CHELATING RESINS IN ANALYTICAL CHEMISTRY

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Chelating resins, the polymeric complexing compounds, are specific and selective ion exchange resins. A chelating ion exchange resin consists essentially of two components, *i.e.* a chelating group and a polymeric matrix. The properties of both components affect the selectivity of the synthesized resin. Methods used to synthesize chelating resins are reviewed. The analytical and physical techniques used to characterize the dissociation constant, metal capacity and distribution coefficient of the newly synthesized resin as well as the coordination site, the composition and the formation constant of the metal-resin complexes are discussed. Chelating resins could be used in various forms. Some important features of the analytical application of chelating resins, including selective concentration and separation both in inorganic analysis and organic analysis are also discussed. The techniques by which sorption or separation with the help of chelating resins achieved can be static, dynamic, or chromatographic. After sorptive concentration or separation, the elements can be determined either directly in the sorbent phase, its decomposition residue, the eluent solution after desorption, or the effluent after the solution has been passed through the sorbent. Various objects such as natural waters, geological objects, industrial materials, foodstuffs, coal, fuel oil, shale oil, transuranium elements and biological materials could be analyzed with the help of chelating resins.

INTRODUCTION

The lack of selectivity of the conventional ion exchange resins has led to the discovery and development of a new class of polymers which are now known as specific and selective ion exchange resins. These resins are in fact polymeric complexing and chelating compounds. The idea of using complexing resins originated with the observation of Erlenmeyer and Dahn[1] that mixtures of various cations could be chromatographed on a column of powdered 8-hydroxyquinoline, the suggestion of Meinhardt[2] that complexing agents could be fixed on a supporting solid, and Griessbach's concept of selective ion exchange as a function of pH[3]. Skogseid was the first one to synthesize potassium ion selective resin[4,5], and propagated the theory of ion-specific resins. This initiated a new field of industrially important and useful selective ion-exchange resins. Mellow[6] and Gregor[7] described the preparation of several resins containing a variety of chelating groups known to form complexes with a wide range of metal ions whose selectivity and stability is pH-dependent. At present, a large number of chelating ion-exchange resins incorporating a host of ligands, such as aminocarboxylic acids, hydroxamic acids, oxines, pyridine carboxylic acids, acid hydrazides, arsonic acids, phosphonic acids, dithiocarbamates, thiols, schiff bases, crown ethers and cryptands etc., have been synthesized. These ligands were incorporated into a variety of both organic[8,9] and inorganic[10,11] polymeric supports or matrices.

A chelating ion-exchange resin consists essentially of two components, *i.e.*, a chelating group and a polymeric matrix. Thus, the properties of both components have to be taken into account when designing and synthesizing a chelating ion-exchange resin. Fundamentally, two types of polymeric matrices can be considered, *i.e.*, inorganic and organic. However, inorganic supports have high mechanical strength, high thermal stability, good ability to withstand high pressure and stability both towards organic solvents and to mineral acids. On the other hand, there are several disadvantages associated with the use of inorganic supports, among the most conspicuous being the impossibility of a

high degree of functionalisation, relatively low ion-exchange capacity and low ion-exchange rates. Silica is among the most extensively used inorganic supports[11]. The organic matrices used as supports for ion exchange resins can either originate from naturally occurring polymers or from synthetic polymers. Among the naturally occurring polymers used as supports for chelating ion-exchange resins, cellulose has been used most extensively. The chemistry of cellulose as a polymeric support, its ion exchange properties and the use of chelating cellu-loses for preconcentration of trace elements have recently been reviewed comprehensively by Wegscheider and Knapp[12] and Lieser[13]. Unsub-stituted cellulose has a very low ion exchange capacity. Another important natural-occurring chelating marine polymer is chitin, poly(N-acetyl-D-glucosamine) and its deacetylated derivative, chitosan, which have been useful for removing heavy metal ions from discharge water. The chelating and ion-exchange properties of chitin and chitosan have been studied in deatil[14-16] and reviewed by Muz-zarelli[17,18]. Among the synthetic organic matrices, two types of polymers can be considered, viz. con-densation and addition polymers, which are ex-tensively used as supports or matrices for chelating ion exchangers. Condensation polymers can easily undergo hydrolytic and cleavage reactions and therefore have poor chemical and mechanical stability. Addition polymers are preferred over condensation polymer matrices whenever possible, because of their higher chemical stability and me-chanical strength.
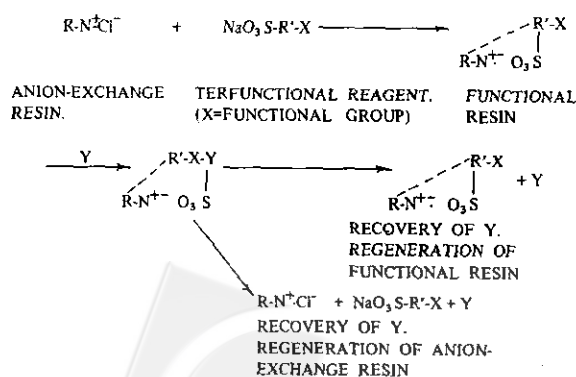
SYNTHESIS OF CHELATING ION EXCHANGE RESINS

The general methods of incorporating active functional groups have been summarised by Akelah and Sherrington[9]. According to them, three methods can be distinguished to incorporate active functional

groups into polymer chains:

a. Direct polymerisation and copolymerisation of monomers containing the desired functional groups.
b. Chemical modification of a preformed polymer.
c. A combination of a and b.

