraction of Zn^{2+} or Mg^{2+} in presence of Ca^{2+} as an interfering metal ion was possible using silica-ERT phase. These metal ions could be separated and preconcentrated using modified silica phase.

Formylsalicylic acid immobilized on silica gel by a direct chemical reaction of the amino group-containing silica gel phase and the aldehyde group of formylsalycylic acid giving various phases of modified silica gel.[37] These modified silica gel phases have been used for extraction

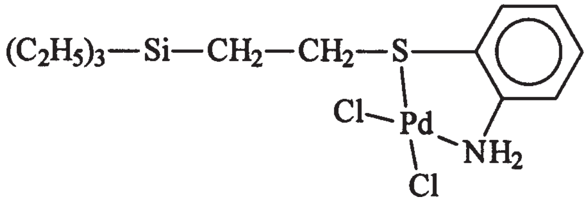


FIGURE 4. Proposed structure of 2-[(2-(triethoxysilyl)-ethyl)thio]aniline complex of Pd^{2+} (Ref. 35).

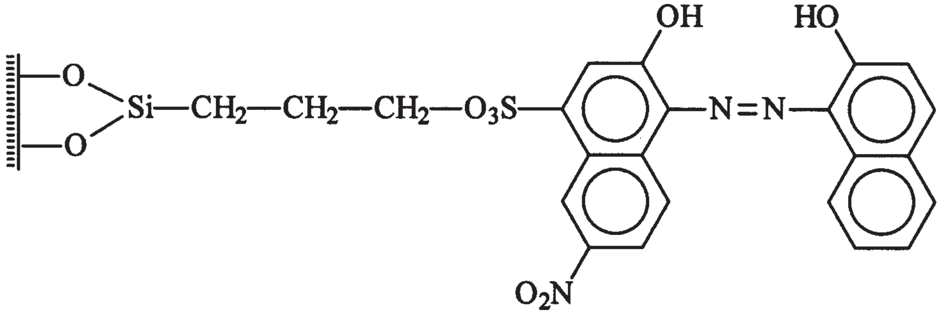


FIGURE 5. Silica gel immobilized with Eriochrome black-T (silica-ERT) (Ref. 36).

of Fe^{3+} at pH 5.5. The metal capacity of Fe^{3+} was 0.96 mmol g^{-1} of the modified silica gel. In the presence of other metals, Fe^{3+} was selectively adsorbed onto the resin with a recovery of about 97%. Immobilized silica gel phases can be recycled by EDTA because of its ability for back-extraction of metal ions from the complex formed.

A solid extractant prepared by loading the liquid-anion exchanger Adogen 464 on silica gel has been used by Battistoni et al. for the sorption and quantitative determination of anionic complexes of Cu^{2+}, Co^{2+}, and Cr^{6+} in sea water, natural water, metal alloys, and industrial electroplating baths.[38] The leaching of the exchanger from the silica gel, studied by differential thermal analysis and infrared spectroscopy (measurement of the 2930 cm^{-1} stretching band), indicated the high retention of Adogen 464 at low pH values. Copper and cobalt, extracted as their thiocyanate complexes, were completely extracted in pH range 1 to 6 and 1.4 to 2.5, respectively, while for Cr^{6+} the optimum pH was 2. The capacity of the 5% Adogen 464/silica gel for Cu^{2+}, Co^{2+}, and Cr^{6+} were 0.028, 0.025, and 0.020 mmol, respectively, per gram of loaded silica. The capacities were, however, lower than those for silylated immobilized reagents. The detection limits for Cu^{2+} and Co^{2+} were 0.2 and 0.40 ng ml^{-1}, respectively. Using this technique, Cr^{6+} can be separated from Cr^{3+}, and a concentration factor of 40 and a detection limit of 0.2 ng ml^{-1} were achieved. A solid support prepared by chemical bonding of 2-pyridinecarboxaldehyde phenylhydrazone on silica (Figure 6.) has been used for the separation and determination of trace amounts of various transition metal ions such as Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}.[39] Metal sorption confirms to the Langmuir isotherm, and the relative orders of the Langmuir constants K' and the column retention-capacity factors, k', for these transition metal ions were found to be the same as the natural order of the stabilities predicted for their metal chelate, that is, $Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$. They have also used this modified silica as a stationary phase for the chromatographic separation of aqueous metal ion mixtures containing various combinations of Mn^{2+}, Fe^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, and Cu^{2+}.[40] The capacity data obtained for the copper sorption study and acid base titration indicate that the basic sites are equally accessible to protons and metal ions, presumably because they are located on the surface rather than in narrow pores. The metal-ligand complex had a stoichiometry of 1:1. At pH 4.5,

