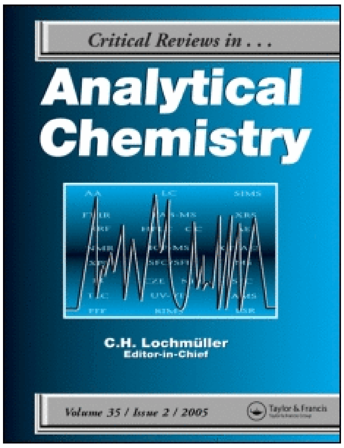

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The State of the Art of Ligand-Loaded Complexing Resins. Characteristics and Applications

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ABSTRACT: This review deals with the most recent investigations on the preparation, characterization, and metal sorption properties of ligand-loaded resins obtained by modification of conventional anion-exchange resins and nonionic sorbents with complexing organic reagents. These resins display a selectivity for metal ions that can be applied for the separation and/or preconcentration of metal ions off-line as well as in on-line techniques. In addition, the increasing application in recent years of new functional-modified resins in certain growing scientific areas, namely, electrochemistry, optical-fiber sensors, pharmaceuticals, biochemistry, etc., is discussed. Finally, the immobilization of chelating reagents in types of supports other than conventional resins is also considered.

KEY WORDS: ligand-loaded resins, complex-forming resins, modified resins, ion exchange, separation of metal ions, metal-ion preconcentration.

I. INTRODUCTION

In trace metal analysis, preliminary analytical procedures, such as preconcentration or selective and sensitive separation of the analyte before its determination, are frequently necessary in order to avoid interferences caused by the matrix. Among a number of preconcentration and separation techniques reported, methods using ion-exchange materials have proved to be very effective.

Many different natural and synthetic products exhibiting ion-exchange properties have been used.[1,2] However, the lack of selectivity of most of these ion exchangers has led to the development of ion-exchange materials containing functional groups that interact strongly with metal cations to form stable complexes.[2]

Many studies have been done on the separation of metal ions in solution using "chelating resins",[2–4] which are conventional resins possessing functional groups, such as iminodiacetate,[5] acid hydrazides, arsonic acids, etc.[1,2,6] chemically joined to an organic matrix. These resins can form chelates with metal ions and thus are potentially more selective than ordinary cation- and anion-exchange resins.[2,3,6,7].

Extensive investigations have been made of chelating resins prepared with selective chelating groups covalently attached to poly(styrene-divinylbenzene) copolymer matrices.[6–14] These resins can be synthesized by direct polymerization and copolymerization of monomers containing the functional groups of interest,[6,8,10,12] by chemical modification of the copolymer[6,9–11,13] (which commonly involves nitration of the copolymer, diazotization, and coupling of the desired ligand), or by procedures derived from both methods.[6,10]. Whichever method is used for their preparation, chelating resins from 8-hydroxyquinoline,[7–10] dithiazone,[11] and

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acetoacetanilide[13] have given good results in selective preconcentration and separation of metal ions. Moreover, an hydrophyllic organic resin gel containing 8-hydroxyquinoline functional groups also has been utilized for separation of trace metals.[15]

In spite of the higher selectivity of these chelating ion exchangers, the application of these resins in the field of analytical chemistry seems to be limited by the complexity of their synthesis, the very often difficult and time-consuming procedures needed for covalently linking the functional group to the skeleton of the resin, and their high cost.[16,17]

In the last decade, the development of new functional resins with chelating properties, prepared by simple immobilization of complexing organic reagents by ion exchange and/or adsorption onto conventional anion-exchange resins or nonpolar sorbents, has acquired great importance. These "ligand-immobilized resins" or "modified resins" can react with a large variety of metal ions by complex formation between the complexing agent and the metallic element. The stability of the resultant complexes differs and depends on the experimental conditions.[6] As a matter of fact, and as would be expected, the stronger the bond between the metal ion and the organic reagent, the more selective is the modified resin.[6]

The use of these modified resins with the aim of preconcentrating in trace metal analysis presents numerous advantages:

1. The active part, namely, the complexing ligand, can be varied easily and thus the same resin can be used for different analytical purposes by varying the type of organic reagent loaded.
2. By using an appropriate resin, a selective complexing ligand to be loaded, and the optimum experimental conditions, it is possible to obtain the desired selectivity with respect to a certain metal ion or a group of metal ions.[6,18]
3. The organic reagent, in general, can be displaced out of the resin and easily recovered.
4. More flexible working conditions are allowed.[16]
5. Good stability.[16]
6. High capacity for metal ions.[16]

The analytical literature provides, at present, an increasing number of works on trace metal preconcentration and separation by using ligand-loaded resins. Most of the highly selective nonconventional resins have been prepared by modifying common resins with the sulfoderivatives of aromatic complexing agents (SACA), which display selectivity for metal ions depending on the complexing ability of the complexing agent used for the modification (References 19 to 23, for example). In addition, a method involving incorporation of 2-ethylhexyl hydrogen 2-ethylhexylphosphonate,[24-26] 4-(2-pyridylazo)resorcinol (PAR),[27,28] 1-(2-pyridylazo)-2-naphthol (PAN),[29] thioglycolate,[30] etc., has also been reported.

Conventional resins as well as anion-exchange membranes have been modified, thus providing ligand-loaded membranes that can chelate metal ions.[31]

In analytical chemistry, ligand-immobilized resins are mainly used for selective preconcentration and separation of metal ions preceding the determination of these elements by different methods. Due to their high concentration efficiency and operational convenience, ligand-loaded resins have been used mainly as a technique for trace metal preconcentration and matrix isolation prior to metal-ion determination by atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), ultraviolet/visible (UV/vis) spectrometry, etc., or as an appropriate stationary phase in high-performance liquid chromatography (HPLC), in flow-injection systems (FI), and in ion-exchanger phase absorptiometry.

The literature on ligand-loaded resins studied from 1974 to 1984 was reviewed by Marina et al.[32] However, the number of investigations on this subject is increasing rapidly and, for this reason, a review of the most relevant literature published in the last nine years is considered useful.

This review deals with the mechanism of formation of ligand-immobilized resin, the types of conventional resins and complexing ligands employed, the physicochemical properties of these new functional resins, and their most important applications for preconcentration and/or separation of traces of metal ions. Finally, the more recent investigations on the application of modified resins to the determination of inorganic anions in electrochemistry, fiber-optic sensing techniques, biochemistry, clinical analyses, and the pharmaceutical–chemical industry have been reported.

II. COMPLEX-FORMING RESINS: CHARACTERISTICS, PROPERTIES, AND THEIR APPLICATION TO METAL-ION ANALYSIS

A. Modification of Ion Exchangers with Organic Reagents

A large number of chelate-forming resins have been prepared and employed for a great diversity of studies on preconcentration, separation, and/or analytical determination of chemical components present in solution. The nature of the two constituents of a ligand-modified ion-exchange resin, that is, polymeric substrate and organic reagent, is the criterion adopted to group the main scientific studies on this subject. Table 1 summarizes the most important analytical applications of complexing resins for metallic elements in aqueous solution. In this table, the kind of conventional resin used (nature, granulometry, and chemical form), the organic ligands incorporated to the substrate, methods for sorption of these reagents onto the resin, the metallic elements involved in the study, and the analytical applications derived from the use of the modified resin are specified. Table 2 presents an alphabetically arranged compilation of the organic reagents shown in Table 1, their systematic names, empirical formulas, and molecular weights.

As is shown in Table 1, a great variety of conventional resins have been used to prepare selective chelating ion exchangers. These resins are, as previously stated, synthetic organic ion exchangers consisting of a crosslinked hydrocarbon matrix that may carry basic functional groups in their polymeric matrix (anionic exchangers) or, on the other hand, may be non-ionic substrata.

All of the anionic resins that appear in Table 1 are addition polymers characterized by their monofunctionality, reproducible degree of crosslinking, and high chemical stability and mechanical strength.[1,6] The two most widely used crosslinked styrene anionic resins are made with trimethylamine and dimethylethanolamine, respectively, and contain the following basic functional groups:

$$-(CH_2)(CH_3)_3\,N^+$$

(a)

$$-(CH_2)(CH_3)_2(C_2H_4OH)\,N^+$$

(b)

Resins of type (a) are, for example, Amberlite IRA-400[23,39] and Dowex 1,[36–38] whereas the resin Dowex 2[16] is illustrative of the second type of strong-base resins.[1]

Nonionic synthetic organic resins also appear to be excellent supports for the preparation of chelating exchangers by deposition of certain ligands because they present good physical properties such as porosity, uniform pore size distribution, and a chemical homogeneous nonionic structure.[45]

For several applications, macroporous (macroreticular) ion-exchange resins, which have higher porosities, are needed. These substrata are characterized by spherical beads with wide pores of several hundred angström units; they guarantee the successful deposition of water-soluble organic chelating reagents.[1,29,41] Sometimes it is advantageous to use macroporous substrata instead of microporous resins, for example, for sorption of aromatic complexing agents of great size, because the use of macroreticular ion exchangers makes it possible to avoid the partial exclusion of large molecules by sieve action that might occur if a microporous exchanger were used.[32] In this way, anionic and nonionic macroporous resins, such as Amberlyst A-26[19–21,40–42] and Amberlite XAD,[18,22,24–27,29,36,37,43–45] respectively, have become valuable tools for preparing a great

TABLE 1
Characteristics and Applications to Metal-Ion Determination of Resins Loaded with Aromatic Organic Compounds