Some special methods have also been used to synthesize many individual resins. Tanaka *et al.*[19] developed highly selective functional resin by simple modification of common ion exchange resin with appropriate reagent. These reagents should have three functional properties, namely selective reaction with the determinant of interest, an ion exchange reaction with the resin and physical adsorption of the ion exchange resin matrix. The preparation and regeneration of the functionalized resin was shown as Scheme 1. The various methods for the synthesis of these exchange resins have been reviewed recently by several authors[20-25]. The synthesis of polymers with macrocyclic chelating ligands as pendant or anchor groups has also been discussed by a number of authors[26-29]. The method involving incorporation of chelating ligands into preformed polymers or matrices to synthesis chelating ion-exchange resins is preferred to other methods in view of the fact that the degree of functionalisation can be controlled by varying the amount of cross-linking agents and the

Scheme 1 Preparation and regeneration of anion-exchange resin functionalized with terfunctional reagent.
- - - - - physical interaction

extent of modification in preformed matrices.

CHARACTERISATION OF CHELATING ION-EXCHANGE RESINS AND THEIR METAL COMPLEXES

The characterisation of newly synthesized chelating ion-exchange resins and their metal complexes is of prime importance. In the case of chelating ion-exchange resins, characterisation has to be in terms both of its analytical and physical properties and its characterization involves the use of analytical and physical techniques. Various analytical methods are used for the characterisation of chelating resins. They are used to determine density, grain size, water content, ash content, capacity, distribution coefficient and selectivity coefficient. Both the distribution and selectivity coefficients depend on the degree of cross-linking, specific capacity and on the nature of the chelating group[30-39]. Acidic and basic properties of chelating resin are usually characterized by determing the content of chelating groups and the dissociation constants. The protonation process of complex-forming resins can be expressed as Scheme 2. In the solution phase, there are water; protons; and the electrolyte, G^+G^-, it is used to adjust the ionic strength. The components in the resin phase are as follows: the water; the fixed basic group, which can be either a basic anion or a neutral base; the conjugate acid formed in the protonation reaction; and the counter ions. When the active group is a negative base, its protonation is accompanied by the release of the positive counter ions, G_K^-. When, however, the base is neutral, its protonation is accompanied by the uptake of the negatively charged counter ions, G_K^-. The electrolyte, $G_I^+G_I^-$, in the resin phase has migrated from the solution by the so-called electrolyte invasion process. The concentration of the counter ions in the resin phase is the sum of the chemically bound and the invaded amount of the counter ions divided by the
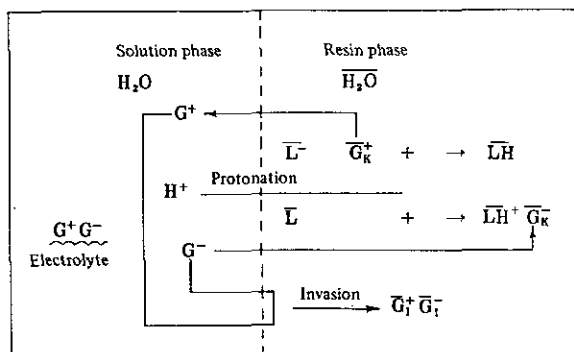
$$(G) = \frac{\overline{G_K} + \overline{G_I}}{\overline{H_2O}} \qquad C_L^- = (L) + (LH) = \frac{Q}{\overline{H_2O}}$$

$\overline{G_K}$
$\overline{G_I}$ mmol per gram dry resin

Q

$\overline{H_2O}$ gram per gram dry resin

Scheme 2   Protonation process of compex-forming resins.

water content of the resin. The analytical concentration of the base, C_L, is the ratio of the capacity, Q, and the water content of the resin. Since the protonation process is a heterogeneous system, the protonation constant can be expressed as the following equations.

1. The protonation of a negatively charged base, L^-, taking the counter-ions into account; the reaction is:

$$L^- + G^+ + H^+ + G^- = HL + G^+ + G^-$$
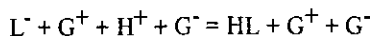
The protonation constant is:

$$K_{L^-} = \frac{a_{HL} \; a_{G^+}}{a_{L^-} \, a_{G^+} \; a_{H^+}}$$

2. The protonation of a neutral base, L, then the reaction is:

$$L + H^+ + G^- = HL^+ + G^-$$

The protonation constant is:

$$K_L = \frac{a_{HL^+} \, a_{G^-}}{a_L \; a_{H^+} \; a_{G^-}}$$

3. The protonation of a positively charged base, L^+, the reaction is:

$$L^+ + G^- + H^+ + G^- = HL^{2+} + 2G^-$$

The protonation constant is:

$$K_{L^+} = \frac{a_{HL^{2+}} \, a_{G^-}}{a_{L^+} \, a_{G^-} \, a_{H^+}}$$

The general equation describing the protonation equilibria can be written as:

$$\sum_{j=0}^{N} (\overline{\alpha^*} - N + j) \beta_j' (\overline{H})^j = 0$$

This equation applies when the fully protonated base is an N-basic acid and is titrated with a strong base, where $\overline{\alpha}^*$: the molar fraction of the free, non-protonated base, β_j' is the overall protonation constant: $\beta_j' = K_1' K_2' \ldots K_j'$.