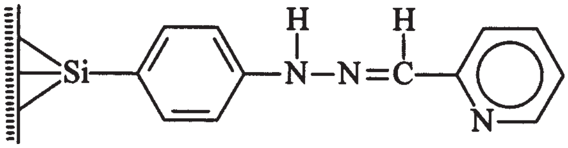


FIGURE 6. Silica immobilized 2-pyridinecarboxaldehyde phenylhydrazone (Ref. 39).

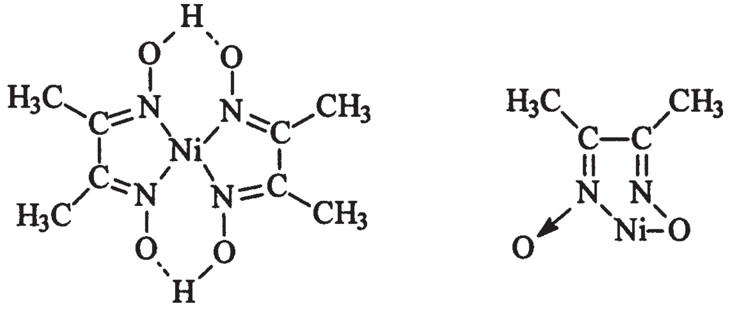
optimal chromatographic retention and separation of these metal ions were achieved. Using the present method, the metal ions were determined in various synthetic samples, tomato leaves, and vitamin tablets. The results obtained were in agreement with known amounts of metal present in each type of sample.

Solid phase extraction using 1-(2-pyridylazo)-2-naphthol (PAN) loaded on silica gel has been used for the extraction and preconcentration of rare earth elements, Pr^{3+}, Nd^{3+}, Sm^{3+}, Y^{3+} mixtures.[41] The metal ions were subsequently determined by energy-dispersive X-ray fluorescence spectrometry. The procedure permitted complete recovery of rare earths and significant sensitivity enhancement in comparison with the direct determination in the aqueous phase. The maximal extraction of these metal ions were observed between pH 7.5 and 9.5. There is a possibility of hydrolysis of trivalent lanthanide elements at these pH values, but the distinguished purple color of the lanthanide-PAN complexes was observed. Also, the physical phenomena that characterize the hydrolysis were not observed, indicating that no hydrolysis was observed in the present case. The preconcentration procedure permitted an enhancement of sensitivity of about 200 times for Pr^{3+}, Nd^{3+}, Sm^{3+}, and nearly 100 times for Y^{3+}. The determinations in quaternary mixtures showed typical precisions and accuracies of 3 and 5%, respectively.

Selective solid phase extraction of Ni^{2+} was accomplished with dimethylglyoxime (DMG) doped silica.[42] The pore width of silica, prepared by sol-gel chemistry to have pore widths in micropore and mesopore domains, demonstrated to influence the chemistry of material. With microporous silica, the stoichimetery of the Ni^{2+}-DMG complex was 1:1 as was evident from the green shift in the visible absorption spectrum. This is contrary to 1:2, which is the value observed in aqueous solution (Figure 7).

The capacity of the DMG-doped mesoporous silica was only 9 μmol Ni g^{-1} because of leaching of the complexing agent. The microporous material showed no loss of DMG, but low permeability lowered the capacity.

1-(2-Thiasolylazo)-2-naphthol (TAN) loaded on silica gel has been used by Zaporozhets et al. for the adsorption and preconcentration of Cu^{2+} and Zn^{2+} from aqueous solution and detection of these elements by visual and diffused reflectance spectroscopy.[43] The adsorption of TAN on silica surface was carried out from the hexane solution of the reagent, and the time required for equilibration was 5 min. Zn^{2+} and Cu^{2+} were completely recovered from the loaded silica gel by batch process in the pH range 5.5 to 6.8 and 3.3 to 4.6 with an equilibration time of 10 and 15 min, respectively. The isotherms of Zn^{2+} and Cu^{2+} were shaped L-type, indicating chemical interaction between Zn^{2+} and TAN. The chelating capacity of



(A) (B)

FIGURE 7. Structure of Ni^{2+}-DMG complexes (A) 1:2 complex is formed in aqueous solution, (B) 1:1 complexes is proposed to form in the microporous sol-gel material (Ref. 42).