Resin	Ligand	Method for ligand sorption	C_E of loaded resin (mmol ligand per gram resin)	Metal-ions studied	Method for metal-ions sorption	Stripping agent	Analytical technique	Applications	Ref.
Anionic, microporous									
Bio-Rad AG 1 X8 (100–200 mesh; Cl^- form)	Chromotrope 2B	Batch, 30min	1.60	Al(III)	Batch 1 h at 25°C Column, *flow rate:* 0.5–1.0 ml/min, 20 × 0.8 cm i.d.	0.01 *M* HCl	Visible spectrophotometry	Determination of Al in tap water. Preconcentration and separation of Al from Pb, Zn, Ni, Cd, Ca, and Mg	33
Bio-Rad AG MP-1 (100–200 mesh; Cl^- form)	T-azo-R	Batch, 30 min	0.10	Th(IV)	Batch		Visible spectrophotometry		34
Bio-Rad AG MP-1 (100–200 mesh; NO_3^- form)	T-azo-R T-azo-C	Batch, *30 min*		Ga(III), Al(III)	Batch, 1 h	0.2 *M* HNO_3 for Ga	Anodic stripping voltammetry DP (for Ga^{3+}). Visible spectrophotometry (for Al^{3+})	Separation of GaAl. Preconcentration of Al	35
Seralite SRA-400 (100–200 mesh; Cl^- form)	Pyrogallolsulfonic acid	Batch, 8 h	0.80	Cu(II), Ni(II), Be(II), Mn(II) Fe(III), V(V), Mo(VI)	Batch 24 h. Column, flow rate: 0.5 ml/min, 10 × 0.5 cm i.d.	Column: citrate buffer/ascorbic acid/ $HCl/HClO_4$, in different proportions	UV/vis spectrophotometry, with the exception of Mo(VI) analyses (ICP–AES)	Separation of synthetic binary and ternary mixtures: Cu–Fe, Ni–Fe, Mn–Fe, Fe–Mo, Mn–V, V–Mo, and Mn–Cu–Fe	17
Dowex 1 X8 (Cl^- *form)*	Chrome azurol S Calmagite Xylenol orange	Batch, overnight		Mg(II), Co(II), Mn(II), Zn(II), Ca(II)	Column, mobile phase for metal retention: 1 *M* KNO_3	0.2–1.0 *M* KNO_3 + trace amounts of lactic acid	HPLC with postcolumn reaction and UV/vis detector	Separation of Zn, Co, and Mn from Mg and Ca	36
		Batch, overnight		*Zn(II), Co(II),* Mn(II), Mg(II), Cu(II), Cd(II)	*Column,* mobile phase for metal retention: *1 M* KNO_3	*1 M* KNO_3 Gradient elution	HPLC with postcolumn reaction and UV/vis detector	*Separation of* transition metals from high concentrations of alkaline earth metals	37

	Xylenol orange	Batch, 48 h, 50°C		Mg(II), Ca(II), Sr(II), Ba(II)	Column, flow rate: 2.5 ml / min	Mobile phase: 0.2 *M* lactic acid +0.15 *M* ethylene-diamine, pH 2.8	HPLC	Separation of Mg, Ca, Ba, and Sr in concentrated brines	38
Dowex 2 (200–400 mesh; Cl^- form)	Pyrocatechol violet Xylenol orange	Batch, 3–8 h	25.7 (XO)[a] and 23 (PV)	Cd(II), Cu(II)	Batch 20–30 min	1 *M* HNO_3, for Cd and 1 *M* HCl, for Cu	FAAS	Preconcentration of Cd and Cu prior to their determination by FAAS in river waters	16
Amberlite IRA-400	Xylenol orange	Batch, 24 h	0.04	Pb(II), Cd(II) Cu(II), Zn(II), Co(II), Ni(II), Cr(III), Mn(II)	Batch 24 h. Column, flow rate: 0.3 ml / min, 4.7 × 0.45 cm i.d.	Column: ammoniacal buffer, for Cd. 0.04 *M* EDTA, for Pb	FAAS	Preconcentration and separation of Cd / Pb	39
Amberlite IRA-400 (Ac^-, Cl^- form)	SPADNS	Column	1.26	Cu(II), Ni(II), Co(II), Zn(II), Fe(III), Pb(II)	Column, flow rate: 0.75 ml / min	HNO_3, pH 1.4	GF–AAS Visible spectrophotometry	Preconcentration and determination of metal ions from synthetic and natural samples (water)	23
Amberlite CG-400 (100–200 mesh)	Xylenol orange	Batch, 24 h	1.05	Pb(II), Cd(II), Cu(II), Zn(II), Co(II), Ni(II), Mn(II), Cr(III)	Batch 24 h		FAAS	Preconcentration of trace metals	39
Anionic, macroporous									
Amberlyst A-26 (0.45–0.55 mm, 0.1–0.2 mm)	SPADNS Nitroso-R salt	Batch. Column	Batch method: 1.0–1.7 (SPANS) and 1.8 (NRS). Column method: 0.6 (orange II), 1.8 (SPADNS)	Cd(II), Co(II), Ni(II), Cu(II), Fe(III), Zn(II), Cr(III), Al(III), Pd(II), Mn(II) Pb(II), Bi(III)	Batch 12 h. Column, 0.58 cm i.d.; flow rate: 0.5 ml / min (0.1 g resin loaded with 0.25 mmole SPADNS / g resin) and 1 ml / min (0.5 g resin loaded with 0.2 mmol orange II / g resin	Column: 10^{-3} *M* HNO_3 for foreign metals and 1.0 *M* HNO_3 for Bi(III) (SPADNS-loaded resin). Mixtures 0.25 *M* NaOH + 0.20 *M* HCl (XO-loaded resin)	AAS	Separation of metal cations	40

TABLE 1 (continued)
Characteristics and Applications to Metal-Ion Determination of Resins Loaded with Aromatic Organic Compounds

Resin	Ligand	Method for ligand sorption	C_E of loaded resin (mmol ligand per gram resin)	Metal-ions studied	Method for metal-ions sorption	Stripping agent	Analytical technique	Applications	Ref.
Amberlyst A-26 (0.45–0.55 mm, 0.1–0.2 mm)	Eriochrome blue-black R	Batch. 30 min. Column, flow rate: 1 ml / min, 0.8 cm i.d.	Batch: 3.70	Mn(II), Co(II), Ni(II), Cu(II), Pb(II), Cd(II), Zn(II), Ga(II), Fe(III), In(III), Bi(III), Cr(III)	Batch, 6 h.		GF–AAS	Trace metal preconcentration in conventional AAS	41
Amberlyst A-26 (20–50 mesh, Cl^- form)	Pyrocatechol violet	Batch, 8–9 h	99[b]	Pb(II), Cd(II)	Batch, 6–7 h (Cd^{2+}) and 4–5 h (Pb^{2+})	1 *M* HNO_3 (Cd). 1 *M* HCl (Pb)	FAAS	Determination of Cd and Pb in river waters	42
Amberlyst A-26 (0.1–0.2 mm, Cl^- form)	Xylenol orange	Batch	0.4	In(III), Zn(II), Pb(II)	Column, flow rate: 0.67 ml / min, 4 cm bed height	Water acidified to pH 4.0 with H_2SO_4 for Zn and 0.2 *M* HNO_3 for In.	GF–AAS	Fast separation of In from an excess of Pb and Zn and determination of this metal ion	21
Amberlyst A-26 (0.4–0.5 and 0.1–0.2 mm, Cl^- form)	ANS	Batch. Column	Batch[c]: 3.41 and 3.81 for 0.4–0.5 and 0.1–0.2 mm bead sizes, respectively. Column[c]: 3.95 (0.1–0.2 mm bead size)	Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), Cr(III), Mn(II), Fe(III), Ca(II), Mg(II), Ag(I)	Batch, 8 h. Column, flow rate: 0.5 ml / min, 5 × 0.8 cm i.d. 0.25 g ANS-loaded resin	Column: $NH_3(Ag^+)$ and 0.1 *M* HNO_3 for metal ions others than Ag(I)	GF–AAS and F–AAS	Determination of silver in copper ore	20

	Thoron	Batch	Batch: 1.1 and 1.5 for 0.4–0.5 and 0.1–0.2 mm bead sizes, respectively. Column: 1.6 (0.1–0.2 mm bead size)	Fe(III), Cu(II), Co(II), Ni(II), Zn(II), Pb(II), Ca(II), Mg(II)	Batch, 8 h. Column, flow rate: 1 ml / min, 0.58 cm i.d.	Column: 0.1 *M* trien for metal ions others than Fe(III). 1.0 *M* HCl (or 1.0 *M* HNO_3) for Fe(III).	GF–AAS and F–AAS	Analysis of iron in brass. Preconcentration and determination of iron in natural waters.	19
Varion AT-400 (0.4–0.5 mm, Cl^- form)	Orange II	Batch. Column, flow rate: 1 ml / min	Batch: 0.8. Column: 0.6	Cd(II), Co(II), Ni(II), Cu(II), Fe(III), Zn(II), Cr(III), Al(III), Pd(II), Mn(II) Pb(II), Bi(III)	Batch 12 h		AAS	Separation of Al–Ni; Pb–Mn(II); Al, Pb, Zn–Ni; Al, Pb, Zn–Mn(II)	40
D296 porous alkaline anion exchanger (40–50 mesh, ASO_4^{3-} form)	Arsenazo III	Batch		Rare earth metals	Column, at pH 1–2.5	1.5 *M* HNO_3	Visible spectrophotometry	Determination of rare earths in geological sediments by preconcentration with Arsenazo-III resin.	43
Nonionic, macroporous									
Amberlite XAD-2	Chrome azurol S Calmagite Xylenol orange	Batch, overnight		Zn(II), Co(II), Mn(II), Mg(II), Ca(II)	Column, mobile phase for metal retention: 1 *M* KNO_3	0.2–1.0 *M* KNO_3 +trace amounts of lactic acid	HPLC with postcolumn reaction and UV / vis detector	Separation of Zn, Co, and Mn from Mg and Ca	36
Amberlite XAD-2 (20–60 mesh)	Pyrocatechol violet	Batch, 12 h	0.05	In(III), Bi(III), Fe(III), Co(II), Cd(II), Cu(II), Pb(II)	Batch, 12 h. Column, flow rate: 1.7 ml / min, 6 × 0.8 cm i.d.	Column: 1 *M* HNO_3 (Bi). 0.5 *M* HNO_3 (In).	GF–AAS	Separation of Bi(III) or In(III) from excess of Cu(II) and Ni(II). Preconcentration of In(III) and Pb(II).	44
Amberlite XAD-2 (0.3–0.78 mm)	Chrome axurol S Calmagite Xylenol orange	Batch, overnight		Zn(II), Co(II), Mn(II), Mg(II), Cu(II), Cd(II)	Column, mobile phase for metal retention: 1 *M* KNO_3	1 *M* KNO_3. Gradient elution	HPLC with postcolumn reaction and UV / vis detector	Separation of transition metals from high concentrations of alkaline earth metals	37