1. If the base is a negatively charged ion:

$$\overline{\alpha^*} = \frac{\overline{G_K^+}}{Q} + \frac{(\overline{H}) - (\overline{OH})}{C_{\overline{L}}}$$

2. If the base is neutral:

$$\overline{\alpha^*} = N - \frac{\overline{G_K^-}}{Q} + \frac{(\overline{H}) - (\overline{OH})}{C_{\overline{L}}}$$

Here the proton activity, $(\overline{H})$, in the resin phase is given by

$$(\overline{H}) = [H] \left[\frac{(G)}{aG} \right]^{\nu}$$

$\nu = +1$ if the counter ion is $\overline{G^+}$ and -1 if the counter ion is $\overline{G^-}$, [H] and a_G are the proton activity and the counter ion activity in the solution phase, respectively, (G) is the concentration of the counter ions in the resin phase. For the practical application of the general equation it is necessary to establish the inter-relationships between the experimentally accessible parameters: $\overline{\alpha^*}$, $\overline{G_K}$, $\overline{G_1}$, $\overline{Q}$, $\overline{H_2O}$, etc. Some parameters determined for the β-hydroxydi-

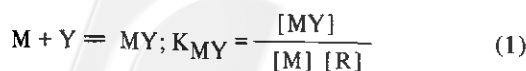Table 1   Determination of the dissociation constants of β-hydroxy-dithiocinnamate resin

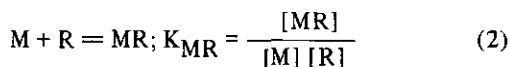| pH	$\overline{G_K}$	$\overline{G_1}$	[G]	pH	$\overline{\alpha^*}$	pK_a
6.35	0.27	0.06	0.43	6.72	0.45	6.44
6.50	0.36	0.08	0.55	6.76	0.58	6.62
6.80	0.40	0.09	0.64	6.99	0.67	6.68
7.03	0.49	0.10	0.76	7.15	0.81	6.40

Amount of resin: 0.2 g; volume of solution: 25 mL; ionic strength: 1.0 mol/1; water regain: 0.77 g g^{-1}; temperature: 25°C.

thiocinnamate resin were listed in Table 1[41].   From this table, the dissociation constant of the resin being $10^{6.53}$ could be calculated.   The heterogeneous protonation equilibria of chelating ion exchange resins has been studied by several workers[30-34,36-38,40].

A number of physico-chemical methods mainly based on the spectral and magnetic properties of chelating ion-exchange resins and their metal complexes are now used for characterising these polymeric compounds.   Infrared spectroscopy in conjunction with their elemental analysis provides an excellent tool for characterising chelating ion-exchange resins and to locate the coordination or bonding sites in the metal complexes of chelating resins[33,34,36-38,40].   Other methods, such as ESR, Diffuse reflectance electronic spectra, magnetic susceptibility measurements, EXAFS, ESCA, SEM, TGA, DTA, solid NMR and Mössbauer spectroscopy could also be used for the study of chelating resins and their metal complexes.

The methods applied to study the stability constants of chelating resins could be roughly divided into three methods, that is ligand competition method, metal competition method and proton competition method.   In ligand competition method, two competing complexation reactions take place

$$M + Y \rightleftharpoons MY; \quad K_{MY} = \frac{[MY]}{[M][R]} \qquad (1)$$

Chelating Resins in Analytical Chemistry

J. Chin. Chem. Soc., Vol. 36, No. 5, 1989   393

$$M + R = MR; K_{MR} = \frac{[MR]}{[M][R]} \quad (2)$$

$$MY + R = MR + Y; \quad (3)$$

$$K_{over-all} = \frac{[MR][Y]}{[MY][R]} \quad (4)$$

$$\log[R] = \log\frac{[MR][Y]}{[MY]} - \log K_{over-all} \quad (5)$$

where Y is the competing ligand, and R is the chelating resin.

The equilibrium measurements for the iron-EDTA-hydroxamate resin system were shown as Table 2[42]. The conditional formation constant could be obtained from the plot of $\log[R]$ vs. $\log [MR][Y]/[MY]$. Since the K_a value is $10^{-6.47}$, the formation constant could be calculated as 1.62×10^{10}.