TAN-SG for Zn^{2+} and Cu^{2+} indicated 1:1 complexation in each case. The method was applied for the determination of trace amounts of Zn^{2+} and Cu^{2+} in natural and tap water samples, and the results were in agreement to the reported values. They have also used silica gel loaded with dithiazone and zinc dithiazone for the determination of Ag^+, Hg^{2+}, Pb^{2+} present in buttermilk, natural, mineral, and wastewater samples.

Silica gel chemically modified with benzimidazole has been used by Filho et al. for preconcentration of Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+} in ethanol solution.[45] Adsorbed metal ions were eluted with 0.1 *M* HCl in ethanol-water mixture having a mole fraction of water of 0.8. The adsorption isotherms obtained for these systems follow the Langmuir adsorption model, and the retention capacity of metal ions on modified silica gel follow the sequence, $Fe^{3+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Mn^{2+}$. It was also proposed that the sorption of the metal from solution by the solid phase occurs with the metal directly coordinating with the unsubstituted benzimidazole nitrogen. The recovery of Fe^{3+} from a mixture of ions was about the same as in the individual ion experiment, whereas for Cu^{2+}, Zn^{2+}, and Cd^{2+} the recoveries were lower, indicating that the presence of one of the ions in excess did not significantly affect the recoveries of the others. The method was applied for the preconcentration of trace amounts of these metal ions from commercial alcohol used as engine fuel.

Recently, sorption of high-molecular-weight quaternary ammonium salt, Didecylaminoethyl-β-tridecyl-ammonium iodide (DDATA), on silica gel was reported.[46] This modified silica gel was used for the sorption of thiocyanate complexes of Co^{2+}, Cu^{2+}, and Zn^{2+}, with a recovery of 98.8%. Modified sorbent was applied to cobalt chemiluminescence and determined in natural water and a nickel preparation with a detection limit of 2 $\mu g\ l^{-1}$.

1,10-Phenanthroline adsorbed on silica gel (Phen-SG) has been used for the adsorption of Fe^{2+}, Cu^{2+}, and Ag^+ from aqueous solutions.[47] Loaded silica gel was applied for reflectance spectroscopy in water with detection limits 0.08, 0.03, and 0.01 ppm, respectively. The adsorption of Fe^{2+} on Phen-SG was maximum at pH 5.5 forming a colored complex requiring 5 min for equilibration. The chelation capacity of Phen-SG was 0.1 mmol g^{-1} Fe^{2+} for 0.1 mmol g^{-1} Phen, and it was spectrophotometrically proven that $Fe(Phen)^{2+}$ complex has been formed on the surface. Cu^{2+} was not adsorbed from aqueous solution on Phen-SG, so the adsorption Cu^{2+} was carried out from ammonia solution because it has a small radius and escapes the steric hindrance. The concentration of ammonia was so chosen by the authors in order to avoid the difficulties with soluble hydroxide of Cu^{2+}. The time taken for maximum Cu^{2+} adsorption was 10 min. Ag^+ formed a colorless complex at pH 2.0. The time required for equilibration was 10 min. The chelating capacity of Phen-SG was 0.2 mmol g^{-1} Ag^+ for 0.2 mmol g^{-1} Phen, thus proving the fact that the Ag:Phen complex has an stoichiometry of 1:1 on the surface of Phen-SG.

The separation and preconcentration of trace amounts of Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, and Pb^{2+} can also be carried out using silica gel modified with sodium diethyldithiocarbamate (Na-DDTC) and ammonium hexamethylenedithiocarbamate (HMDTC) as column packing material.[48] The adsorbed metal ions can be quantitatively eluted with iso-butylmethyl ketone. Using this preconcentration procedure followed by instrumental analysis, trace amounts of these metal ions can be determined in natural water samples. The chromatographic behavior of alkaline earth metals, Cu^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} on chelating aminomethylphosphonic acid-functionalized silica column was studied by Nesterenko and workers in eluents with high ionic strength.[49]