TABLE 1 (continued)
Characteristics and Applications to Metal-Ion Determination of Resins Loaded with Aromatic Organic Compounds

Resin	Ligand	Method for ligand sorption	C_E of loaded resin (mmol ligand per gram resin)	Metal-ions studied	Method for metal-ions sorption	Stripping agent	Analytical technique	Applications	Ref.
Amberlite XAD-2 (20–60 mesh)	PAR	Batch, 12 h	0.04	Ag(I)	Batch 24 h. Column (4.5 cm): off-line method (flow rate: 0.5 ml / min); on-line method (flow rate: 8 ml / min)	0.5 *M* thiourea in 0.2 *M* HNO_3	GF–AAS FAAS (on-line method)	Rapid and selective separation and determination of silver in copper ores	27
	PAR Eriochrome blue-black R Pyrocatechol violet	Batch		Cu(II)	Column, flow rate: 6.8 ml / min. Column of 7.0 × 0.3 cm i.d., flow rate: 6.7 ml / min for FI–AAS with PV-loaded resin	2 *M* HNO_3	FAAS FI–AAS	Preconcentration and determination of Cu(II) by flow injection AAS in natural waters	18
Amberlite XAD-2 (20–60 mesh)	Eriochrome blue-black R	Batch, 30 min. Column, flow rate: 1 ml / min, 0.8 cm i.d.	Batch[d]: 0.6. Column[d]: 0.47	Mn(II), Co(II), Ni(II), Cu(II), Pb(II), Cd(II), Zn(II), Ga(III), Fe(III), In(III), Bi(III), Cr(III)	Batch 6 h. Open-column chromatography and flow-injection AAS (flow rate: 8–11 ml / min, 4.5 × 0.4 cm i.d.) for Ni(II)	Column: 2–4 *M* HNO_3	GF–AAS FI–AAS	Separation of metal cations and nickel preconcentration in conventional open-column chromatography and in flow-injection AAS	41

	Pyrocatechol violet	Batch, 12 h		Zn(II), Cd(II)	Batch, 8–12 h	4 *M* HCl or 4 *M* HNO_3	FAAS	Determintion of Zn(III) and Cd(II) in river water. Preconcentration and separation of both metals.	22
Amberlite XAD-4	Chrome azurol S Calmagite Xylenol orange	Batch, overnight		Zn(II), Co(II), Mn(II), Mg(II), Ca(II)	Column, mobile phase for metal retention: 1 *M* KNO_3	0.2–1.0 *M* KNO_3 +trace amounts of lactic acid	HPLC with postcolumn reaction and UV / vis detector	Separation of Zn, Co, and Mn from Mg and Ca	36
Amberlite XAD-4 (0.3–0.78 mm)	Chrome azurol S Calmagite Xylenol orange	Batch, overnight		Zn(II), Co(II), Mn(II), Mg(II), Cu(II), Cd(II)	Column, mobile phase for metal retention: 1 *M* KNO_3	1 *M* KNO_3. Gradient elution	HPLC with postcolumn reaction and UV / vis detector	Separation of transition metals from high concentrations of alkaline earth metals	37
Amberlite XAD-4 (0.3–0.78 mm)	PAN	Batch, 1 h. Column, flow rate: 1 ml / min	Column: 0.054	Cu(II), Zn(II), Cd(II), Ni(II), Pb(II), Fe(III)	Batch, 1 h. Column, flow rate: 1.5–20 ml / min, 0.6–0.9 cm i.d.	Batch: 2–4 *M* HCl	FAAS	Analysis of metal cations in river water	29
Amberlite XAD-4 (100 mesh)	Oxine 5ClDMPAP	Batch, 1 h (oxine); 12 h (5ClDMPAP)		Ce(III), La(III), Pr(III)	Batch, 30 min		Visible spectrophotometry. X-ray fluorescence	Preconcentration of trace rare earths in aqueous samples for analyzing by X-ray fluorescence	45
Amberlite XAD-7 (20–60 mesh)	PC-88A	Batch, under pressure, 30 min	1.60	Rare earth elements	Batch, > 5 h. Chromatographic column, flow rate: 20 ml / h, 95.5 × 1.0 cm i.d.	Column: 0.9 *M* HCl	ICP–AAS	Separation of rare earth elements	24

TABLE 1 (continued)
Characteristics and Applications to Metal-Ion Determination of Resins Loaded with Aromatic Organic Compounds

Resin	Ligand	Method for ligand sorption	C_E of loaded resin (mmol ligand per gram resin)	Metal-ions studied	Method for metal-ions sorption	Stripping agent	Analytical technique	Applications	Ref.
		Batch, under pressure 30 min	1.60	Rare earth elements	Batch > 5 h. Chromatographic column, flow rate: 15 ml / h (Ho-Er-Tm) and 20 ml / h (La-Pr-Nd), 94.5 × 1.0 cm i.d., 47°C	1.4 *M* HCl (Ho-Er-Tm) and 0.1 *M* HCl (La-Pr-Nd)	ICP−AES	Separation of rare earth elements	26
		Batch, under pressure, 30 min	1.60	Sc(III)	Batch, 5 h. Column, flow rate: 16−20 ml / h, 0.8 cm i.d.	3 *M* HCl. 4-methyl-2-pentanone	ICP−AES	Separation of Sc(III) from acidic leached solution of wolframite	25
Small particle size HPLC grade resins									
PLRP-S neutral 8 μm polystyrene-divinylbenzene substrate	Chrome azurol S Xylenol orange	Stainless-steel column, 10 × 0.46 cm i.d.		Ba(II), Mg(II), Sr(II), Ca(II), Mn(II), Co(II), Zn(II), Cd(II), Pb(II), Ni(II), Cu(II)	Column, mobile phase: 1 *M* KNO_3	1 *M* KNO_3, gradient elution	HPLC with post column reaction and UV / vis detector	Separation of selective groups of metal ions, in high ionic strength media, by gradient elution	36, 37

Note:

C_E = exchange capacity for complexing agent; ICP = inductively coupled plasma; AES = atomic emission spectrometry; HPLC = high-performance liquid chromatography; FAAS = flame atomic absorption spectrometry; GF − AAS = graphite furnace atomic absorption spectrometry; FI = flow injection system.

[a] C_E given in milligrams of reagent per gram of dry resin.

[b] C_E given in milligrams per milliliter of reagent per gram of dry resin.

[c] C_E given in moles of reagent per gram of dry resin.

[d] C_E given in millimoles of reagent per gram of dry resin.

TABLE 2
Systematic Name, Empirical Formula and Molecular Weight of Organic Compounds