In proton competition method, the following reaction was considered:

$$M^{n+} + iAH = iH^+ + A_iM^{(n-i)+} \quad (6)$$

The complex formation equilibrium constants Bi could be determined by a modification of Bjerrum's method.

$$B_i = \frac{[A_iM^{(n-i)+}][H^+]^i}{[AH]^i[M^{n+}]} \quad (7)$$

$$\bar{n} = \frac{\sum_{i=1}^{N} iB_i(\frac{[AH]}{[H^+]})^i}{1 + \sum_{i=1}^{N} iB_i(\frac{[AH]}{[H^+]})^i} \quad (8)$$

$$B_i = (\prod_{i=1}^{i} k_i)K_a^i \quad \text{and} \quad \beta_i = \prod_{i=1}^{i}K_i \quad (9)$$

where $K_i = [MA_i]/[MA_{i-1}][A]$ is the stepwise constant for the ith step, β_i is the overall stability constant for the ith complex, and K_a is the dissociation constant of the functional group of the chelating resin. Eq. (8) could be solved graphically in the form $XP_1 + YP_2 = 1$.

$$\frac{\bar{n}}{(1-\bar{n})\frac{[AH]}{[H^+]}} \cdot \frac{1}{B_1} + \frac{(\bar{n}-2)[AH]}{(1-\bar{n})[H^+]}\frac{B_2}{B_1} = 1 \quad (10)$$

Table 2   Equilibrium measurements for the iron-EDTA-hydroxamate resin system*

No.	Fe^{3+} taken (mmol)	EDTA taken (mmol)	Resin (g)	Fe^{3+} in Resin (mmol)	Fe-EDTA/soln (mmol)	EDTA/soln (mmol)	log R	log [MR][Y]/[MY]
1	9.80×10^{-4}	2×10^{-3}	0.25	7.60×10^{-4}	2.20×10^{-4}	1.78×10^{-3}	−0.358	−2.21
2	1.96×10^{-3}	4×10^{3}	0.40	1.26×10^{-3}	7.00×10^{-4}	3.30×10^{3}	−0.153	−2.23
3	4.90×10^{-4}	1×10^{-3}	0.15	4.28×10^{4}	6.20×10^{-5}	9.38×10^{-4}	−0.580	−2.19
4	1.96×10^{-3}	4×10^{-3}	0.35	1.27×10^{-3}	5.95×10^{-4}	3.31×10^{-3}	−0.211	−2.22
5	2.49×10^{-3}	1×10^{-3}	0.50	1.58×10^{-2}	8.70×10^{-4}	3.13×10^{-3}	−0.056	−2.25

*Sample volume: 25 mL
 Acidity of solution: in 0.2 N $HClO_4$
 Maximum capacity of the resin: 1.76 mmol/g
 R: amount of resin uncomplexed
 MR: Fe^{3+} in resin
 MY: Fe-EDTA/soln
 Y: EDTA/soln

Table 3 *Potentiometric determination of the formation constant of copper(II)-N-(hydroxymethyl)thioamide resin complex*

Cu(II) added mmol	pH of solution	[Cu] mmol	[$\overline{Cu}$] mmol	[AH] mmol	[A_{Cu}] mmol	$\overline{n}$	$\dfrac{[AH]}{[H^+]}$	$\dfrac{\overline{n}}{(1-\overline{n})\dfrac{[AH]}{[H^+]}}$	$\dfrac{(\overline{n}-2)[AH]}{(1-\overline{n})[H^+]}$
0.202	4.16	0.152	0.050	0.674	0.022	0.444	1094.76	7.294×10^{-4}	-3.063×10^3
0.404	3.49	0.342	0.062	0.673	0.023	0.371	268.31	6.793×10^{-4}	-2.249×10^3
0.505	3.63	0.448	0.057	0.670	0.026	0.456	844.76	9.922×10^{-4}	-2.398×10^3
0.707	3.44	0.645	0.062	0.670	0.026	0.419	752.89	9.580×10^{-4}	-2.720×10^3
0.909	3.21	0.861	0.048	0.673	0.023	0.479	698.75	1.330×10^{-3}	-1.833×10^3

Volume of solution: 25 mL

Amount of resin: 0.3 g

Here, B_1 and B_1/B_2 could be calculated from the intercepts of X and Y coordinate respectively. Table 3 showed the result of potentiometric determination of the formation constant of copper-N-(hydroxymethyl)thioamide resin complex[42]. By the graphic method mentioned above, the formation constants obtained for copper-N-(hydroxymethyl)thioamide resin complex was $10^{8.80}$. The equilibria for the complex formation of chelating ion exchange resin toward some metal ions have been studied by several workers[36,37,39,40,43-46]. The values of stability constants obtained are highly useful in estimating the selectivity of chelating resins and their analytical potentialities.

USE OF CHELATING RESINS IN INORGANIC ANALYSIS

In analytical chemistry, chelating resins are mainly used for selective concentration and separation of elements preceding the identification of elements by different methods. The possibility of selective sorption of certain elements in the presence of others is based on the different stability of complexes formed by the element ions with the chelating groups of the resin. Normally, chelating resins can react with a large variety of elements, but the stability of the resultant complexes differs and depends on the experimental conditions. The stronger the bond between the elements of interest and the resin groups, the more selective is the concentration method. By choosing an appropriate resin with the specific chelating groups and the optimum sorption conditions, one can obtained the required selectivity with respect to a certain element or a group of elements. For instance, chelating resin containing thioglycolic acid[33], cysteine[34], hydroxamic acid[36], thiohydroxamic acid[37], histidine[38], β-hydroxydithiocinnamic acid[40] and N-hydroxymethylthioamide[42] group can be used to concentrate numerous metal groups, resulting in their separation from alkaline and alkaline-earth metals at higher pH. While, in highly acidic solutions, some of the mentioned resins can be used for selective concentration of some noble metal ions[33,34,37,38,40-42]. A high selectivity can also be reached by combining sorptive concentration of chelating resins with other concentration methods, *e.g.,* coprecipitation, extraction, and fire assaying[47-49].