In our research group, we have exploited the capabilities of 3-hydroxy-2-methyl-1,4-naphthoquinone (HMNQ) immobilized silica gel for the separation and preconcentration of trace amounts of Fe^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+}, by both batch and column techniques.[50] We have earlier demonstrated the strong chelation behavior of HMNQ with transition and lanthanide metal ions,[51–53] which prompted us to use it as a chelating agent for immobilization on silica gel. Maximum adsorption of Cu^{2+}, Co^{2+}, Fe^{2+}, and Zn^{2+} occur in the pH ranges 3.0 to 7.0, 4.5 to 6.5, 5.0 to 7.0, and 5.0 to 8.0, respectively. The adsorbed metal ions can be eluted either with 1 N HCl or with HNO_3 prior to their determination by AAS. The modified silica gel showed fast metal ion-exchange kinetics, with just 10 min required for Zn^{2+}, Fe^{2+}, and Cu^{2+} to reach the equilibrium, while this time was 12 min in case of Co^{2+} requiring 0.1 g of modified silica gel. We have developed methods for the estimation of trace amounts of these metal ions in various commercial samples such as, vitamin, steel, and milk samples. We have also immobilized *o*-vanillin on the surface of silica gel (Figure 8) and used it for the extraction of trace amounts of these metal ions present in the commercial samples.[54] Cu^{2+} was quantitatively adsorbed in the pH range 4.0 to 6.0, whereas Fe^{2+}, Zn^{2+}, and Co^{2+} were adsorbed in ranges 4.5 to 6.0, 6.0 to 8.0, and 5.0 to 6.0, respectively. The solid phase extraction method showed fast metal ion-exchange kinetics and high sorption efficiency.

2-Mercaptobenzothiazole (MBT) supported on silica gel (MBT-SG) has been used for the chromatographic concentration of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+}.[55] These metals were retained on the MBT-SG at pH vales 4.8, 2.5, and 6.5, respectively, with a recovery of 100%. MBT-SG was found to be useful for the analysis of these metal ions present in river and sea water samples. This resin was used for the concentration of Hg^{2+}, CH_3Hg^+, $C_2H_5Hg^+$ from sea-water samples at pH 4.0, 4.5, and 5.0, respectively.[56] The adsorbed mercury was eluted with 25:1 acetone-HCl mixture or 1% thiourea solution in 0.1 *M* HCl and determined by atomic absorption spectrometry after reductive vaporization.

p-Dimethylaminobenzilidenerhodanine (DMABR) supported on silica gel (DMABR-SG) was used for the preconcentration of Ag^{+}, Au^{3+}, and Pd^{2+} from water samples.[57] These metal ions were retained at pH 1.0 to 6.5, 1.0 to 3.5, and 1.0 to 5.0, respectively, and eluted with 0.1% thiourea in 0.1 *M* HCl. The chelating capacity of DMABR-SG was 23, 11, and 11 μmol g^{-1} for Ag^+, Au^{3+}, and Pd^{2+}, respectively. Silver and gold were determined spectrophotometrically as its 1-(2-pyridylazo)naphthol complex in chloroform. Thallium (0.02 to 0.20 μg) was successfully preconcentrated on C_{18} silica gel from 0.1 *M* HCl in the presence of various cationic surfactants as ion pairs with tetrachlorothallate (III) and subsequently eluted with 96% ethanol.[58] Crown ethers with pendent carboxylic acid groups immobilized on silica gel (Figure 9) have been used for selective column concentration of alkali metal ions by means of a chromatographic stripping technique.[59]

The selectivity and efficiency for the column concentration of these ions was found to be influenced by the cavity size of crown ether unit and the conformational positioning of the proton-ionizable side arm with respect to the crown ether cavity.

IV. CONCLUSION

An accurate analysis of metal ions at trace levels is one of the most difficult and complicated analytical tasks. The targeted ion has to be separated and preconcentrated prior to its estimation by instrumental methods. Of the various methods available for this purpose, the solid phase extraction method, using chelating resins based on silica gel as solid support, offers many advantages over

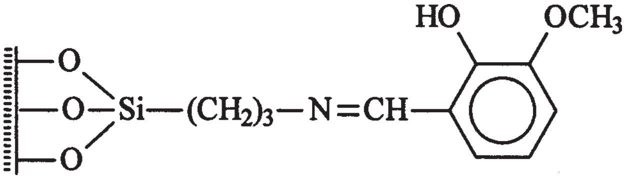


FIGURE 8. *o*-Vanillin immobilized silica gel (Ref. 54).

