Michal J (1973) *Inorganic Chromatographic Analysis*. New York: Van Nostrand.

Moshier RW and Sievers RE (1965) *Gas Chromatography of Metal Chelates*. Oxford, London: Pergamon.

Schwedt G (1981) *Chromatographic Methods in Inorganic Analysis*. Heidelberg, New York: Huthig Verlag.

Uden PC (1995) Element specific chromatographic detection by atomic absorption, plasma atomic emission and plasma mass spectrometry. *Journal of Chromatography* 703: 393.

Uden PC and Henderson DE (1977) Determination of metals by gas chromatography of metal complexes – a review. *Analyst* 102: 889.

# METAL COMPLEXES

## Ion Chromatography

**D. J. Pietrzyk**, University of Iowa, Iowa City, IA, USA

### Introduction

Many different and clever methods have been reported in the literature for the separation of metal ions. Most involve chemical reactions in which complexes are formed between the hydrated metal ions and an inorganic or organic ligand. If an organic ligand is employed coordination is usually through oxygen, sulfur or nitrogen atoms, individually or in combination.

In a simplified representation the stepwise and overall formation of metal–ligand complexes can be represented by the following:

$$\mathrm{M}^{2+} + \mathrm{HL} = \mathrm{ML}^{+} + \mathrm{H}^{+} \qquad [1]$$

$$\mathrm{ML}^{+} + \mathrm{HL} = \mathrm{ML}_2 + \mathrm{H}^{+} \qquad [2]$$

$$\mathrm{M}^{2+} + n\mathrm{HL} = \mathrm{ML}_n^{+2-n} + n\mathrm{H}^{+} \qquad [3]$$

where $M^{2+}$ is a divalent hydrated cation (acceptor) and HL is a monoprotic weak acid ligand (donor) that replaces the waters of coordination in a series of steps. The formation and dissociation of the metal–ligand (donor–acceptor) complexes proceeds, often rapidly, by a series of equilibrium reactions, each of which is defined by a formation constant. Because of the metal ion coordination number, the stepwise equilibria, the formation constant, and concentrations of the metal ion and ligand, a series of complexes (see the expression of the total equilibrium steps in eqn [3]) may coexist in the solution. When the ligand is neutral the charge of the resulting complexes are positive. However, the complexes may associate with solution anions to produce neutral species. Ligands can also be anions, eqns [1]–[3], and thus the complexes that form can be cations, neutral or anionic, depending on the coordination number of the metal ion, the number of ligands bound to the metal ion, the formation constants for the complexes that form, and the metal ion and anionic ligand concentrations.

Conversion of a metal analyte into a complex is important in separations for two major reasons. First, the chemical and physical properties of the metal–ligand complex are sharply different than those of the metal ion hydrate. Solubility, ionic or polar character, and even volatility can be different. Formation constants for the metal–ligand complexes will differ and pH is often an important variable. Thus, the number of separation strategies that are applicable to the separation of metal ions are broadened and the number of variables that can be altered to bring about resolution in the separation of a complex mixture of metal ions is increased. Second, some metal–ligand complexes can be more easily detected, which improves quantitative estimation and even identification, than the metal ion hydrate. For example, metal–ligand complexes can be highly coloured, while some will fluoresce and/or have electrochemical properties that can be monitored.

Using complex formation between a ligand and metal ion to facilitate metal ion separations was an important strategy in the development of low efficiency liquid column chromatographic separations of metal ions, particularly in separations by ion exchange and partition column chromatography. Similarly, complex formation is a key elution parameter in high efficiency liquid column chromatographic separations. Each of these column strategies is briefly described in the following.

### Ion Exchange

In ion exchange column chromatography the column is packed with either a cation exchanger, which will exchange cations, or an anion exchanger, which will exchange anions. The exchangers are like insoluble electrolytes and exchange ions rapidly, reversibly and stoichiometrically. Cation exchange is represented in eqn [4] while eqn [5] illustrates anion exchange.

$$R^-C^+ + M^+ = R^-M^+ + C^+ \quad [4]$$

$$R^+A^- + X^- = R^+X^- + A^- \quad [5]$$

Here R is the ion exchanger matrix containing either an anionic or cationic ionogenic group, $C^+$ and $A^-$ are co-cation and co-anion, respectively, and $M^+$ and $X^-$ are the analyte cation and anion, respectively. The direction of the equilibrium in eqns [4] and [5] is determined by the selectivity coefficient for the exchanger towards the two competing ions. Thus, in the absence of mass action effects the exchanger will prefer the ion with the highest selectivity coefficient. For a mixture of analytes, for example a mixture of metal ions and a cation exchanger, the metal ion with the smallest selectivity coefficient would elute first and the metal ion with the largest selectivity coefficient would elute last when using a mobile phase containing an electrolyte that provides a cation of appropriate selectivity and concentration. To increase elution of the metal ion the electrolyte concentration in the mobile phase is increased, or a different electrolyte that provides a cation of higher selectivity is used.

While low efficiency metal ion separations are possible on cation exchangers, resolution is improved considerably when a ligand is included in the mobile phase and the separation occurs because of the properties of the metal complex. For example, elution of $M^+$ from the cation exchanger is enhanced with a mobile phase containing the ligand, HL, because of the formation of metal ion–ligand complexes. As shown in eqn [4], $M^+$ is retained on the cation exchanger through competition with the mobile phase cation $C^+$. When the ligand is in the mobile phase, the ligand will form a complex with the metal ion, causing the equilibrium in eqn [4] to shift to the left with the formation of the metal ion–ligand complex. The overall effect of the ligand can be represented by eqn [6]:

$$R^-M^+ + 2HL + C^+ = R^-C^+ + ML_2^- + 2H^+ \quad [6]$$

From eqn [6] the best mobile phase ligand, assuming formation constants and solubility are favourable, will be one that forms anionic complexes with the metal ion.

On the other hand, if the metal ion–ligand complex that forms is anionic, the complex can be retained by an anion exchanger, or

$$M^+ + 2HL = ML_2^- + 2H^+ \quad [7]$$

$$R^+C^- + ML_2^- = R^+ML_2^- + C^- \quad [8]$$

In this case the metal ion is subsequently removed from the anion exchanger by reversing the equilibrium in eqn [7], which is done by reducing the concentration of the ligand in the mobile phase. This causes the equilibrium in eqn [8] to shift to the left, thus removing the metal ion from the anion exchanger.

## Low Efficiency Ion Exchange Separation of Metal Ions

In the 1940s ion exchange was recognized as an excellent strategy for the separation of metal ions. The advantages of including ligands in the mobile phase were soon realized and many different types of inorganic and organic ligands were evaluated to aid metal ion separations. Chloride ion was one inorganic ligand that was studied extensively. Many metal ions complex with $Cl^-$ stepwise and the equilibria describing the stepwise formation of metal ion–chloride complexes are summarized by eqn [9]:

$$M^{2+} + nCl^- = MCl^-, MCl_2, MCl_3^-, MCl_n^{2-n} \quad [9]$$

where the complexes that are present depend on the formation constants for the individual steps, the coordination number of the metal ion, and the $Cl^-$ concentration. Depending on these factors, the metal analyte may be a cation, a neutral species or an anion. Thus, the charge of the metal-containing species may not only be altered but actually reversed and separation of the metals can become one of cations from anions.