Ligand	Systematic name	Empirical formula	Molecular weight (g / mol)
Alizarin	1,2-dihydroxyanthraquinone	$C_{14}H_8O_4$	240.21
ANS	8-amino-naphthalene-2-sulfonic acid	$C_{10}H_9NO_3S$	223.25
Arsenazo III	3,6-bis[(*o*-arsonophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulfonic acid	$C_{22}H_{18}N_4O_{14}S_2As_2$	777.37
Bromothymol blue	3′,3″-dibromothymolsulfonephthalein	$C_{27}H_{28}Br_2O_5S$	624.40
Calmagite	3-hydroxy-4-(2-hydroxy-5-methylphenylazo)-1-naphthalene-sulfonic acid	$C_{17}H_{14}N_2O_5S$	358.37
Chlorophenol red	3′,3″-dichloro-phenolsulfonephthalein, sodium salt		445.26
Chrome azurol S	5-[α-(3-carboxy-5-methyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,6-dichloro-3-sulfobenzyl]-3-methylsalicylic acid, trisodium salt	$C_{23}H_{16}Cl_2O_9S$	539.34
Chromotrope 2B	1,8-dihydroxy-2-(*p*-nitrophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid	$C_{16}H_9N_3Na_2O_{10}S_2$	513.37
5ClDMPAP	2-[2-(5-chloropyridylazo)-5-dimethylaminophenol]		
Eriochrome blue-black R (EBBR)	1-(2-hydroxy-1-naphthylazo)-2-hydroxy-4-sulfonic acid, sodium salt	$C_{20}H_{13}N_2NaO_5S$	416.39
Nitroso-R salt	disodium 3-hydroxy-4-nitroso-2,7-naphthalene disulfonate	$C_{10}H_5NNa_2O_8S_2$	377.26
Orange II	4-(2-hydroxy-1-naphthylazo)benzene-sulfonic acid, sodium salt	$C_{16}H_{11}N_2NaO_4S$	350.33
Oxine	8-hydroxyquinoline	C_9H_7NO	145.16
PAMB	2-[2-(3,5-dibromopyridyl)azo]-5-dimethylamino benzoic acid		
PAN	1-(2-pyridylazo)-2-naphthol	$C_{15}H_{11}N_3O$	249.27
PAR	4-(2-pyridylazo)resorcinol	$C_{11}H_9N_3O_2$	215.20
PC-88A	2-ethylhexyl hydrogen 2-ethylhexylphosphonate		
PGS	pyrogallol sulfonic acid		
Pyrocatechol violet (PV)	3,3′,4′-trihydroxyfuchsone-2″-sulfonic acid	$C_{19}H_{11}O_7S$	386.38
SPADNS	trisodium 2-(*p*-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate	$C_{16}H_9N_2Na_3O_{11}S_3$	570.40
T-azo-C	2-(tetrazolylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid		
T-azo-R	1,2-(tetrazolylazo)-2-hydroxynaphthalene-3,6-disulfonic acid		
Thoron	1-(2-arsonophenylazo)-2-hydroxy-3,6-naphthalenedisulfonic acid sodium salt	$C_{16}H_{11}N_2O_{10}S_2Na_2As$	576.20
Thioglycolate	mercaptoacetic acid, sodium salt	$C_2H_3O_2SNa$	114.10
Xylenol orange (XO)	3,3′-bis[*N*,*N*-di(carboxymethyl)aminomethyl]-*o*-cresol-sulfonephthalein	$C_{31}H_{32}N_2O_{13}S.2H_2O$	706.70

variety of ligand-loaded resins. Amberlyst A-26 is a macroporous copolymer of styrene and divinylbenzene of structure similar to XAD-2 that contains additional trimethylammonium ion-exchange groups.[22] XAD-4 and XAD-7 are, respectively, representative examples of styrene and polyacrylate adsorbents that have a high surface area (725 and 450 m^2/g) for immobilizing organic reagents.

Recent investigations into chelating ligand-coated HPLC resins have been carried out by Challenger et al.[36] and Jones et al.[37] in accordance with prior investigations developed by Jones and Schwedt.[46] They found that dyestuff-coated small particle size HPLC grade resins packed into stainless-steel columns also behave as very efficient columns for separating selective groups of metal ions.

The reagents retained on or sorbed onto the substrate should present a high selectivity for a given reaction with the species of interest,[6,39] properties of ion exchange with the resin,[6] and/or physical adsorption.[6,39] Several types of reagents have been loaded onto or immobilized on a polymeric matrix in order to prepare the highly selective chelating resins. It is evident from Table 1 that these ligands should be strong complexing agents of the metallic elements founded in the solution that is in contact with the resin phase.[47,48] At present, the ligands most commonly incorporated into ion-exchanger materials are aromatic organic compounds such as:

1. Naphthalene-sulfonic acids, that is, arsenazo III, calmagite, chromotrope 2B, EBBR, nitroso-R salt, orange II, SPADNS, T-azo-R, T-azo-C, and ANS.
2. Sulfonephthaleins, that is, bromothymol blue, chlorophenol red, phenol red, and xylenol orange.
3. Anthraquinones, such as alizarin.
4. Pyridylazo compounds, such as 5ClDMPAP, PAMB, PAN, and PAR.
5. 8-Hydroxyquinoline derivatives

However, organic nonaromatic compounds, such as EDTA, ethylenediglycol dibutyl ether, or dimethylglioxime, also have been used by several authors because of their strong metal-ion complexing properties (Reference 32 and references within).

The majority of the main organic reagents listed in Table 1 have a common characteristic: the molecules of such ligands possess one or more functional group such as $-OH$, $-COH$, NH_2, $C{=}O$, $-SO_3^-$, $=NH$, $-NO$, with donor atoms O—, N—, O, N—, S, N—, O, O—. Some of these groups are capable of forming links or interacting with the organic matrix of the resin, whereas the other groups can be involved in the ionic or electrostatic chemical bonds that are typical of complexes of transition and nontransition metals with chelating ligands.[47,48] A common case is ligands that possess two or more donating groups. These ligands, generally called chelating ligands, have a chelate ring structure instead of a linear structure and may share more than one pair of electrons with a single metal ion by coordinating two or more sites around the central metal ion.[47]

Attempts to study the mechanisms of both the sorption of the chelating ligand on the substrate and the fixation of the metallic ion on the chelating resin are considered extremely important and thus are presented next.

B. Procedure for Sorption of Chelating Reagents on Conventional Resins. Mechanisms of Retention

It is evident from Table 1 that two main procedures have been employed in the preparation of chelating resins: on the one hand, the "batch" or static method; on the other hand, the column or dynamic technique.

In the "batch" procedure, the ion exchanger is added to a given volume of reagent solution and the mixture is shaken until the resin is saturated. If the ligand to be sorbed is a chromogenic agent, the equilibrium concentration of this reagent is measured spectrophotometrically and the total sorption capacity of the sorbent may be determined. Some of the experimental conditions employed in the static preparation of several ligand-loaded resins for retention of metal ions (in principle, concentration and volume of reagent solution, amount of resin, and optimum pH for loading) are listed in Table 3.

In the dynamic method, columns are packed with conventional resin and a solution of organic reagent of an appropriate concentration is passed through the ion exchanger. Then, the amount of ligand immobilized on the resin is estimated by determining spectrophotometrically the amount of this reagent left in the effluent.[23,29,40,41]

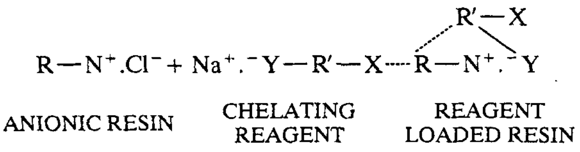
Several authors have discussed the mechanisms of ligand loading onto conventional resins. From their investigations, it may be suggested that in the immobilization of chelating reagents on a polymeric matrix, in order to prepare ligand-immobilized resins, in general, the mechanisms of ion exchange and/or adsorption may be involved.[6,16,18-20,22,27,32,38,39,41,44]

Dealing with anion-exchange resins, the retention of an organic reagent according to the mechanism of ion exchange illustrated in

TABLE 3
Experimental Conditions for Loading of Several Chromogenic Agents on a Conventional Resin by the Static Method

Chromogenic agent	Resin	Concentration and volume of reagent solution	Amount of resin (g)	Optimum pH for loading	Wavelength (nm) for measuring equilibrium concentration of reagent[a] by UV/vis spectrophotometry	Ref.
ANS	Amberlyst A-26	$1 \times 10^{-3}-2 \times 10^{-2}$ *M*, 20 ml	0.200			20
5ClDMPAP	Amberlite XAD-4 Amberlite XAD-7	4.11×10^{-4} *M*, 10 ml	0.010	4.0 - 4.5	440	45
EBBR	Amberlite XAD-2 Amberlyst A-26	5% ethanol-water solution of $1 \times 10^{-4}-8 \times 10^{-4}$ *M*		3.0	569	41
Orange II	Amberlyst A-26	0.02 *M*, 20 ml	0.200			40
Oxine	Amberlite XAD-4 Amberlite XAD-7	5×10^{-4} *M*, 10 ml solution	0.010	4.0 - 8.0	318	45
PAR	Amberlite XAD-2	5×10^{-4} *M*, 20 ml	0.200	4.0	395	27
PC-88A	Amberlite XAD-7	5.25 ml PC-88A (95% purity) +30 ml acetone	5.0			24 - 26
PGS	Seralite-400	2% PGS solution, 20 ml	0.500	5.0 - 9.0	438	17
Pyrocatechol violet	Amberlite XAD-2	5×10^{-4} *M*, 20 ml	0.200	2.0	450	22, 44
	Amberlyst A-26	5×10^{-4} *M*, 28 ml	0.200	8.0 - 8.5	441	42
	Dowex 2	6×10^{-4} *M*, 20 ml	0.100	7.5 - 8.0		16
SPADNS	Amberlite IRA-400 Amberlite IRA-910		0.300	5.3	508	30
	Amberlyst A-26	0.02 *M*, 20 ml	0.200			40
Thoron	Amberlyst A-26	1×10^{-3} *M*, 20 ml	0.200			19
Xylenol orange	Dowex 1 X8	100 mg in 25 ml of 40% methanol solution	3.0			37, 38
	Dowex 2	1.4×10^{-4} *M*, 75 ml	0.300	7.0 - 7.5		16

Scheme 1 would occur by means of the exchange of the Cl^-, NO_3^-, or Ac^- ions attached to the tertiary or quaternary ammonium groups of the resin and the negatively charged functional groups of the ligand (not hindering in the chelation) such as sulfonate groups.[16,22,32,38] As an example, Pesavento et al.[49] proved that sorption of T-azo-R and T-azo-C on Dowex 1 X8 resin (which had benzyltrimethylammonium groups as the active fixed group) in chloride form meant the displacement of three counterions by each azo-dye molecule, because the capacity of the Dowex 1 X8 resin (3.20 meq/g dry resin) was approximately triple the capacity of the ligand-loaded resin obtained for the two mentioned dyes (1.07 meq/g dry resin). Moreover, the maximum capacity of AG 1 X8 for Chromotrope 2B was 1.60 mmol/g, and sorption of a molecule of the organic reagent released two chloride ions.[33] Analogous findings were reported by Petit Dominguez et al.[39] in their study on the deposition of xylenol orange on strongly basic microporous Amberlite CG-400.



$$R{-}N^+.Cl^- + Na^+.{}^-Y{-}R'{-}X \cdots \overset{R'-X}{R{-}N^+.{}^-Y}$$

(R: polymeric skeleton; X, Y: functional groups)

Scheme 1. Preparation of a ligand-loaded resin, - - - - -, interaction by forces of adsorption.