Concentration of microelements from natural water by sorption on chelating resins can be performed both by batch and column methods. The batch method is normally used for small water samples of 100 to 500 mL. It is particularly advantageous when the microelements are determined
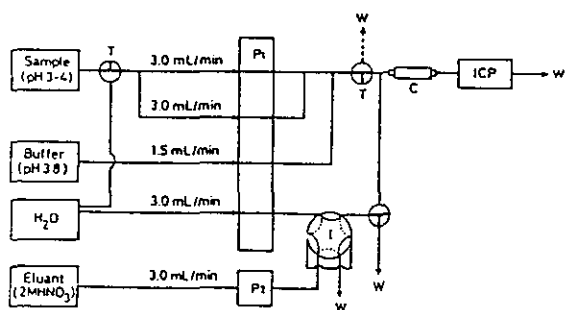
Fig. 1 Schematic manifold for on-line preconcentrating FIA-ICP system: (P_1, P_2) pumps; (I) six-way valve; (c) Muromac A-1 (3.2 mm i.d., 8 mm); (ICP) inductively coupled plasma atomic emission spectrometer; (W) waste; (T) three-way stopcock.

directly in the resin phase after concentration by means of X-ray fluorescence[50], neutron activation method or UV-visble methods[39]. The method is simple and unnecessary to desorb the elements after concentration or separation, as well as when sorption is performed in heated solution, or in some other cases. Column concentration is used chiefly for large sample volumes of 1 to 5 L and more. If resins based on hydrophilic and porous matrices are used, the concentration can be performed with a higher solution flow rates, than that in the hydrophobic resin. Fibrous sorbents hold great promise for the concentration of microelements from natural waters. The large surface area, the high kinetic properties of these sorbents and the possibility of using them in different sorption modes, as filters, films etc., are useful in concentrating and determing various micro-elements[50-52]. The apparatus for collection and elution of metal ions with Expapier F-2 was shown as Fig. 1[52], where Expapier F-2 is 2-hydroxypropy-liminodiacetic acid loaded on cellulose fiber. By a filtration procedure, Th(IV), Zr(IV), Fe(III), Sc(III), Y(III), and rare earth ions(III) were quantitatively retained on the Expapier F-2 from acetate buffer sulutions at pH 4 − 5. The quantitative retention pH of various metal ions were as follow; Th(IV):

2.0 − 2.5, Sc(III): 3.0 − 4.0, Y(III): 3.0 − 5.2, Al(III): > 5.0, Fe(III): 1.7 − 2.0, rare earth metal ions(III): 2.0 − 6.0. The complexing capacity of Expapier F-2 for these metal ions was $(6.35\pm0.25) \times 10^{-2}$ meq g^{-1} at optimal pH. Current ICP-MS detection limits in dilute aqueous acid solution are in the range from 0.01 to 0.1 $\mu g/L$ for most elements[53,54], often 1−3 orders of magnitude lower than that for ICP-AES. However, determination of trace metals in sea water by inductively coupled plasma mass spectrometry have also involved a preconcentration procedures on a silica-immobilized 8-hydroxyquinoline. McLaren *et al.* achieved a 50-fold enhancement prior to instrumental determination[58]. With the growth of nuclear power, new uranium resources other than uranium ores have been explored in order to secure a supply of uranium for the future. Many studies have been made on the recovery of uranium from seawater, since the estimated reserve of uranium in seawater is 4.5 x 10^9 tons, which is about one thousand times the terrestrial resources. Another important alternate source of uranium is the phosphoric acid solution from the manufacture of fertilizers. Phosphoric acid from fertilizer plants usually contains 10−300 ppm uranium as compared to 3 ppb contained in seawater. An amidoxime-group-containing fibrous adsorbent was found to have excellent properties for the adsorption of uranium from seawater and a high stability when contacted with acid[55]. The same material was also used for the recovery of vanadium and titanium[55].

Flow injection analysis (FIA) was originally designed as a vehicle for homogeneous conversion of a sample component into a measurable species, and this feature is still viewed today as the main function of the technique. Nowadays, heterogeneous conversion is also used extensively. Depending on their purpose, various types of column materials are used in packed reactors, such as (a) solid reagents, (b) ion-exchangers and (c) catalysts. Ion exchangers could be used for preconcentrating an analyte, or

removing matrix components which might interfere, or converting a sample constituent into a detectable species. The columns used have contained a variety of immobilised chelating functions, including Chelex-100[56], Muromac A-1[57], quinolin-8-ol on controlled-pore glass[58], poly (dithiocarbamate)[59] and poly (phenyl urea)/poly (ethylenediaminediacetic acid)[60] as well as Amberlite IRA-400[61] and alumina[62]. Hirata *et al.* used the on-line preconcentrating FIA-ICP system (Fig. 2) and found the signal enhancements were 34–113 times better than for a conventional continuously aspirated system for Al(III), Cr(III), Fe(III), Ti and V[63]. The results also showed that the detection limits were at least one order of magnitude better than conventional continuous aspiration ICP, and two orders of magnitude lower detectability than those by EA-ICP.