Separation of metal ions is possible on either a strong acid cation exchanger or a strong base anion exchanger using a HCl mobile phase. With the cation exchanger increasing the HCl concentration shifts the equilibria represented by eqn [9] to the right, thus causing the metal analytes to elute from the cation exchange column as the metal chloro complexes (see eqns [4] and [6]). Those metals that form chloro complexes more readily (more favourable formation constants) will elute first.

The better resolution for metal ion separations is actually obtained when using a strong base type anion exchanger with $Cl^-$ as the mobile phase ligand. For the separation on an anion exchanger the mixture of metal ions is placed on the anion exchanger from a concentrated HCl solution. This converts the metal ions into chloro complexes (see eqn [9]) and these complexes are retained by the anion exchanger. The HCl concentration is then progressively reduced, the equilibria in eqn [9] shifts to the left, and the metal ions are removed from the column (see eqns [7] and [8]). In this case the more stable metal chloro complexes stay on the anion exchanger the longest and the least stable metal chloro complexes come off the earliest.

The retention of all the metal ions, some at several oxidation states, was determined on a strong base anion exchanger as a function of HCl concentration from $< 0.001\ \mathrm{mol\ L^{-1}}$ to $12\ \mathrm{mol\ L^{-1}}$ HCl. These data allow one to predict elution order and conditions for the separation. **Table 1** summarizes some of these results by listing the elution order for several metal ions on the anion exchanger from $12\ \mathrm{mol\ L^{-1}}$ HCl to dilute HCl. As HCl concentration in Table 1 is reduced, those metal ions above the HCl concentration listed are eluted while those below are retained on the exchanger. Many metal ion separations, including complex mixtures, are possible with the HCl eluent. **Figure 1** shows the separation of the transition elements on a strong base anion exchanger by a successive decrease in mobile phase HCl concentration. The column was 26 cm × 0.29 $\mathrm{cm^2}$ and about 6 mg of each cation was separated. Each metal ion was collected and its quantity was determined by chemical or instrumental methodology. $Mn^{2+}$ was determined spectrographically, $Fe^{3+}$ and $Zn^{2+}$ were radioactive tracers and were determined by radioactivity, and $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ were determined spectrophotometrically.

**Table 1** Elution order for common metal ions on a strong base anion exchanger with an HCl mobile phase

| *Mobile phase HCl concentration* (*mol L* $^{-1}$) | *Metal ion* |
|---|---|
| 12 | Not retained: $Ni^{2+}$, $Al^{3+}$, lanthanoids, $Th^{4+}$ Slight retention: $Sc^{3+}$, $As^{5+}$, $Cr^{3+}$, $Mn^{2+}$ |
| 9.5 | $Ti^{4+}$ |
| 8 | $Hf^{4+}$ |
| 7.5 | $Zr^{4+}$ |
| 7 | $Fe^{2+}$ |
| 6 | $U^{4+}$ |
| 4.5 | $Co^{2+}$, $As^{3+}$ |
| 3 | $Cu^{2+}$ |
| 1 | $UO_2^{2+}$, $Fe^{3+}$ |
| 0.02 | $Zn^{2+}$ |
| 0.001 | $Cd^{2+}$ |

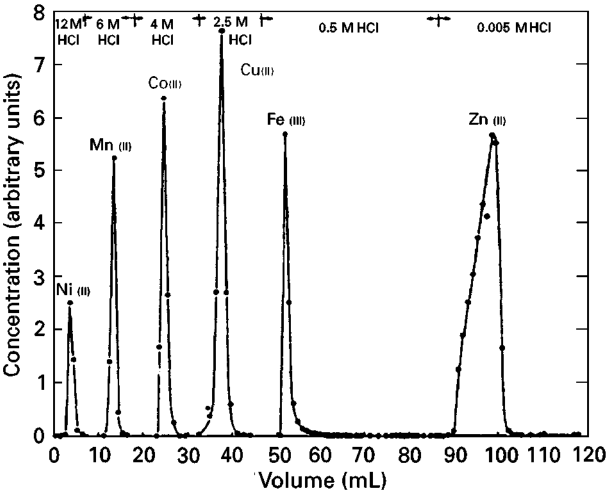

**Figure 1** Separation of transition elements on a strong base anion exchanger from an HCl mobile phase. M = $\mathrm{mol\ L^{-1}}$. (Reproduced from Kraus and Moore, 1953. Reprinted by permission of American Chemical Society.)

Success with chloride ion as the eluent ligand led to studies with many other inorganic ligands. Like $Cl^-$, $F^-$ is also an important mobile phase ligand and was employed in a mobile phase that was $1\ \mathrm{mol\ L^{-1}}$ HF as a function of HCl concentration. The presence of the $F^-$ is particularly useful because it forms complexes with Group IV and V elements such as $Zr^{4+}$, $Hf^{4+}$, $Nb^{5+}$ and $Ta^{5+}$ and aids their separation. Other inorganic ligands have also been shown to be useful but typically do not have the broad scope of applications characteristic of the HCl and HCl/HF elution systems. These ligands include $NO_3^-$, $SO_4^{2-}$, $Br^-$, $I^-$, $SCN^-$, $CO_3^-$ and $CN^-$. While the analytical applications of these ligands may be limited, several have been shown to be particularly useful in commercial recovery and purification applications, for example the isolation of uranium and thorium from low grade ores. **Figure 2** illustrates an elution diagram that was used for the separation of a multicomponent high temperature alloy on a strong base anion exchanger using a combination of the HCl and HCl/HF elution scheme. Note that the column dimensions and sample size of 1 g are large and by today's standards this would be called a prep column and separation. Because each metal analyte was separated in such a large quantity each metal ion was determined by chemical methodology, namely by ethylenediaminetetraacetic acid (EDTA) titration or by gravimetry.