However, ion exchange is not the sole mechanism responsible for ligand loading on anionic resins. In most cases, the deposition of organic reagents, in addition to ion exchange, is due to the adsorption process.[16,20,22,32,39] In fact, Singh and Dhingra[16] suggested that pyrocatechol violet and xylenol orange, which have a conjugated π-electron system and a sulfonate group, are immobilized on the Dowex 2 resin by an ion-exchange/π-π interaction. Moreover, data from the study of Brajter and Dabek-Zlotorzynska[20] showed that the difference between the capacity of the anionic macroporous Amberlyst A-26 (0.1 to 0.2 mm bead size) for ANS as determined by the dynamic method (3.95 meq/g dry resin) and that of the resin in chloride form (3.48 meq/g) may be due to the superposition of both mechanisms of ligand loading on the resin. Similar considerations were made for the modification of Amberlyst A-26 with eriochrome blue-black R,[41] SPADNS, and orange II.[40]

Immobilization of chelating agents on the hydrophobic surface of nonionic resins seems to be due to the mechanism of adsorption.[38,45] Furthermore, according to Handley et al.,[38] the phenomenon of adsorption should proceed *via* a combination of two processes: attraction forces between the aromatic rings of most ligands and those of the resin backbone, and the subsequent physical trapping of these ligands within the pores of the resin beads. It is difficult to predict accurately just which materials will be adsorbed well by a given nonionic substrate. In effect, nonionic resins such as Amberlite XAD-2 are excellent supports for retaining molecules of a given organic reagent and also ionic compounds.[41] Studies on the retention of pyrocatechol violet,[18,22,44], PAR,[18,27] and EBBR[18] on Amberlite XAD-2 resin showed that the deposition of these ligands occurred due to the physical attraction, namely, π-π dispersion forces, arising from the aromaticity of the styrene-divinylbenzene-type resin and the benzene rings in the dye molecule. In most cases, for sorption of large anions, structures with a permanent porosity with aliphatic hydrocarbons in their backbone are more suitable.[45] Moreover, acrylic components have a favorable influence on the retention of organic reagents.[32]

Adsorption isotherms of PAR,[27] pyrocatechol violet,[44] and EBBR[41] on Amberlite XAD-2 resin have been reported. In all cases, the adsorption isotherm fits the equation of Langmuir well. The time necessary for equilibrium to be reached was 12 h for PAR and pyrocatechol violet and 30 min for EBBR. As shown in Table 1, a maximal sorption of chelating agents is obtained if resins are equilibrated for a time below 16 h, although in most cases the rate of uptake of these ligands on the resin is very fast and half-saturation occurs in a very short time.[40,45] On the other hand, longer shaking times do not adversely modify the immobilization process.[16,22,27,42] In addition, adsorption isotherms and thermodynamic studies for 8-hydroxyquinoline and 5ClDMPAP immobilization on Amberlite XAD-4, a hydrophobic resin, and XAD-7, a resin of intermediate polarity or hydrophobicity, have also been reported.[45]

In either the ion-exchange process nor in the physical adsorption are covalent links between the reagent and the resin formed. Thus, the regeneration of the resin and the recovery of the reagent are feasible.[6,32]

The capacity of conventional resins for ligand sorption may be modified by the acidity of the external solution over a wide range of pH whether the ligand retention takes place by ion exchange or by the mechanism of adsorption. Dealing with anionic microporous resins, sorption of T-azo-R and T-azo-C on Dowex 1 X8 resin was found to be independent of the acidity of the external solution over the pH 2 to 12 range.[49] Moreover, Petit Dominguez et al.[39] reported that maximum immobilization of xylenol orange on Amberlite CG-400 was reached within the pH 3 to 10 range. On the contrary, sorption of xylenol orange and pyrocatechol violet on a Dowex 2 sorbent[16] and Amberlyst A-26 resin[42] proved to be pH dependent, and maximum sorption for the dyes was obtained at pH 7.0 to 8.0[42] and pH 8.0 to 8.5.[2] Finally, the pH of the external solution did not affect the amount of eriochrome blue-black R sorbed onto an anionic macroporous resin, such as Amberlyst A-26.[41]

As might be expected, the pH of the external solution should exert a significant effect on the deposition of ligands on nonionic resins due to the nonpolar properties of the substrata and the acidic-basic character of most ligands.[32] In effect, Brajter et al.[27,44] explained this behavior by means of the theory postulated by Cantwell and Puon and based on the Stern-Gouy-Chapman electrical double-layer theory for retention of organic ions on nonionic sorbents. According to this proposition, if a large organic anion (ligand) is used with a small cation (H_3O^+, at low pH), the anion will be adsorbed as the potential-determining ion and the cation will act as a counterion. Thus, in acidic media, the maximum adsorption of both PAR ($pK_{a1} = 2.7$, $pK_{a2} = 5.5$, $pK_{a3} = 12.3$, in 10% MeOH)[47] on Amberlite XAD-2 resin and 8-hydroxyquinoline ($pK_{a1} = 5.01$, $pK_{a2} = 9.9$)[47] on XAD-4 and XAD-7 resins occurred at pH 3 to 6[27] and 6.0,[45] respectively. Moreover, the adsorption of pyrocatechol violet ($pK_{a1} < 1$, $pK_{a2} = 7.82$, $pK_{a3} = 9.76$, and $pK_{a4} = 11.7$)[47] on the same resin was maximal at pH 2.[44] In both cases, specific interaction of the anion increased the aforementioned effect.[44] On the other hand, an examination of EBBR retention on XAD-2 sorbent in static conditions showed that the maximum loading capacity of this resin did not depend on the pH of the ligand solution.[41]

C. Characteristics of Ligand-Loaded Resins

The characterization of resins modified with organic reagents has been carried out in terms of their physical and chemical properties. Among these properties, the breakthrough capacity (dynamic capacity), chemical and physical stability, and acidic and basic properties will be discussed.

1. Breakthrough Capacity

Capacity and related data on ion-exchange materials are interesting both for characterizing resins and for use in the numerical calculation of the ion-exchange operation.[1] Data of maximum capacity or ion-exchange capacity, defined as the number of ionogenic groups per specified amount of ion exchanger, are compiled in Table 1 for the main works on ligand-loaded resins found in the recent literature. Because many ion-exchange operations are carried out in columns, data on breakthrough capacity are of considerable interest. It is evident that concepts usually applied to conventional resins are also useful for ligand-loading resins, as will be shown next.

By definition, the capacity that is utilized until breakthrough occurs (before the bed has come to complete equilibrium with the feed) is called the breakthrough or dynamic capacity and it depends on the operating conditions.[1] The capacity, as determined by the dynamic method, of Amberlyst A-26 for ANS,[20] EBBR,[41] orange II,[40] and SPADNS[40] was 3.95 mol/g and 3.70, 0.6, and 1.8 mmol/g, respectively, and the data for retention of orange II on Varion AT-400[40] and PGS on Seralite SRA-400[17] were 0.6 and 0.8 mmol/g, respectively. Total amounts of ANS and EBBR loaded on Amberlyst A-26 were higher than the total capacity of this resin and, thus, the potential of these chelating resins for the separation of metal ions is evident.

On the other hand, with respect to nonionic resins, the obtained elution curves showed a low breakthrough capacity for PAR- and EBBR- loaded Amberlite XAD-2: 0.2[43] and 0.47[41] mmol/g, respectively.

2. Chemical Stability

The chemical, thermal, and mechanical stability of the chelating resins depends mainly on the structure and number of the fixed ionic groups.

The resistance of modified ion-exchange resins to mineral acid or base solutions has been investigated widely. In fact, it is important to know the conditions for total elution or release of ligands from chelating resins in order to predict the potential application of these resins to the separation and analysis of mixtures of metallic ions.[32]

The stability of modified resins depends on the type of sorbent used and the nature of the organic reagent retained. The chemical resistance of chelating resins is usually studied by spectrophotometrically measuring the concentration of complexing reagent in the effluent when a solution of acid, base, or salt is passed through a column containing the modified sorbent[17,19,20,27,40,41] or by determining the loss of ligand upon shaking the impregnated resin with a solution of mineral acid or base.[14,38,39,49]