Chelating resins could also be used in speciation studies[63-66]. Florence found that solutions of col-

loidal hydrated ferric oxide and bulky organic dyes are quantitatively rejected by the resin[63,64]. Itoh *et. al.* found that selenium(IV) and other forms of selenium in sea water could be determined by anion-exchange resin loaded with sulfonic acid derivative of bismuthiol-II[66]. We also found that selenium(IV) and selenium(VI) could be separated and determined simultaneously by N-(hydroxymethyl)-thioamide resin column, even in the presence of high concentration of electrolyte (Fig. 3)[66].

Some methods that use of high performance liquid chromatography to determine metal ion concentration at low levels in complex matrices are: (a) Ion chromatographic method: This method is most commonly applied, but often requires the use of a metal-complexing additive in the buffered eluent. (b) HPLC on reversed columns: In this method, sample mixture must be converted into neutral metal chelates. (c) A hydrid of these two methods, where chelating resins are used as the stationary phase. It is a somewhat more direct approach. In this way, pretreatment of the sample solution is generally not necessary and simpler mobile phases can be used because selectivity is designed into the stationary phase. The separation of some metal ions may serve as examples to demonstrate the efficiency of the third technique. For instance, separation of copper(II), cadmium(II) and lead(II) (Fig. 4) or copper(II) and gold(III) (Fig. 5) or gold(III) and platinum(IV) (Fig. 6) could be effected by sorption of them with a resin containing β-hydroxydithiocinnamic acid group[41]. Separation of gold(III) from cobalt(II), copper(II) and zinc(II) (Fig. 7) or separation of mercury(II), gold(III), and platinum(IV) from iron(III) and copper(II) (Fig. 8) could be effected by sorption on the N-(hydroxymethyl)thioamide resin[42].

In short, chelating resins can be used in the analysis of different objects, including natural waters, geological objects, industrial materials, foodstuffs, coal, fuel oil, shale oil, transuranium elements and other biological materials.
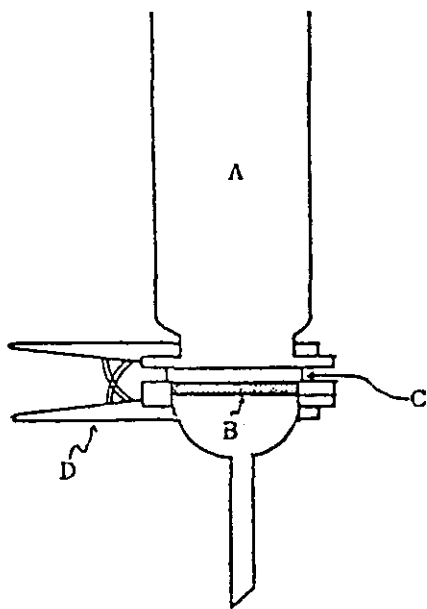

Fig. 2 Apparatus for collection and elution of metal ions with Expapier F-2.
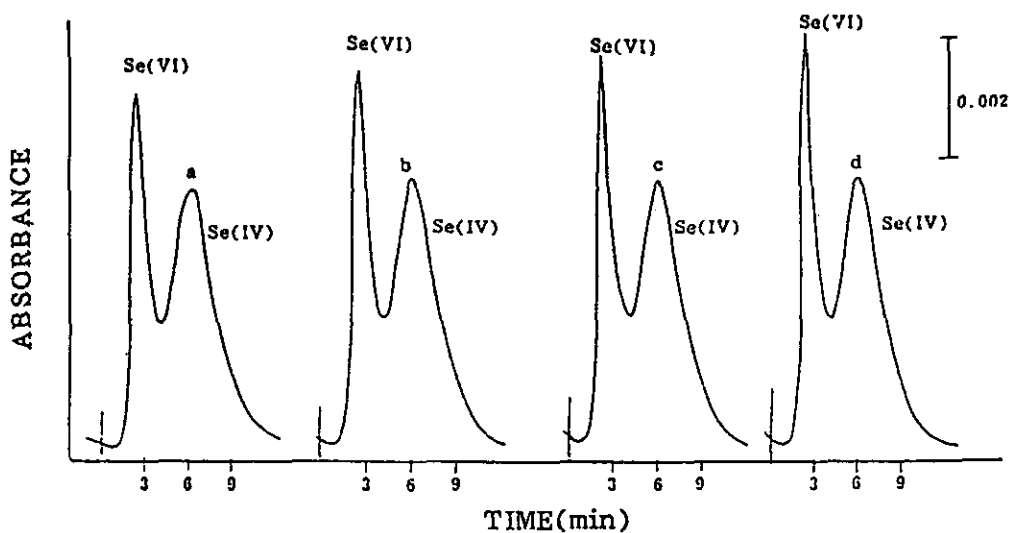A: funnel, B: glass filter, C: Expapier F-2, D: clamp.