Organic ligands have been used in eluents to improve resolution in low efficiency ion exchange metal ion separations. Iminodiacetic acid, nitrilotriacetic acid and EDTA are examples of mobile phase ligands that have been used that form very stable complexes with many metal ions, while citric

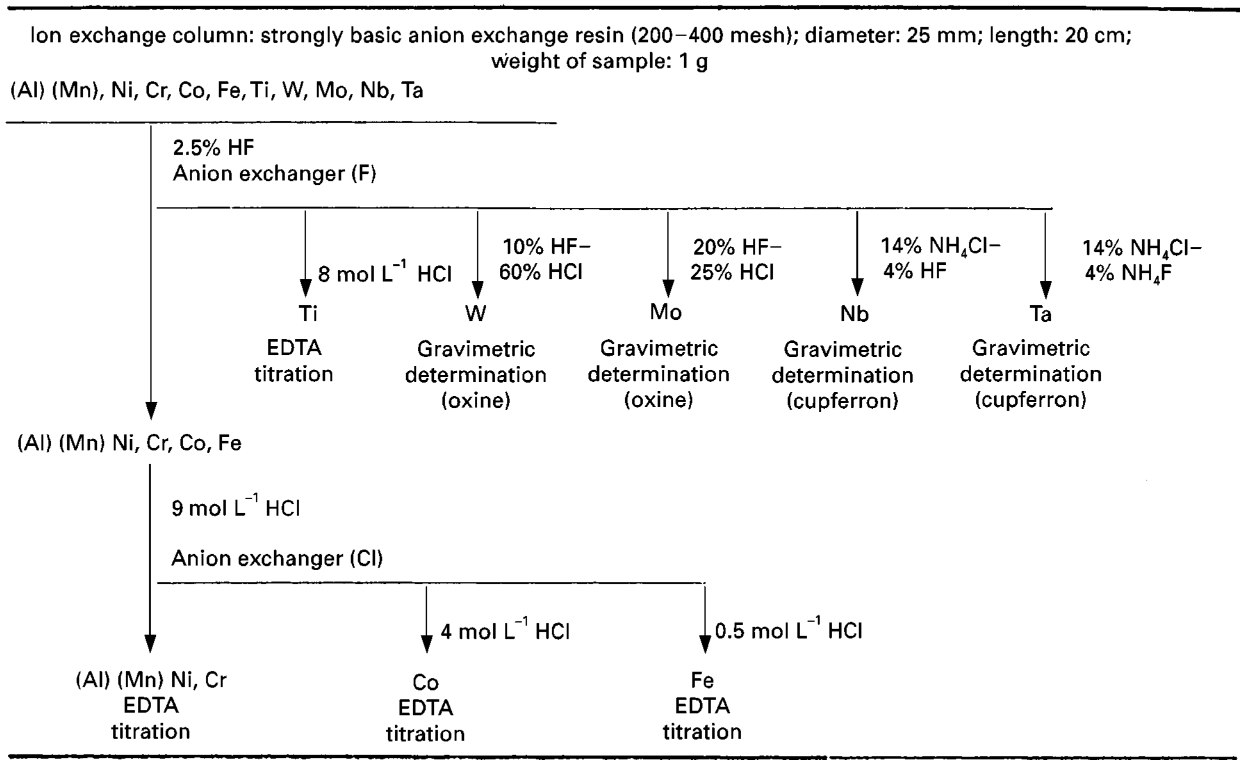

**Figure 2** A flow diagram for the separation of a high temperature alloy on a strong base anion exchanger. The anion exchanger is a 40–75 μm, 2.5 cm × 20 cm strong base anion exchange column and the sample size is about 1 g. (Reproduced from Wilkins, 1959. Reprinted by permission of Pergamon Press Ltd.)

acid, tartaric acid, malonic acid, oxalic acid, diglycolic acid and α-hydroxyisobutyric acid (HIBA) are examples of useful ligands that form metal ligand complexes of modest stability. In addition to formation constants, pH is also an important mobile phase variable that can be optimized to enhance resolution because all of these ligands are weak acids. Another mobile phase parameter that can be altered to influence elution is to use a mixed solvent for the mobile phase. The presence of the organic solvent in the mixture has a pronounced effect on the formation constants for the complexes as well as the exchange equilibrium with the exchanger. The type of organic solvent and its concentration then become variables in influencing elution time and resolution.

The unique complexing properties of organic ligands have been used to isolate and concentrate metals from ores and other geological samples. For example, one of the more successful applications of this kind was the isolation and separation of the lanthanoids on cation exchangers from mobile phases containing an organic ligand. Prior to this development individually pure lanthanoids were not readily available. Similar success was subsequently achieved in the isolation and purification of uranium and other actinoids, hafnium and zirconium, and many other less familiar metals from natural occurring ores and minerals.

Table 2 lists several elution conditions that have been used for the low efficiency separation of lanthanoids on anion or cation exchangers using a ligand in the mobile phase. The separation of the lanthanoids on a strong acid cation exchanger with lactate as the mobile phase ligand and a small pH increase during the elution is shown in **Figure 3**. Each lanthanoid was collected in a series of fractions and the lanthanoid in each fraction was determined spectrophotometrically by complex formation with 1-(2-pyridylazo)-2-naphthol (PAN). The pH and the formation constants for the lactate complexes determine the elution order. When HIBA is used as the ligand instead of lactate, the same elution order is obtained for the lanthanoids. In another example cation exchange was used to separate 35 metal ions into six separate groups by using mobile phase ligands citric acid, *N*-hydroxyethyl(ethylenedinitrilo)triacetic acid, EDTA, HCl and pH control in a predetermined elution programme.

## Ligands in the Separation of Metal Ions by Partition Chromatography

Column liquid–liquid partition chromatography of metal ions can be one of two types. In one case the stationary phase is a nonaqueous immiscible solvent

**Table 2** Mobile phase ligand conditions used for the separation of the lanthanoids on anion and cation exchangers

| *Mobile phase conditions* | *Exchanger* | *Application* |
|---|---|---|
| HIBA at pH = 5.2 | Cation | Early lanthanoids |
| HIBA at pH = 4.7 | Cation | Lanthanoid radionuclides |
| HIBA, pH gradient from 3.4 to 4.0 | Cation | Lanthanoids and fission products |
| 0.24 mol $L^{-1}$ lactate at 87°C | Cation | Lanthanoids |
| 1.1–1.25 mol $L^{-1}$ lactate and 3.1 to 3.25 pH gradient at 87°C | Cation | Lanthanoids |
| Ammonium lactate gradient at pH 5 and 95°C | Cation | Radiochemical separation of lanthanoids from fission products |
| 26 mmol $L^{-1}$ EDTA at pH 3.62 and 87°C | Cation | Ce, Pr, Nd, Sm, La |
| 5–6 mol $L^{-1}$ $HNO_3$ | Anion | La, Ce, Pr group separation |
| EDTA | Anion | Lanthanoids |
| Citrate | Anion | Lanthanoids |

held up by an inert support and the mobile phase is usually an aqueous solution containing elecrolyte, buffer, and a ligand. This type of column chromatography is called liquid–liquid reversed-phase partition chromatography (RPPC). The other strategy is the opposite – the stationary phase liquid is a polar or aqueous solvent held up by the inert support and the mobile phase is an immiscible organic solvent or solvent mixture of less polarity. In both cases the additives cause the metal ions to distribute between the two phases as the metal ions pass through the column. Separation occurs because of differences in the equilibrium positions imposed by the additives, namely the ligand, the resulting formation constants, the pH, and the properties of the two solvents that make up the two phases.