As a general rule, for most ion exchangers and organic reagents, the resistance of the ligand-loaded resins to mineral acids depends on the affinity of the acid anions for the sorbent. The affinity sequence follows the order of the hydrophobic character of the anions involved:[19,33,49] perchlorate > nitrate > bromide > chloride > acetate. The interferences become more important as the concentration of the inorganic reagents involved increases.[19,20,39,40] In this way, the interference of several anions present in a solution containing chromotrope-2B-loaded AG 1 X8 resin (1.60 mmol of reagent per gram of dry resin) followed the order stated above.[33] Additionally, it was found that chloride and perchlorate did not cause any release of this sulfonated azo dye up to concentrations of 1 *M* and 10^{-3} *M*, respectively, and di- and trivalent ions did not interfere at all. Analogous results have been reported for xylenol-orange-loaded Amberlite CG-400 resin,[39] for which it was found that 1 *M* nitrate and chloride caused a ligand release of 51.2 and 31.4%, respectively. The chelating resin was resistant to 5 *M* sodium hydroxide and 1 *M* acetate. Moreover, the percentage elution of SPADNS from loaded Amberlyst A-26 resin[40] in dynamic conditions (capacity of chelating agent 0.2 mmol/g) observed for 1 *M* concentrations of HCl, HNO_3, and $HClO_4$ was 1.0, 16.0, and 99.0, respectively. The resistance of nitroso-R-salt-loaded resin was lower (94% of the organic reagent was eluted with 0.1 *M* $HClO_4$). Minimal influence of chloride anions on the retention of PGS on Seralite SRA-400 was found[17] when this chelating resin was treated with diluted HCl or NaCl solutions. However, when the electrolyte concentration was increased up to 1 *M*, more than 80% of the PGS was leached out. In addition, ANS-modified Amberlyst A-26 is resistant to 0.2 *M* HNO_3 (< 10% reagent released).[20]

Olbrych-Sleszynska et al.[41] examined the resistance of XAD-2-EBBR sorbent for $HClO_4$, HNO_3, and HCl in dynamic conditions , as compared with the stability of EBBR-loaded Amberlyst A-26 resin. For all examined acids, the elution of EBBR from XAD-2 resin was negligible up to 2 *M* concentration of acids; ligand-modified Amberlyst A-26 exhibited a slightly better resistance toward the mineral acid solutions studied. The PAR-modified Amberlite XAD-2[27] was found to be resistant to mineral acids at concentrations up to 6 *M* (less than 40% of PAR was released), although NaOH exerted an important effect on the stability of this chelating resin (50% release of PAR at 1 *M* NaOH in solution). In addition, Chwastowska and Mozer[29] reported the high stability of PAN-loaded Amberlite XAD-4 resin. In effect, according to these authors, all attempts to remove the PAN from the sorbent with organic solvents failed. However, the influence of inorganic acids in the chemical resistance of this modified resin was not tested. Finally, leakage and loss of PC-88A from ligand-modified Amberlite XAD-7 resin (maximum loading of 1.6 mmol reagent per gram of resin) was less than 3% upon shaking the impregnated resin with 0.01 *M* HCl.[24-26]

The results show clearly that chelating resins exhibit reasonably good chemical resistance together with high thermal stability[31] and repeatability.[29,41] This is because such resins can be recommended for preconcentrating and determining metal ions in a wide variety of samples.

3. Acidic and Basic Properties of Ligand-Loaded Resins

Conventional cation exchangers in H^+ form and anion exchangers in OH^- form can be considered as insoluble acids and bases.[1] In the same way, chelating resins have acidic and basic properties[6,34,35,49,50] and thus they can be titrated with bases and acids.[6] Protonation characteristics of the modified resins depend on the nature of the ligand to be loaded, the type of resin, crosslinking, swelling, the nature of the counterion, the solution phase in contact with the resin, etc.[6,51] In the protonation process, the modified resins remain insoluble, but come to equilibrium with the solution to which the titrant is added.[1] The protonation of the ligand-loaded resins can be followed by recording the pH of the supernatant solution while the titration is progressing. From the protonation curve, the content of chelating groups and the numerical value of the proton selectivity coefficients can be determined.[1,6,34,49,52]

Knowledge of the sorbing properties toward protons (protonation coefficients) is quite useful for predicting the best conditions for analytical operations such as separation, preconcentration, and determination of metal ions in solution.[49] In effect, a correlation has been found between the protonation and complexation properties of the ligand in aqueous solution and the chelating characteristic of the resins loaded with the same ligand.[6,34,49,50,52]

In-depth research into the protonation equilibria of modified resins has been carried out in recent years.[6,34,49,50,52] At first, Pesavento et al.[53] applied the model proposed by Marinsky for the protonation and ion exchange of different resins to particular chelating resins consisting of a strong anion-exchange resin loaded with a sulfonated azo-dye.[33,34,49] This system had the advantage of being characterized by a constant ionic composition of the resin and the homogeneity of its active and well-characterized functional groups, which are easily introduced into the substrate by ion exchange.[52]

The theoretical model starts from the assumption that the resin can be treated as an aqueous phase separated from the external solution by a boundary across which all the molecular and ionic components of the system, except the fixed quaternary ammonium groups, can diffuse. At the boundary, the Donnan potential between the ion exchanger and the solution is set up,[1,49] The resin is assumed to contain the sorbed ligand $H_{r-1}L$. Thus, in the resin phase, by applying the Gibbs-Donnan model to the proton exchange, the reaction

$$\overline{H_{r-1}L} + \overline{H^+} \rightleftharpoons \overline{H_rL}$$

takes place with an intrinsic protonation constant

$$K_{\mathrm{ip}} = \frac{[\overline{H_rL}]}{[\overline{H_{r-1}L}][\overline{H^+}]} \qquad (1)$$

The degree of dissociation α and the *pH in the resin* are defined according to:

$$\alpha = \frac{[\overline{H_{r-1}L}]}{[\overline{H_{r-1}L}] + [\overline{H_rL}]} \qquad (2)$$

$$\mathrm{pH} = -\log\,[\overline{\mathrm{H}^+}] \qquad (3)$$

where symbols with overbars indicate the species in the resin. Note that pH has been defined by the Stockholm school convention.

The proton concentration on the resin $[\mathrm{H}^+]$ depends on the composition of the external solution. As a first approximation, it can be assumed that

$$[\overline{H^+}] = \frac{[H^+][A^+]}{[\overline{A^+}]} \qquad (4)$$

where A proceeds from the dissociation of a given strong electrolyte A_aC_c in the solution.

For the protonation reaction

$$H^+ + \overline{H_{r-1}L} \rightleftharpoons \overline{H_rL}$$

the experimental protonation coefficient K_p, is given by

$$K_p = \frac{[\overline{H_rL}]}{[H^+][\overline{H_{r-1}L}]} \qquad (5)$$

Thus, the intrinsic protonation constant K_{ip} and the observed protonation constant are related by the equation

$$K_{\mathrm{ip}} = K_p \frac{[\overline{A}]}{[A]} \qquad (6)$$

Defining n (the fraction of protonated ligand in the resin) as

$$n = \frac{[\overline{H_rL}]}{[\overline{H_{r-1}L}] + [\overline{H_rL}]} \qquad (7)$$

from Eqs. (1) and (7), n can be given by

$$n = \frac{K_{\mathrm{ip}}[H^+][A][\overline{A}]}{K_{\mathrm{ip}}[H^+][A][\overline{A}] + 1} \qquad (8)$$

from which plots of $n = f(\mathrm{pH} + \mathrm{pA})$ are independent of the ionic composition of the external solution[49] and allow us to determine K_{ip} and, thus, K_p and α. Considering the activity coefficients in both phases, the foregoing equations can be transformed by taking into account the molal coefficients of each species (Y_H, $Y_{\overline{H_{r-1}L}}$, $Y_{\overline{H_rL}}$) and the activity of the species A (a_A, $\overline{a_A}$), giving the equation

$$K_{\mathrm{ip}} = K_p \frac{\overline{a_A}}{a_A} \frac{Y_{\overline{H_rL}}}{Y_H Y_{\overline{H_{r-1}L}}} \qquad (9)$$

where the activity coefficients can be determined by applying the specific interaction theory.[34,35,49,50]

Most of these equations have been applied to the characterization of several ligand-loaded resins. In this way, protonation of sulfonated azo dyes containing a nitrogen donor atom in the diazo group (i.e., T-azo-R, T-azo-C, and chromotrope 2B) sorbed onto AG MP-1, Dowex 1 X8, and AG 1 X8 resins, respectively, has been studied using conventional analytical methods.

Pesavento et al.[49] applied the equations we already have shown for determining the protonation constants of T-azo-C and T-azo-R immobilized on a Dowex 1 X8 resin. Starting from titration curves of these chelating resins and assuming that (a) the ionic invasion was practically negligible up to about 1 *M* electrolyte concentration and (b) $[A]$ did not vary both during titration and at different ionic strength in the aqueous phase, the mean values of the first protonation constants obtained were 8.93 ± 0.08 (T-azo-C) and 9.62 ± 0.09 (T-azo-R). These values were in good agreement with those found in aqueous 0.1 *M* $\mathrm{NaClO_4}$: 8.30 and 9.10, respectively.

Moreover, the second protonation constant of T-azo-R sorbed on AG MP-1 was determined potentiometrically at different sodium chloride concentrations in solution.[34] The computed mean value (2.94 ± 0.10) was similar to that found in aqueous solution.

Protonation of chromotrope 2B sorbed onto AG 1 X8 resin in sodium chloride solutions of different concentrations (from 0.019

to 1.053 mol/Kg) and in sodium nitrate (from 0.017 to 0.373 mol/Kg), for comparison, has been studied.[50] The findings indicate that K_p depends on the ionic strength, according to Eq. (9). The average value of $\log K'_p = \log(K_{ip} Y_{\overline{H_{r-1}L}} / \overline{a_A} Y_{\overline{H_rL}})$ was 8.57 ± 0.10 in the chloride solutions. This value was similar to that of Chromotrope 2B in solution.

Other models, such as that suggested by Muraviev and Högfeldt[54] to describe the equilibrium properties of systems in which the composition of the resin varies during the ion-exchange process, have been applied to ligand-loaded resins. This model is simple to use and requires the knowledge of three parameters that can be determined experimentally from potentiometric acid-base titrations at various electrolyte concentrations in the aqueous phase. Results obtained on the protonation equilibrium of T-azo-R and Chromotrope 2B sorbed on Dowex 1 X8 or AG 1 X8[51] by applying this model were in good agreement with those found with the method of Marinsky and Helfferich and require less experimental information, such as water uptake, ionic strength, etc.