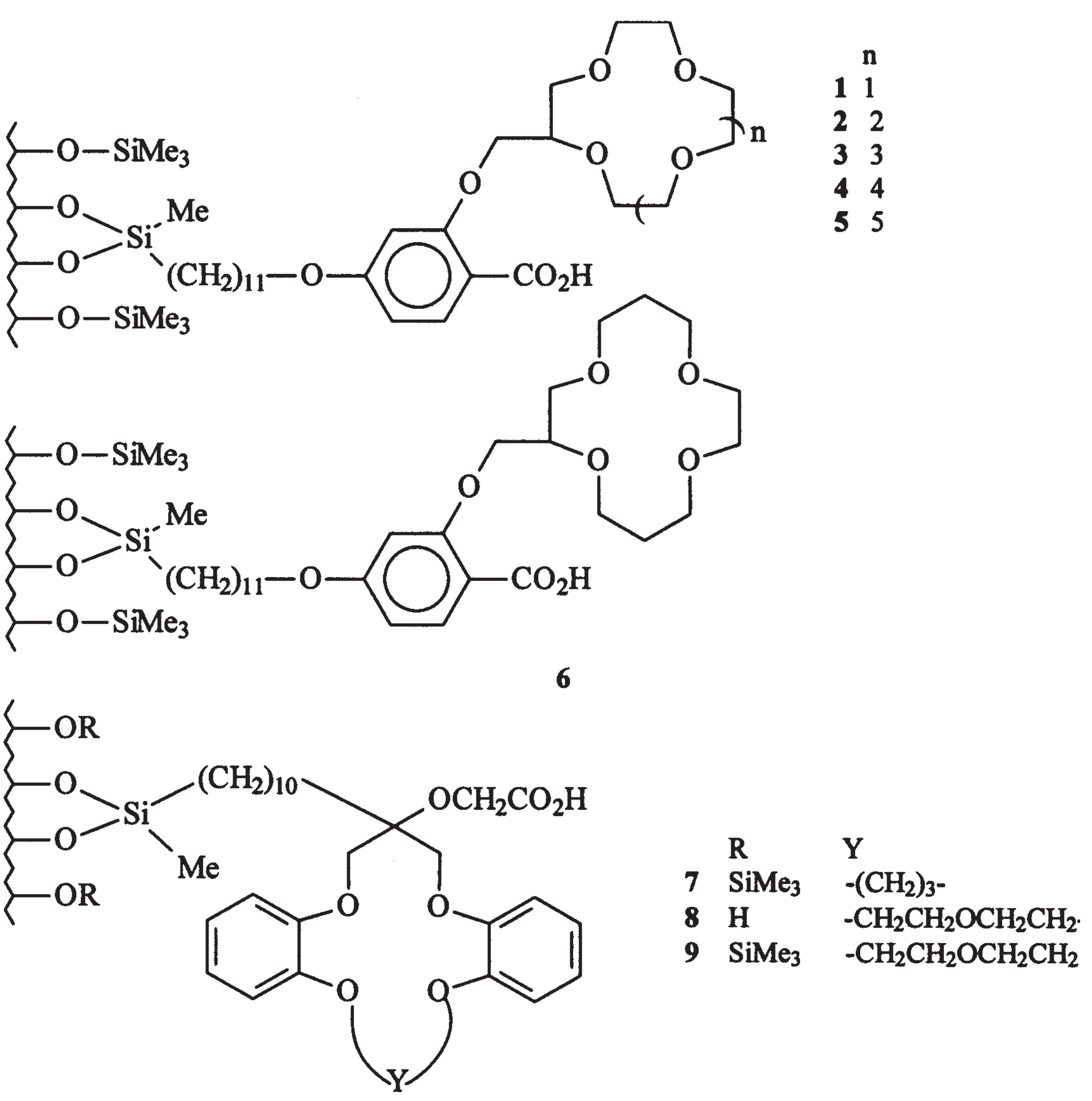


FIGURE 9. Structure of silica gel-bound crown ether carboxylic acids (Ref. 59).

conventional methods. The process of chelation in the solid phase presents a challenge both for basic research and to the industrial chemist looking for new analytical methods. If any advances are to be made in this field, a great deal of synthetic work must be invested with a view to enlarging the variety of chelating resins having different ligands. The aim of such synthesis should be to devise substances of high selectivity and rapid exchange for targeted metal ions. Silica based chelating resins offer such a potential. The synthetic procedures are simple and reproducible. Generally, these resins show fast metal ion exchange kinetics and have high sorption efficiency. Modified silica gel can be applied to a variety of samples, because the solid support is stable over a wide pH ranges. Above all, this method is a green analytical method because it does not involve the use of large amounts of toxic and chlorinated solvents, as in the case of conventional methods.

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