These techniques, which may also be carried out with solvent combinations that are partially miscible suffer from gradual changes in the stationary phase liquid over prolonged column use. This means it is difficult to maintain or reproduce a uniform, constant stationary liquid phase, sometimes even in a single elution run and often over repeated runs. Even solvents that are thought to be completely immiscible will have a low level equilibrium distribution of one solvent into the other when they are brought together. Thus, the stationary liquid phase will be slowly removed (solvent bleed) from the inert support.

Because of solvent bleeding high efficiency liquid–liquid partition chromatography is rarely used and as a separation strategy it has been replaced by high efficiency reversed-phase and normal-phase column chromatography. Nevertheless, many difficult separations of metal ion mixtures are possible by RPPC and RPPC can be readily applied to cases where the chromatographer needs to separate large quantities of metal ions and is not faced with requirements of short analysis times, the best detection limits, and/or regulatory method controls. Several examples of RPPC described below illustrate the scope of using ligands in RPPC separations of metal ions.

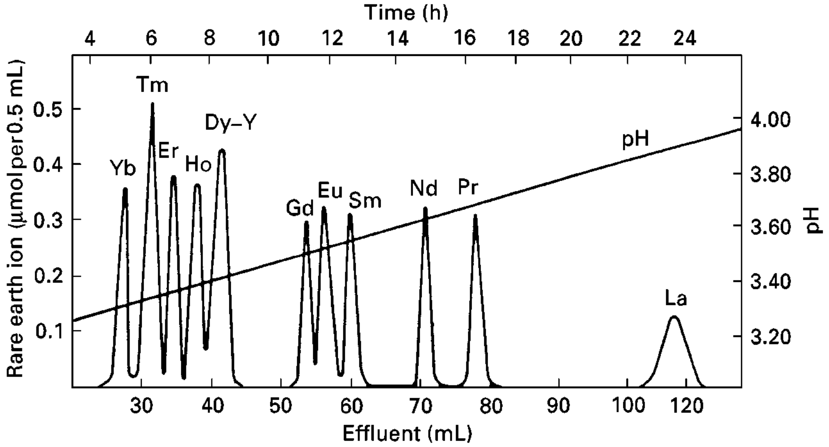

**Figure 3** Separation of the lanthanoids on a strong acid cation exchanger. The cation exchanger column is a 40–75 μm, 0.5 cm × 100 cm column at 80°C and the mobile phase is a lactate buffer solution and pH gradient at about 0.7 mL $min^{-1}$. (Reproduced from Inczédy, 1966, p. 166. Reprinted by permission of Pergamon Press Ltd.)

**Table 3** Selected applications of porous organic copolymers as support materials for the partition chromatographic separation of metal ions[a]

| *Metals* | *Porous polymer* | *Extraction system* |
|---|---|---|
| 27 metal ions | XAD-2 | Isopropyl ether/HCl<br>Isobutylmethyl ketone/HCl<br>Trioctylphosphine oxide/HCl |
| Ga, In, Th | XAD-2 | Isobutylmethyl ketone/HBr |
| $U^{6+}$ | XAD-2 | Dioctyl sulfoxide/1,2-dichloroethane |
| $Mo^{6+}$, $W^{6+}$, $V^{6+}$ | XAD-2 | Aliquat 336 liquid anion exchanger/ toluene/$H_2SO_4$ |
| Cu | XAD-2 | Aliphatic $\alpha$-hydroxyoxime/toluene |
| $Mo^{6+}$ | XAD-2 | 5,8-Diethyl-7-hydroxydecane-6-one oxine/toluene |
| Au | XAD-2 | HCl/$H_2O$ |
| Fe, Cu | XAD-7 | Kelex 100/$H_2O$ |
| Zn, Cd, Hg | Macroporous polystyrene–divinylbenzene | Dithiozone/dibutyl phthalate |
| Ni, Fe, Co | Ethylstyrene–divinylbenzene | Monothiobenzoylmethane/heptane |

[a] Reproduced from Pietrzyk, 1989, p. 144. Reprinted by permission of Wiley-Interscience.

RPPC shares many features with solvent extraction and a wealth of information is available in the literature on the solvent extraction of metal–ligand complexes from one phase to another. In most cases a successful extraction depends on the properties of the complex that forms between the ligand and the metal ion. Complex formation constants, metal coordination, solubility of the ligand in the aqueous phase and the nonaqueous phase, solubility of the complex in each of the two phases, and pH are the main factors that determine the percent extraction and the selectivity in the extraction, and consequently the ability to resolve one metal ion from another. These same factors influence metal ion resolution in RPPC and must be optimized to obtain a successful separation.

Two of the more successful inert stationary phases for RPPC are polystyrene–divinylbenzene and acrylic acid-based macroporous copolymers. These are capable of holding up appreciable quantities of nonpolar organic solvents, many of which are desirable for partitioning procedures. **Table 3** lists several RPPC quantitative metal ion separations that have been carried out where an inorganic or organic ligand is employed in the two-phase system to complex metal ions and bring about resolution on either the styrene or acrylic acid-type copolymers as the inert stationary phase.

## Chelating Ion Exchanger

Instead of adding a ligand to the mobile phase, a chelating group can be chemically bound to a solid, inert matrix. In this case coordination occurs between the metal ion and the bound chelating group. Resolution is possible because of differences in formation constants for the differential metal complexes that form with the stationary phase-bound chelating group, the mobile phase pH, and the ionic strength. Employing a second chelating group or ligand in the mobile phase to establish a competition between the bound chelating group and the mobile phase ligand towards the metal ion analytes is also an excellent elution procedure to effect resolution of the metal ion mixture.

Chelating ion exchangers often have several disadvantages, even though metal ion retention can be high and selectivity can be favourable. First, the kinetics for the exchange or dissociation of the metal ion from the chelating group bound to the stationary phase can be slow, and this causes poor elution behaviour. Second, few chelating ion exchangers are commercially available. One notable exception is a chelating ion exchanger that has the iminodiacetic acid group, $-CH_2N(CH_2CO_2H)_2$, attached to a polystyrene–divinylbenzene copolymer. And third, because most chelating ion exchangers have to be synthesized in the laboratory, reproducibility from column to column is only fair. Furthermore, column efficiency in analytical separations is rarely exceptional because the kinetics are usually not favourable.

The major advantage of a chelating ion exchanger, which is very important to environmental and ultratrace metal analysis, is that the exchanger can be used to isolate trace levels of metal ions from samples and/or to concentrate the trace metal ions prior to their determination. This has been proven to be particularly valuable for the isolation/concentration of metal ions other than the Group I metal ions, particularly transition metal ions, the lanthanoids and the actinoids. Often this can be done from solutions that may contain substantial quantities of

**Table 4** Chelating ion exchangers

| *Chelating group* | *Chelating group* |
|---|---|
| Anthranilic acid | *N*-substituted hydroxylamine |
| Arsonic acid | 8-Hydroxyquinoline |
| Crown ether | Iminodiacetic acid |
| *β*-Diketone | Isothiuronium |
| Dimethylglyoxime | Nitrilotriacetic acid |
| Dithiocarbamate | Rescorinol |
| Dithioizone | Salicylic acid |
| Ethylenediaminetetraacetic acid | Thioglycolate |
| Hydroxyamic acid | |

monovalent electrolyte, for example brine solution, boiler water and sea water. **Table 4** lists several chelating ion exchangers that have been synthesized in the laboratory and some typical applications of these chelating ion exchangers.