D. Retention of Metal Ions on Ligand-Loaded Resins

An extensive literature deals with the use of ligand-loaded resins in metal-ion analysis. In fact, three main applications of modified resins for separating and determining metal cations present in solution at low levels have been described:

1. Preconcentration, selective separation, and analysis of numerous metal ions present in solution by an off-line procedure, that is, under static conditions or by using column performances. From this point of view, the potential of modified resins as an effective method of separation in the analysis of synthetic[27,35,39-41,44,45] and real[16,19-23,27-30,42-44] samples may be demonstrated.
2. Preconcentration and separation of metal ions from the matrix of a given sample on-line. Recent investigations into dye-coated columns for separation of trace metals by chromatographic techniques have been carried out.[36-38] Moreover, the possibility of using ligand-loaded resins in a flow-injection system, usually with detection by atomic absorption spectrometry (18, 27, 41), has also been examined. In this way, the advantages of ion-exchange resins and nonionic sorbents modified with complexing ligands are combined with the preconcentration facility, detectability, and selectivity of the on-line sample processing methods FI-AAS.[18]
3. Ion-exchanger phase absorptiometry or "ion-exchanger colorimetry" for trace analysis is based on the direct measurement of the degree of light absorption by the ligand-loaded resin phase that has sorbed a sample component. In spite of the interest of this technique, it is one of the less investigated applications of modified-conventional resins to the analysis of metal ions, although there are various studies with the ligand immobilized in other types of sorbents.[55-60] Nevertheless, this review deals only with those works on ion-exchanger absorptiometry in which a complexing resin obtained by previous retention of a ligand on an anionic acid and nonionic exchanger is employed, excluding those in which the retention of metal complexes directly in the conventional resin is achieved (the modified resin is not previously prepared).

The mechanisms that describe metal-ion sorption onto resins loaded with chelating agents and the most significant studies on the application of these resins to preconcentration, separation, and analysis of metal elements will be presented and discussed next.

1. Mechanisms of Retention of Metal Ions on Modified Resins

Knowledge of the mechanism of retention of metal ions on ligand-loaded resins is of utmost importance for predicting the distribution of these species between an aqueous solution and a conventional resin containing a complexing organic reagent.

Almost all the reports dealing with the mechanism of sorption of metal ions on ligand-modified resins started from the assumption that all the ligands immobilized on a conventional resin keep the same molecular structure and complexing properties as in aqueous solution. For this reason, the metal ion should be sorbed only by complexation with the free chelating groups of the ligand.[32,61] Thus, sorption of metal ions on modified resins takes place by the reaction

$$M + \overline{H_xL} \rightleftharpoons \overline{MH_rL} + qH \qquad x = q + r$$

On the basis of this equilibrium and by applying a model of the resin based on the Donnan equilibrium concept,[33,35,49,50] it was proved that the complex formation constants of a given ligand loaded onto an anion-exchange resin were equal to those of the ligand in the aqueous phase, despite the fact that the apparent constants altered as the reaction proceeded and the composition of the aqueous solution changed.[49] According to this model and by assuming that the metal ion could enter the resin phase only by reacting with the ligand and was present in the solution phase only as the aquo-ion, the fraction (f) of total metal ion sorbed onto the resin is given by

$$f = 1\Big/\left(1 + \frac{[H]^q[\overline{A}]V}{\overline{L_t}[A]K_c}\right) \qquad (10)$$

where V is the volume of the solution, $\overline{L_t}$ is the total amount of sorbed ligand, and K_c is the equilibrium complexation constant inside the resin phase ($K_c = [\overline{MH_rL}][\overline{H}]^q/[\overline{M}][\overline{H_xL}]$). Thus, the quantities that must be known are the total amount of chelating reagent sorbed, the composition of the aqueous solution and the resin phase (capacity and water sorbed), and the volume and acidity of the aqueous phase.[49] Because f at a particular acidity of the external solution can be experimentally determined, the evaluation of $\log K_c - \log[\overline{A}]$ could be evaluated as a function of pH for different metal ions sorbed on a properly loaded anion-exchange resin.

In fact, the results obtained by use of Eq. (10) for the chelates of Cu(II) and Ni(II) with T-azo-C or T-azo-C immobilized on a Dowex 1 X8 resin[49] and Al(III) with chromotrope 2B[33] showed acceptable agreement with the complex formation constants of the corresponding complexes in aqueous solution.

To a first approximation, the Donnan model could also describe the complexation of Cu(II), La(III) and Ni(II) with chromotrope 2B loaded onto AG 1 X8 resin.[50] Quantitative information with regard to the stability constants and complex stoichiometries was obtained from titration curves of the resin loaded with and without metal ions. For both copper and lanthanum, the 1:1 and 1:2 complexes were formed depending on the ligand concentration on the resin (the 1:2 complex of copper was not observed in aqueous solution). However, the sorption of nickel was unexpected because complexation in water is negligible.

Similar conclusions could be drawn when the Gibbs-Donnan model (with the evaluation of the activity coefficients of the species in aqueous solution by means of the specific interaction theory) was applied for predicting the distribution of Ga(III)[35] and Th(IV)[34] between aqueous solution and AG MP-1 resin containing T-azo-R.

From all of these studies with sulfonated azo dyes, Pesavento and Profumo[62] stated that the charge of this organic reagent should be considered as globally distributed on the molecule, and the binding of the metal ion to the ligand could be due to either a purely electrostatic, coordinative interaction between the metal ion and the phenolic oxygen, strictly localized at the complexation site, or an outer-sphere ion pairing.

Starting from the similarity between the retention of metal ions on modified resins and the stability of the metal-ligand complexes in solution, an equation was derived by Marina et al.[61] to relate the distribution coefficient of the metal ion between the resin and the aqueous phase and the pH of the external solution. This equation included the selectivity constant corresponding to the ion exchange between the metal ion in solution and protons in the resin, the first dissociation constant of the ligand in the resin phase, the complex formation ligand-metal ion in the aqueous solution, the ion-exchange capacity of the nonloaded resin, and the complexation coefficient of the metal ion in solution. All of these quantities was perfectly known from data in the literature. In this way, the selectivity of various loaded resins and the theoretical range of pH in which a metal ion goes from null fixation to quantitative retention were established for several resins loaded with SPADNS, 8-quinolinol-5-sulfonic acid, SSA, and tiron.

From a very different point of view, Wakui et al.[24-26] proposed the use of a modified resin as a stationary phase that could readily be prepared by impregnation of a commonly employed extractant (PC-88A) into porous polymer beads of Amberlite XAD-7 resin. Starting from this assumption, these authors gave an equation that predicted the variation of the distribution ratio as a function of pH and reagent concentration. Analysis of the distribution behavior of rare earth elements between the resin phase and the acid aqueous solution revealed the increase in the distribution ratio at a given pH with the decrease of ionic radii of lanthanides, in analogy with the trend observed for the solvent extraction systems with other commonly employed extractants.

2. Preconcentration and Separation of Metal Ions Off-Line

a. Experimental Procedure

As shown in Table 1 and as we have already mentioned, static (batch) and dynamic methods are effective procedures for equilibrating the ligand-immobilized resins with a solution of metal ions and determining the sorption of these elements.

When sorption of metal ions on modified resins is carried out by the static procedure, a sample of the loaded resin is shaken with a given volume of the metal-ion solution. After reaching equilibrium, the residual concentration of the metallic cation in solution is measured by atomic absorption spectrometry,[16,19-22,27,29,39-42,44] visible spectrometry[17,28,33-35,43,45,63] inductively coupled plasma atomic emission spectrometry[17,24-26,41] or electrochemical methods.[35,45] Thus, the capacity of sorption or the percentage retention of several metal ions on modified resins can be given. Desorption of metal ions from the resin is usually carried out with mineral acids such as HNO_3 and HCl (see stripping agents in Table 1) once the resin is separated from the supernatant solution by filtration.

In the dynamic technique, the metal-ion solution is passed through a column packed with the resin, at a constant flow rate. The effluent fractions are collected and analyzed for the presence of metal ions by any of the mentioned analytical techniques. Frequently, the sorbed metals are eluted with a stripping agent and the eluate is collected and also analyzed for determining metal ions.[17,19,20,23,27,29,38-41,43,44] The dynamic method is particularly advantageous for more efficient separations of microelements and with large volumes of sample.[6]

In metal-ion retention by modified ion exchangers, it is of the utmost importance to select a ligand that, once it is immobilized in the resin, may form complexes of different stability with the various metal ions in solution. The stronger the stability of the complex with the element of interest, the more selective is the sorption. In addition, the dependence of the complexation ability of ligand-loaded resins on the pH of the solution should be considered.[6,32] Furthermore, in the experiments of preconcentration of metal ions by the dynamic method, the effectiveness of metal retention is affected not only by the pH of the solution, but by the eluent and also by the solution flow rate.[29,41]

By choosing the appropriate experimental conditions for the specific ligand deposited on the resin, one can obtain the required selectivity with respect to a given metal ion or group of metal ions.[6]

b. Applications

The investigations on the application of ligand-loaded resins to metal ions (Table 1) proceeded from the study of sorption of a sole element, through preconcentration and separation of mixtures containing two metal ions, to selective separation of a great number of metal ions in solution.

With respect to the first application, sulfonated azo dyes, such as chromotrope 2B[33] or T-azo-R,[34] immobilized on strong base anion-exchange resins were used for theoretical studies on sorption of aluminum and thorium, respectively.