Fig. 3   Separation of Se(IV) and Se(VI) on N-(hydroxymethyl)-thioamide resin column.[66]
Eluant: 0.05 M HCl; Eluant flow: 0.8 ml/min.   Detector: 0.02 AUFS, 215 nm.
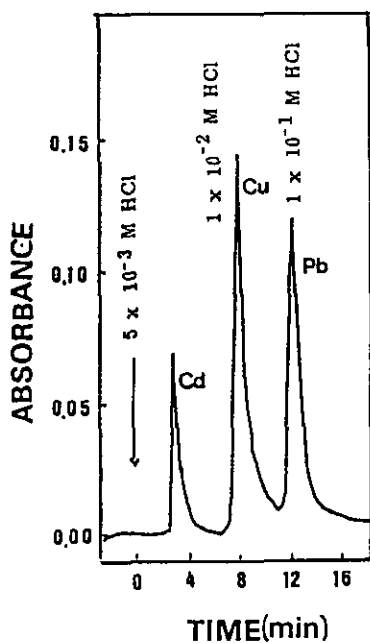a: in deionized water   b: in 0.1 M NaCl   c: in 0.5 M NaCl   d: in 0.75 M NaCl

Fig. 4   Separation of metal ions on β-hydroxydithiocinnamate resin column.[41]
Eluant flow: 1 mL/min.
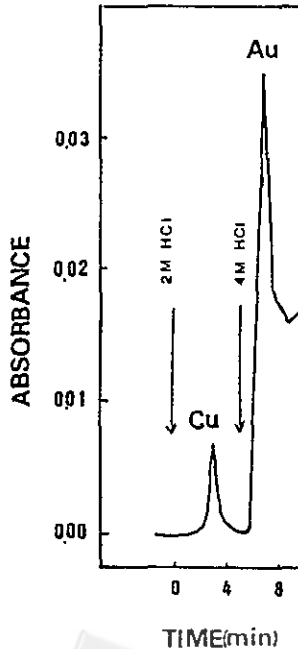Detector: 0.4 mM PAR; Reagent flow: 0.5 mL/min, 0.5 AUFS, 520 nm.

Fig. 5   Separation of metal ions on β-hydroxydithiocinnamate resin column.[41]
Eluant flow: 1 mL/min.
Detector: 0.2 AUFS, 215 nm.
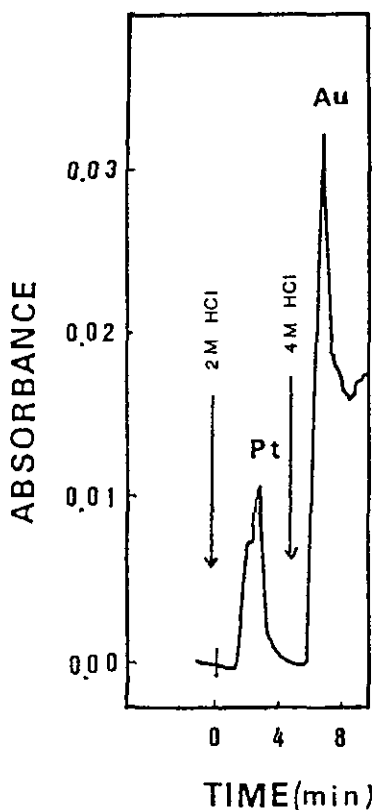
Fig. 6 Separation of metal ions on β-hydroxydithiocinnamate resin column.[41]
Eluant flow: 1 mL/min. Detector: 0.1 AUFS, 215 nm.
Detector: 0.1 AUFS, 215 nm.

Fig. 7 Separation gold(III) from cobalt(II), copper(II) and zinc(II) on a N-(hydroxymethyl)thioamide resin column.[42]
Eluant flow: 1.2 mL/min.
Detection: Photometry at 520 nm after reaction with PAR.