## High Efficiency Column Chromatographic Separation of Metal Ions and the Influence of Ligands on their Resolution

The analytical chemistry and role of the ligand in high efficiency or high performance liquid column chromatographic (HPLC) separations of metal ions is much the same as in low efficiency liquid column chromatographic separations. Mobile phase concentration of reagents including the ligand and metal ion analyte concentration are much lower due to more favourable chromatographic properties of high efficiency columns. Selectivity, retention, and particularly detection limits are improved. Formation constants, stepwise equilibria, coordination number, and formation of positive, anionic or neutral complexes are still crucial factors that influence separation. In addition, the rate of complex formation and dissociation is a major contributing factor because of the significant increase in linear velocity of the analyte in the high efficiency column.

Cation exchangers, anion exchangers, chelating exchangers, and reversed stationary phases are the major column stationary phases that are employed in high efficiency metal ion analyte separations. These modern, high efficiency stationary phase particles are available as small (5 and 10 μm), uniform, and spherical-sized particles of considerable physical strength that can be packed uniformly and reproducibly into columns to yield very favourable mass transfer, and thus high efficiency. All of these are properties that the column must possess in order to exhibit high efficiency. Columns that satisfy these criteria are commercially available. Examples illustrating the scope of modern applications of ligands to improve the resolution in the separation of metal ions on high efficiency columns of cation and anion exchangers, reversed stationary phases and chelating exchangers are outlined in the following sections.

### High Efficiency Cation Exchangers

Metal ions, particularly multivalent cations, are highly retained on high efficiency strong acid-type cation exchangers, even though exchange capacities may be very low. One approach to elute metal ions, particularly multivalent cations, from the cation exchanger is to use a mobile phase cation derived from ethylenediamine, $H_2NCH_2CH_2NH_2$, (En). In an acidic solution En, which is basic, will exist as the dication, $^+H_3NCH_2CH_2NH_3^+$ ($H_2En^{2+}$), providing the pH is low enough. Thus, the eluent strength of the mobile phase is determined by the mobile phase $H_2En^{2+}$ concentration and metal ion analyte elution on a typical high efficient cation exchanger follows ordinary cation exchange. A second approach is to use a ligand in the mobile phase. A successful ligand is one that will form neutral or anionic complexes with the analyte metal ions that are stable (formation constants will influence elution order) and form and dissociate rapidly. It should be noted that although En is a ligand for many multivalent cations, in the diprotonated form its complexing ability is sharply reduced. When a ligand, for example citric acid, which forms complexes with metal ions, is included in the buffered mobile phase along with the $H_2En^{2+}$, resolution now depends on pH. This influences dissociation of citric acid (and also the eluent cation $H_2En^{2+}$ and its potential complexing ability), the formation constants for the metal ion citrate complexes (and metal ion En complexes if they form), and the concentration of the citric acid ligand. The more stable the metal ion citrate complex and the higher the concentration of the citrate, the more quickly the metal ions are eluted. **Figure 4** illustrates the high efficiency separation of several divalent metal ions on a strong acid high efficient cation exchanger using the combined effect of citrate as the ligand and $H_2En^{2+}$ as a divalent mobile phase cation. A similar separation is possible using tartrate or oxalate rather than citrate as the mobile phase ligand.

Because complex formation constants differ, small differences in selectivity and elution order are obtained when the elution behaviour of citrate, tartrate and oxalate as ligands are compared. Consequently, metal ion elution order and selectivity for given metal ions, for example for transition metals, can be changed through the selection of the ligand.

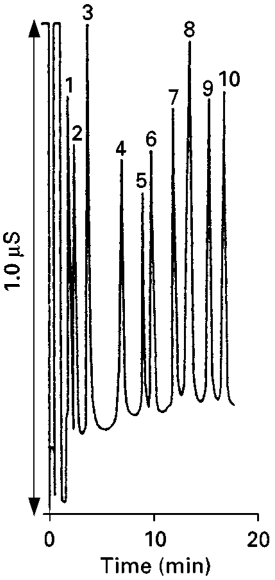

**Figure 4** Separation of alkali, alkaline earth, and transition element metal ions on a cation exchanger. The column is a TSK IC cation SW column and the mobile phase is 3.5 mmol $L^{-1}$ $H_2EN^{2+}$, 10 mmol $L^{-1}$ citric acid, pH 2.8, at a flow rate of 1.0 mL $min^{-1}$ with conductivity detection. Peaks are: 1, $Na^+$; 2, $K^+$; 3, $Cu^{2+}$; 4, $Ni^{2+}$; 5, $Co^{2+}$; 6, $Zn^{2+}$; 7, $Fe^{3+}$; 8, $Mn^{2+}$; 9, $Cd^{2+}$; 10, $Ca^{2+}$. (Reproduced from Timberbaev and Bonn (1993). Reprinted by permission of Elsevier Science Publishing.)

Figure 5 illustrates the separation of several transition metals using a mobile phase that contains both oxalate and citrate as ligands and gives an elution order slightly different from the order obtained in Figure 4. Metal ion complex formation is also very important in detection in high efficiency ion exchange separations of metal ions. In Figure 5 the metal ions are converted into complexes postcolumn online by reaction of the metal ion with 4-(2-pyridylazo)resorcinol (PAR) and the complex is detected by absorbance at 520 nm.

HIBA at pH 4.6 is a good ligand to use to separate lanthanoids on a cation exchanger. This separation is shown in **Figure 6**, where a gradient of 0.018–0.070 mol $L^{-1}$ HIBA is used for the elution of the lanthanoids on a Nucleosil SCX column, a sulfonated bonded phase-type cation exchanger. In Figure 6 detection was by a postcolumn reaction, which produces the highly coloured complex between the ligand, 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid trisodium salt (Arsenazo 1) and each of the lanthanoids as they are separated. If $H_2En^{2+}$ is also included in the mobile phase with HIBA, separation of the first seven lanthanoids is obtained without employing an HIBA mobile phase gradient.

The properties of the cation exchanger used in the column will also influence the selectivity, even causing a reversal. For example, Figure 5 is a separation on a surface-sulfonated cation exchanger, while the cation exchanger used in Figure 4 is a surface/interior-sulfonated cation exchanger.

The latex-based exchanger affects elution order when ligands are used in the mobile phase because of the exchanger's composition. The latex-based cation exchanger, which is commercially available from the Dionex Corporation, for example Ion Pac CS5, is composed of a surface-sulfonated substrate as its central core, uniformly coated with a thin layer of aminated latex particles. This basic surface is then coated by a thin, uniform layer of sulfonated latex particles. The cation exchanger groups ($-SO_3H$) are on the surface while the aminated or anion exchange groups ($-NR_4^+$) are in the interior

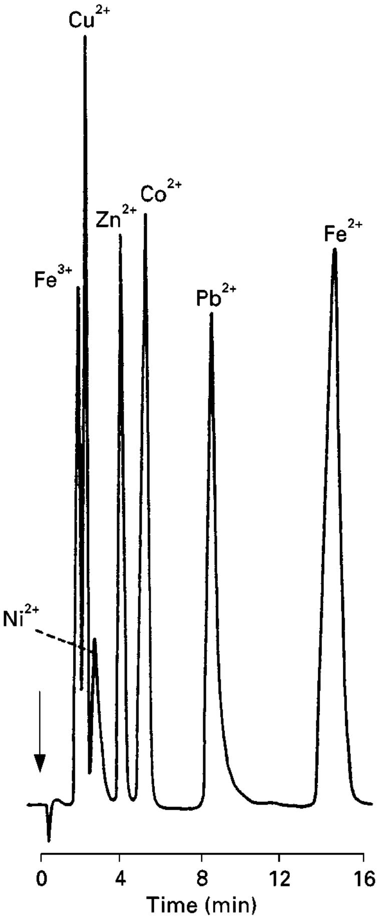

**Figure 5** Separation of the transition element metal ions on a surface-sulfonated cation exchanger. The column is an Ion Pac CS2 column and the mobile phase is 0.01 mol $L^{-1}$ oxalic acid, 0.0075 mol $L^{-1}$ citric acid, pH 4.2, at a flow rate of 1.0 mL $min^{-1}$. Detection is postcolumn absorbance at 520 nm after reaction with PAR. Sample injection is 50 µL containing 5 ppm $Fe^{3+}$, 0.5 ppm $Cu^{2+}$, 0.5 ppm $Ni^{2+}$, 0.5 ppm $Zn^{2+}$, 1 ppm $Co^{2+}$, 10 ppm $Pb^{2+}$, and 5 ppm $Fe^{2+}$. (Reproduced from Weiss, 1995, p. 197. Reprinted by permission of VCH Publishers.)

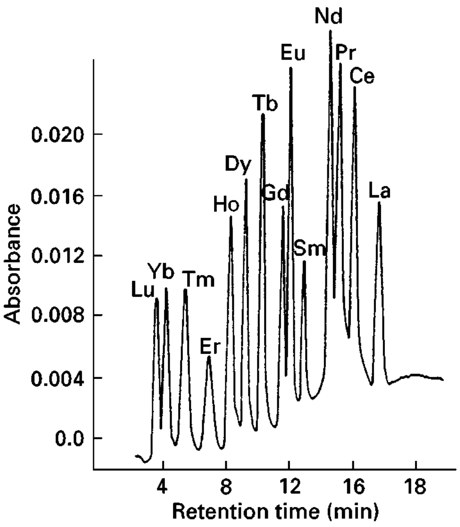

**Figure 6** Separation of the lanthanoids on a sulfonated silica-bonded phase cation exchanger. The column is a 10 μm, 0.4 cm × 10 cm, Nucleosil 10 SA column and the mobile phase is a linear gradient of 0.018 mol $L^{-1}$ to 0.070 mol $L^{-1}$ HIBA at pH 4.6. Sample injection is 10 μL containing about 10 μg $mL^{-1}$ of each lanthanoid. (Reproduced from Elchuk and Cassidy, 1979. Reprinted by permission of American Chemical Society.)

of the particle. Thus, the observed elution for metal ions on the Ion Pac CS5 will be influenced by both cation and anion exchange and the equilibria that favour cationic or anionic metal–complex formation. For example, the transition metal elution order in **Figure** 7 on the Ion Pac CS5 column with oxalate as a mobile phase ligand is quite different from the order found in either Figure 4 or 5 and is due to retention of anionic oxalate complexes that form between several of the transition metal ions and oxalate. When the Ion Pac CS5 column is used with a mobile phase containing pyridine-2,6-dicarboxylic acid (PDCA) as the ligand at pH 4.8, the elution order that is obtained is similar to that obtained by the sulfonated, nonlatex-type cation exchangers used in Figures 4 and 5.

### High Efficiency Anion Exchangers

Some ligands will form very stable complexes with metal ions that are also anionic. It is often possible in these cases to separate the anionic metal–ligand complexes on high efficiency anion exchangers. For example, transition metal–PAR complexes are anionic and these complexes can be separated at high efficiency. Since the complexes are also highly coloured, detection of the separation is readily done at favourable detection limits by absorption. In another example the anionic complexes that form between multivalent cations and EDTA are anionic at the appropriate pH and can also be separated on anion exchangers using an $HCO_3^-/CO_3^{2-}$ mobile phase that is common to ordinary ion chromatographic separation of anionic analytes. The basic requirement of the formation of a very stable anionic complex between the metal ion and the ligand is often a limiting factor and for this reason separation of metal ions in the presence of a ligand on a high efficiency cation exchanger is often a more versatile separation strategy.

The latex-based cation exchanger that possesses both cation and anion exchanger properties, such as the Ion Pac CS5, however, does provide a way to separate metal ion mixtures in the presence of mixed ligands where both cation and anion exchange are involved. This is illustrated in **Figure** 8, where both transition metals and lanthanoids are separated in one run on the high efficiency Ion Pac CS5 column using a complex gradient at the appropriate pH where the concentration of the ligands oxalic acid, diglycolic aci?d and PDCA are varied as a function of elution time. The PDCA causes the elution of the transition metals to be similar to that found on the

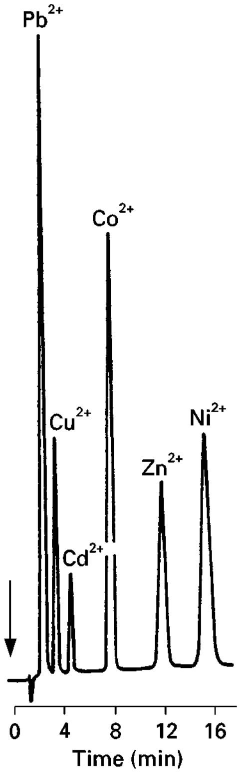

**Figure 7** Separation of several transition element metal ions with oxalic acid as the mobile phase ligand. An Ion Pac CS5 column and a 0.5 mol $L^{-1}$ oxalic acid, pH 4.8, mobile phase at 1 mL $min^{-1}$ was used. Injection volume was 50 μL and contained 4 ppm $Pb^{2+}$, 0.5 ppm $Cu^{2+}$, 4 ppm $Cd^{2+}$, 2 ppm $Co^{2+}$, 2 ppm $Zn^{2+}$, 4 ppm $Ni^{2+}$. (Reproduced from Weiss, 1995, p. 199. Reprinted by permission of VCH Publishers.)