USE OF CHELATING RESINS IN ORGANIC ANALYSIS

Among the variety of separation methods, ligand exchange chromatography (LEC) is one of the most powerful techniques for resolving complex forming substances. Since its introduction in the early 1960s'[67], much work has been done on the separation of isomers or homologues of amines, phenols, amino acids and other organic ligands containing nitrogen or oxygen atoms. LEC is now a very common technique in high per-formance liquid chromatography.
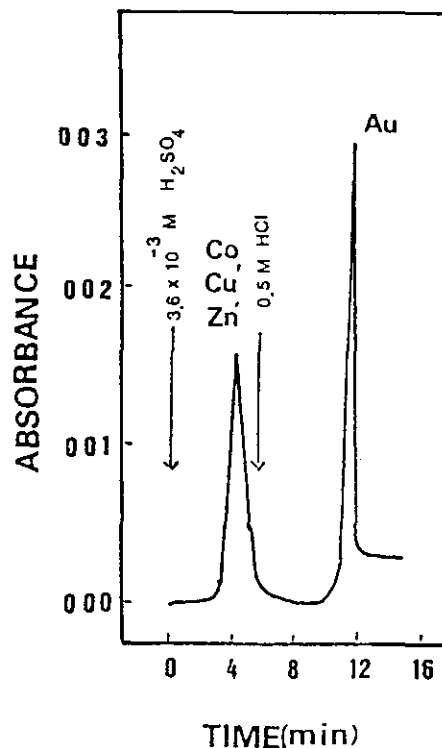
The solid supports commonly used in ligand exchange chromatography are resins with sulfonate, carboxylate or iminoacetic groups which coordinate the metal ions. However, chelating resins were proved to be even better with regard to their ability to retain metal ions. Unfortunately, among the numerous chelating sorbents synthesized so far, resins with iminodiacetate ligands (Chelex 100) and resins with α-amino acid groups are the only ones that have been widely used in LEC. Takayanagi *et al.* loaded an ACDA phase with either copper or silver ions for the separation of dialkyl sulphides[68]. Iminodiacetate phases were loaded with nickel[69], zinc[70] and copper[71] for the separation of peptides, amino acids and proteins. Andersson *et al.* used a cation-exchanger in its silver form for the selective isolation of ethynyl
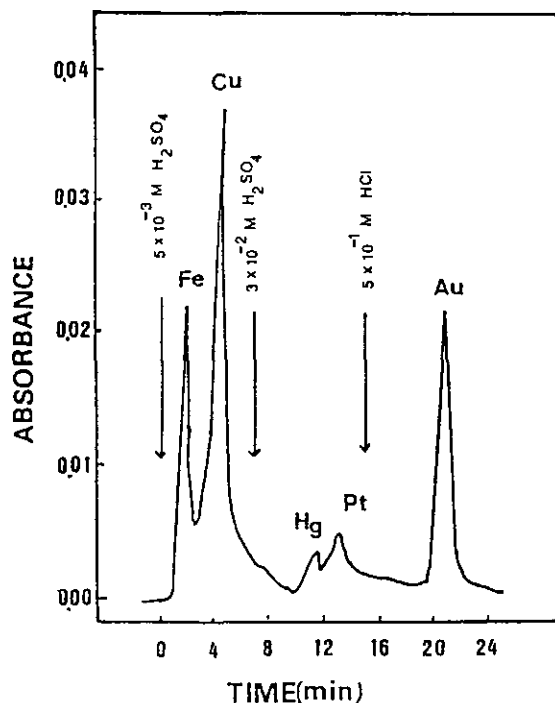
Chelating Resins in Analytical Chemistry

J. Chin. Chem. Soc., Vol. 36, No. 5, 1989   **399**

Fig. 8 Separation of metal ions on a N-(hydroxmethyl)-
thioamide resin column.[42]
Eluànt flow: 1.0 mL/min.
Detection: Photometry at 520 nm after reaction with
PAR.

Fig. 9 Separation of some dialkyl sulfide mixture.[75]
Mobil phase: $CH_3OH:H_2O$ = 3:1 (v/v)
Flow rate: 0.6 mL/min; λ = 210 nm; 0.1 AUFS.
Peak (a)   ter-butyl sulfide
     (b)   isopropyl sulfide
     (c)   allyl methyl sulfide
     (d)   ethyl sulfide
     (e)   methyl sulfide.

steroids from urine[72]. Brinkman *et al.* applied a Pt(IV)
-ACDA phase to the removal of interfering anilines
from a phenylurea herbicide mixture[73] and used a
precolumn packed with Hg(II)-oxine for the on-line
trace entrichment of 2-mercaptobenzimidazole[74]. We
used a precolumn packed with Cu(II)-N-(hydroxy-
methyl)thioamide for the on-line trace enrichment of
2-mercaptobenzimidazole. Excellent selectivity was
demonstrated at low ppb levels (0.2 ppb)[75], which
showed even better than that of Brinkman's result
(1 ppb). Our group also applied Cd-hydroxamate,
Cu-N-(hydroxymethyl)thioamide, Cd-N-(hydroxyme-
thyl)-thioamide and Hg-N-(hydroxymethyl)thioamide
phases for the separation of dialkyl sulfides[75,76].
One of the results was shown as Fig. 7. From the
results of investigation on-line trace enrichment of
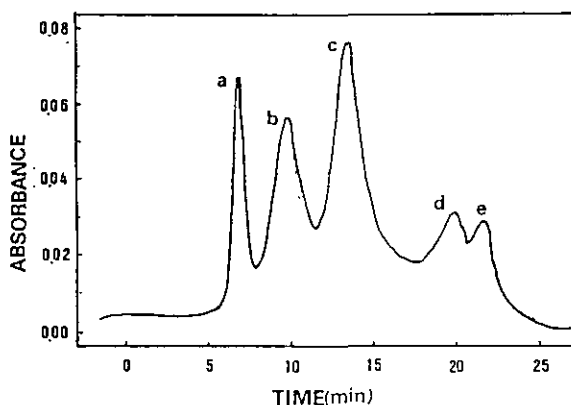2-mercaptobenzimidazole and separation of some

dialkyl sulfide mixture, we found that the softer the
compounds to be tested are, the softer the stationary
phase must be.

CONCLUSION

Nowadays, chelating resins are intensively
investigated in many countries. The high selectivities
of the complexing ion exchangers have enabled a
great expansion in the range of application to the
separation of complicated mixtures, either inorganic
or organic substances, and these resins become of
special importance in the separation of components
present in low concentrations from solution with
complex salt compositions.

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