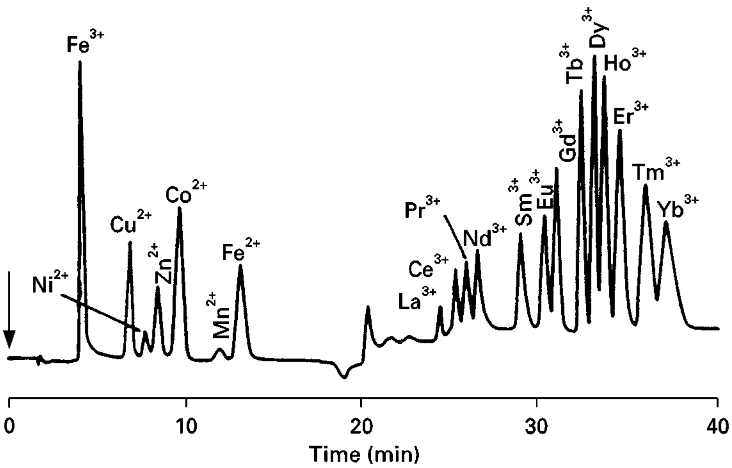

**Figure 8** Separation of the transition elements and lanthanoid metal ions using a three-ligand mobile phase. An Ion Pac CS5 column and a mobile phase gradient of PDCA, oxalic acid, diglycolic acid, and LiOH for pH adjustment at 1 mL min$^{-1}$ was used. Injection volume was 50 μL and contained 2 ppm $Fe^{3+}$, 1 ppm $Cu^{2+}$, 3 ppm $Ni^{2+}$, 4 ppm $Zn^{2+}$, 2 ppm $Co^{2+}$, 1 ppm $Mn^{2+}$, 3 ppm $Fe^{2+}$, 7 ppm of each lanthanoid. (Reproduced from Weiss, 1995, p. 205. Reprinted by permission from VCH Publishers.)

sulfonated cation exchanger (see Figure 5), while the lanthanoids remain on the column as trivalent anions. In the later stages of the gradient oxalic acid and diglycolic acid become more significant in concentration and cause the lanthanoids to be eluted in reverse order to that obtained by the high efficiency cation exchange separation of the lanthanoids (see Figure 6). If only the lanthanoids are to be separated, they can be separated in the order shown in Figure 8 on the Ion Pac CS5 column in about 25 min with the oxalic acid/diglycolic acid gradient. Detection is also made possible by the formation of metal complexes. In this example effluent from the column is combined with PAR to give the highly coloured metal ion–PAR complexes, which are readily detected by absorbance at 520 nm.

## Reversed Phase

Separation of metal ions as anionic complexes on high efficiency reversed stationary phases, such as a $C_{18}$ bonded phase silica or a polystyrene–divinylbenzene copolymer, requires a mobile phase that must also include an ion interaction reagent, for example a quaternary ammonium salt ($R_4N^+C^-$) having lipophilic character. The metal ion–ligand anionic complex interacts with the $R_4N^+C^-$, which in turn interacts with the reversed stationary phase, A, as shown below:

$$A + R_4N^+C^- = A \cdots R_4N^+C^- \qquad [10]$$

$$A \cdots R_4N^+C^- + ML_2^- = A \cdots R_4N^+ML_2^- + C^- \qquad [11]$$

where $M^{2+}$ is the metal ion analyte and $ML_2^-$ represents the anionic metal–ligand complex. The direction of the equilibrium and subsequently the elution of the metal–ligand complex is controlled by the selection of the reversed stationary phase and the $R_4N^+C^-$ salt, the concentration of the $R_4N^+C^-$ salt, the counteranion $X^-$ and its concentration via inert electrolyte, pH, solvent composition, the ligand, and the ligand concentration. This chromatographic strategy, or ion interaction chromatography (IIC), is known by several different terms and has been the subject of many studies to establish the nature of the interactions between the analyte, mobile phase components and stationary phase that are present. Clearly, several equilibria are involved and the success of the separation strategy in analytical applications requires careful control of all the equilibria.

Transition metal–PAR complexes are anionic and separations of these anionic complexes are possible on a reversed stationary phase. Other ligands can be used; the most useful ones are ligands that form kinetically stable anionic complexes with very high formation constants. Often the complexes are highly coloured and/or fluoresce and these properties allow sensitive detection.

Inorganic ligands that form very stable anionic complexes with metal ions can be used in a mobile phase that also contains a $R_4N^+C^-$ salt to separate the metal ions as complexes on a reversed stationary phase. **Figure 9** illustrates the separation of transition metals as anionic cyanide complexes on a $C_{18}$ reversed stationary phase column using a $R_4N^+C^-$ (Waters PICA additive) mobile phase. Detection in this separation is by absorbance at 214 nm.

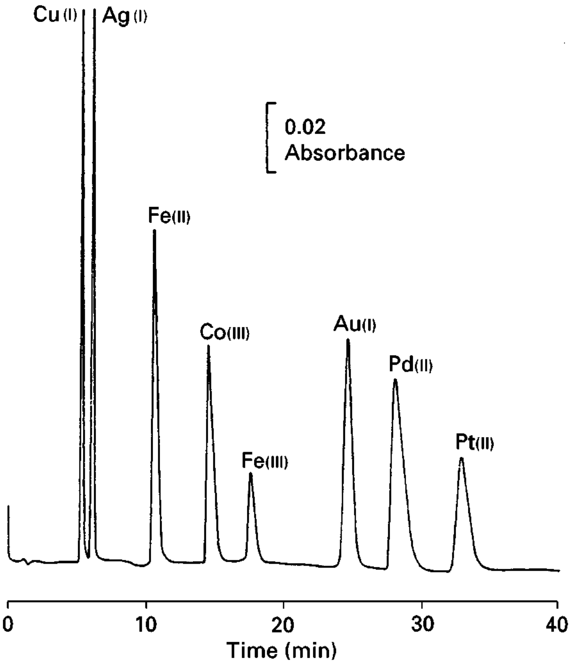

**Figure 9** Ion interaction chromatographic separation of metal ions as cyano complexes. A 5 μm, 0.39 cm × 15 cm, Waters Nova Pak $C_{18}$ column and an $H_2O/CH_3CN$ (23 : 77) 5 mmol $L^{-1}$ tetramethylammonium hydroxide mobile phase at 1.0 mL $min^{-1}$ was used. Sample injection was 10 μL and contained 0.15 μg $Cu^{1+}$, 1.5 μg $Ag^{1+}$, 0.02 μg $Fe^{2+}$, 0.2 μg $Co^{3+}$, 0.3 μg $Fe^{3+}$, 2.0 μg $Au^{1+}$, 0.4 μg $Pd^{2+}$, 0.2 μg $Pt^{2+}$ as cyano complexes. (Reproduced from Hilton and Haddad, 1986. Reprinted by permission from Elsevier Science Publishing.)

IIC with an anionic lipophilic reagent, such as an alkane sulfonic acid ($RSO_3^-H^+$), is also an important strategy for the high efficiency separation of metal ions. However, in this case the ligand in the mobile phase removes the metal ion from the reversed stationary phase according to the metal ion–ligand complex formation constants. The equilibria that are involved and which must be controlled for a successful separation are represented below (equilibria for complex formation are not shown – see eqns [1]–[3] where L is $CN^-$):

$$A + RSO_3^-H^+ = A \cdots RSO_3^-H^+ \qquad [12]$$

$$nA \cdots RSO_3^-H^+ + M^{n+} = (A \cdots RSO_3^-)_n M^{+n} + nH^+ \qquad [13]$$

$$(A \cdots RSO_3^-)_n M^{+n} + xL^{x-} + nH^+ = n(A \cdots RSO_3^-H^+) + ML_x^{+n-x} \qquad [14]$$

where A is the reversed stationary phase, $RSO_3^-H^+$ is the lipophilic ion interaction reagent, $M^{n+}$ is the metal analyte ion, and $L^{x-}$ is the mobile phase liquid.

Examples where this separation strategy has been successfully used are in the separation of transition metals or lanthanoids on a $C_{18}$ stationary phase and octanesulfonic acid as the IIC reagent in the buffered mobile phase. The former metal analytes are eluted with tartrate in the $RSO_3^-H^+$ mobile phase and the elution order is $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Ni^{2+}$ $Co^{2+}$, $Mn^{2+}$, which differs from the tartrate elution of these cations on the sulfonated cation exchange column and the latex-based exchanger (see Figures 4, 5 and 7). The lanthanoids are separated by including the ligand HIBA in the $RSO_3^-H^+$ mobile phase and the elution order is the same as that indicated in Figure 6.

## High Efficiency Chelating Exchangers

Few high efficiency chelating exchangers are commercially available. Even though various chelating groups have been chemically bonded to high efficiency silica or polystyrene–divinylbenzene copolymer particles, and metal ion retention is very high on these stationary phase particles, efficiencies generated on these columns are usually not comparable to efficiencies found for metal ion–ligand separations on ion exchangers or by reversed-phase ion interaction chromatography. In general, high efficiency is difficult to obtain, even when the core particle of the chelating exchanger meets high efficiency properties, because the complex between the metal ion and the bound chelating group often forms and dissociates slowly. Thus, metal ion analyte bands in elution can be broadened appreciably.

Using a ligand in the mobile phase to aid elution can sometimes reduce the analyte peak broadening. For example, the separation of transition metal ions on a high efficiency silica particle containing chemically bound iminodiacetic acid groups was achieved by using citrate, tartrate, nitrilotriacetic acid or PDCA in the buffered mobile phase. Since two complexing reactions are taking place, the metal ion elution order is dependent on the formation constant for the metal ion complex with the bound chelating group and with the mobile phase ligand in addition to pH. Other laboratory synthesized chelating exchangers where the chelating group (several of these are listed in Table 4) is bound to a high efficiency matrix, such as silica, have been evaluated for metal ion separations.

While metal ions can be separated on chelating ion exchangers, the more useful applications of chelating exchangers is still one of isolating and preconcentrating of metal ions from a complex sample matrix. Metal ions can be preconcentrated from biological samples, environmental samples and concentrated electrolyte solutions, such as seawater, brine and other industrial waters, and strong alkali solutions. It is possible to automate fully the preconcentration and separation/analysis procedure. In an example of this trace levels of $Mg^{2+}$, $Ca^{2+}$ and transition metals in biological and environmental samples are preconcentrated on two iminodiacetic acid-type chelating ion exchanger and one strong acid cation exchanger connected in series. The preconcentrated metal ions are then removed from the three columns and the concentrated metal ion mixture is separated on an analytical Ion Pac CS5 column by an elution programme that takes into account pH, ammonia/ammonium ion buffer concentration and PDCA concentration. Detection is by absorption after postcolumn reaction of the metal ions with PAR.

*See also:* **II/Chromatography: Liquid:** Mechanisms: Ion Chromatography. **Extraction:** Analytical Inorganic Extractions. **Ion Exchange:** Theory of Ion Exchange. **III/Ion Analysis:** Liquid Chromatography.

## Further Reading

Barkley DJ, Blanchette M, Cassidy RM and Elchuk S (1986) Dynamic chromatographic systems for the determination of rare earths and thorium in samples from uranium ore refining processes. *Analytical Chemistry* 58: 2222–2226.

Cagniant D (1992) *Complexation Chromatography*. New York: Dekker.

Elchuk S and Cassidy RM (1979) Separation of the lanthanides on high-efficiency bonded phases and conventional ion-exchange resins. *Analytical Chemistry* 5: 1434–1438.

Haddad PR and Jackson PE (1990) *Ion Chromatography Principles and Applications*, p. 232. Amsterdam: Elsevier.

Hilton DF and Haddad PR (1986) Determination of metal-cyano complexes by reversed phase ion-interaction high performance liquid chromatography and its application to the analysis of precious metals in gold processing solutions. *Journal of Chromatography* 361: 141–150.

Inczédy J (1966) *Analytical Applications of Ion Exchangers*. Oxford: Pergamon Press.

Kraus KA and Moore GE (1953) Anion exchange studies. VI. The divalent transition elements manganese to zinc in hydrochloric acid. *Journal of the American Chemical Society* 74: 1460–1462.

Pietrzyk DJ (1989) Macroporous polymers. In Brown PR and Hartwick RA (eds) *High Performance Liquid Chromatography*, p. 244, New York: Wiley-Interscience.

Siriraks A, Kingston HM and Riviello JM (1990) Chelation ion chromatography as a method for trace elemental analysis in complex environmental and biological samples. *Analytical Chemistry* 62: 1185–1193.

Timberbaev AR and Bonn GK (1993) Complexation in ion chromatography – an overview of developments and trends in metal analysis. *Journal of Chromatography* 640: 195–206.

Weiss J (1995) *Ion Chromatography*, 2nd edn, Weinheim: VCH.

Wilkins DH (1959) The separation and determination of nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium, and tantalum in a high temperature alloy by anion exchange. *Talanta* 2: 355–360.

# Use in Gas Separation

*See* **III / GAS SEPARATION BY METAL COMPLEXES: MEMBRANE SEPARATIONS**

# METAL MEMBRANES: MEMBRANE SEPARATIONS

**Y. S. Lin and R. E. Buxbaum**, University of Cincinnati, Cincinnati, OH, USA

## Introduction

The use of metal membranes for hydrogen separation was first demonstrated over a century ago. Graham discovered in 1866 that palladium absorbs a suprising