In relation to the separation of mixtures containing two metal ions, as shown in Table 1, Amberlyst A-26 resin loaded with pyrocatechol violet and Dowex 2 resin loaded with pyrocatechol violet or with xylenol orange were proposed and used for preconcentrating cadmium and lead[42] and copper and cadmium,[16] respectively, prior to their determination by flame atomic absorption spectrometry. In fact, when using the PV-modified Amberlyst A-26 under optimum experimental conditions, the concentration factor (using 1 g of this resin) was 90 for Cd(II) and Pb(II); other cations did not interfere up to ten-fold excesses. Moreover, when this method was applied to determine both metal ions in river water samples, the results obtained (on the order of 5.9 to 6.8 μg/ml cadmium and 10.4 to 14.7 μg/ml lead) were comparable with the values obtained by using the standard addition method in flame atomic absorption spectrometry.[42]

Cadmium and copper could be collected effectively (94 to 97% from solutions having a concentration of 0.01 μg/ml) on either of the two loaded Dowex 2 resins from solutions of these elements having a concentration on the order of 0.01 μg/ml. The metal-ion sorbing capacity of both resins was found to be $\leqslant$ 100 μg metal per 100 mg resin. However, Dowex 2 loaded with xylenol orange had a greater sorbing capacity than the pyrocatechol-violet-modified resin. When applying this ligand-immobilized resin for the analysis of Cd(II) and Cu(II) in river water, the results obtained were similar to those obtained with the standard addition method.[16]

Similar analysis can be done with respect to the preconcentration of cadmium and zinc with PV-loaded Amberlite XAD-2:[22] the concentration factor was 100 for both metals and, furthermore, this method could be applied for determining Zn(II) and Cd(II) by flame atomic absorption spectrometry in river water samples.

Finally, Pesavento et al.[35] reported the possibility of separating Ga(III) traces from Al(III) with T-azo-R-loaded AG MP-1. In fact, the modified resin did not sorb Al(III), and by treating a synthetic sample containing 0.1 *M* Al(III) and 1×10^{-5} *M* Ga(III) with 5 g of resin loaded with 1 mmol T-azo-R, 98% Ga(III) was sorbed; recovery of gallium with 0.2 *M* nitric acid was 99.3%.

When dealing with the applications of modified resins to selective concentration and separation of certain elements in the presence of others, the majority of authors explored, under static conditions, the possibility of the application of modified resins for sorption of the metal ions of interest and the total sorption capacity of the resin. Once the optimum experimental conditions were chosen, the dynamic procedure could be employed for more efficient preconcentration and separation of metal ions. In fact, several authors studied static sorption of divalent and trivalent transition elements on different ligand-resin systems as a function of pH, and the values of percentage metal sorbed,[19,20,27,39-41,44] coefficient of distribution[24-26] or total capacity[17] over the pH range from 1 to 12 were reported in each case. The results obtained in these investigations confirmed that the pH of the solution was an important parameter to be considered due to the modification that it caused to the retention of the metal ion on the modified resin. With few exceptions, the sorption of metal ions increased when the acidity of solution decreased.

According to these studies, SPADNS-loaded Amberlyst A-26 in acid medium (pH 1.3 to 1.5) is selective for Bi(III) and Zr(IV) whereas Co(II), Ni(II), and other metal ions are practically unbound to the resin at this pH.[40] This behavior was confirmed in dynamic conditions because Bi(III) was quantitatively separated from numerous transition elements even when these ions were present in 2500-fold ratio to Bi(III). Moreover, by using a column resin bed modified with two ligands, that is, SPADNS and nitroso-R salt, quantitative separation of cadmium ($\geqslant 0.01$ *M*) from Pb(II), Cu(II), Co(II), Fe(III), and Ni(II) was possible by the reverse separation method, as is shown in Table 4. Results from the dynamic experiments with orange-II-loaded resin showed the separation, at slightly higher pH values than those for the SPADNS resin, of Al-Ni, Pb-Mn(II), Al-, Pb-, Zn-Ni, and Al-, Pb-, Zn-Mn(II) (see Table 1). Moreover, Marina et al.[23] reported that SPADNS immobilized on the anion exchanger Amberlite IRA 400 gave good results in the separation (column performance, pH 6.85) of Cu(II), Fe(III), and Pb(II) from Mn(II) and Zn(II).

Brajter and Dabek-Zlotorzynska[20] reported that Amberlyst A-26 modified with another sulfonated azo dye, ANS, exhibited an exceptionally high affinity for Ag(I) in an acid medium while practically no other metal ions studied (Cu, Pb, Zn, Ni, Co, Fe, or Cd) were retained under the same conditions. For this reason, it was possible to selectively separate these ions [Ag(I) in the concentration of 0.22 to 22.0 μg/ml] in the column. The authors proposed the application of this method to the fast determination of silver in copper ores. Furthermore, this resin loaded with thoron[19] was almost totally selective for Fe(III) in the presence of other transition elements.

Moreover, the study of the pH dependence of the Cd(II), Pb(II), Cu(II), Co(II), Ni(II), and Zn(II) uptake on xylenol-orange-loaded anion exchangers[39] revealed the ability of this resin to sorb these metal ions at pH > 6.0. Good results were obtained for the preconcentration of microamounts of Cd(II) and Zn(II) in the column (pH 7.8) and for selective elution of these species with chelating agents, for example, NH_3 (for cadmium) and EDTA (for lead). Similarly, an anion exchanger (Amberlyst A-26) loaded with xylenol orange (XO) was employed as a separation method, which was a prior step in the determination of mixtures of Zn(II)-In(III) and Pb(II)-In(III) without the inter-

TABLE 4
Separation of Cd From Other Metals on Mixed NRS / SPADNS Resins

Amount of Cd[a]				Amount of Me		
Added (μg)	Found[b] (μg)	Error (%)	Metal ions in mixture	Added (μg)	Found[b] (μg)	Error (%)
20	20	—	Cu	20	20	–
			Fe	20	19.4	−3.0
			Pb	20	19.2	−4.0
			Ni	20	19.6	−2.0
			Co	20	20.1	+0.5
0.5 (corresponds to 0.01 ppm)	0.48	−4.0	Cu	20	20	—
			Fe	20	19.5	−2.5
			Pb	20	19.4	−3.0
			Ni	20	19.8	−1.0
			Co	20	19.9	−0.5

Note: Diameter of column 5.8 mm; 0.2 g of 0.1 − 0.2 m resin beads; 0.1 g of NRS resin (NRS 0.5 mmol / g) + 0.1 g of SPADNS resin (SPADNS 0.1 mmol / g); 50 ml of solution at pH = 6.3 − 7.0 loading and elution at 1 ml / min, other metals all eluted with 10 ml of 2 *M* $HClO_4$; average of 10 determinations. [From Brajter, K; Dabek-Zlotorzynska, E., *Talanta*. **1986**, *33(2)* 149 − 154. With permission.]

[a] Cd passes through the resin bed without being retained if its concentration is $\geqslant$ 0.01 ppm.

[b] For determination by AAS, standards were prepared in the same way as the sample solutions.

ferences of other metal ions in the indium analytical signal.[21] From that point of view, when comparing this method for eliminating matrix interferences with other classical separation methods, namely, coprecipitation and precipitation of the matrix by use of H_2SO_4, the XO-loaded resin permitted the simple and fast separation of the elements of interest using a very short resin bed.

Finally, an arsenazo-III-loaded D296 porous anion exchanger was used for preconcentrating and determining rare earth metal in geological sediments.[43]

The modified anion exchangers as well as the nonionic sorbents immobilized with an appropriate organic reagent may be used as an effective preconcentration procedure for metal ions. In fact, from experiments of retention of several metal ions on EBBR-modified Amberlite XAD-2,[41] a complete retention in specified pH ranges was observed for Cr(III), Fe(III), In(III), Cu(II), and Ni(II); the most favorable results were for Ni(II) (almost 100% metal retained at pH >3). Moreover, the selectivity of this modified resin exhibited a slightly better selectivity than an EBBR-modified anion-exchange resin (Amberlyst A-26); thus, the former could be used for a better selective Ni(II) preconcentration in atomic absorption spectrometry. Under optimum column chromatography conditions, at a preconcentration time not exceeding 1 h and with almost negligible interference of alkaline earth metal salts and transition metals present in solution, Ni(II) could be determined at the 10 μg/ml level.

When Amberlite XAD-2 was loaded with the sulfonated derivative of an aromatic complexing agent, pyrocatechol violet, the observed selectivity sequence of sorption of metal ions at pH 1.0 was Bi(III) $\geqslant$ In(III) $\geqslant$ Pb(II) $>$ Cu(II) $>$ Fe(III) $>$ Co(II) $>$ Ni(II).[44] From the differences in the fixation of the metal ions under study, the separation of Bi(III) from Cu(II) was of practical interest for analysis of copper alloys. In the dynamic method, under the most adequate experimental conditions and by assuming 2 l of 0.5 μg/ml indium solution and 0.05 μg/ml lead solution, the concentration factors of 100 and 80, respectively, were obtained. This method was used for preconcentration and determination of lead in tap water.

According to the results presented in Table 1, the immobilization of heterocyclic azo compounds such as PAN[29] and PAR[27] on Amberlite XAD-4 and XAD-2, respectively, was also useful for separation and preconcentration of metal ions. By a batch procedure, copper and iron were almost quantitatively sorbed on PAN-loaded Amberlite XAD-4, whereas lead, nickel, cadmium, and zinc were only 80 to 85% sorbed. The column method was applied to the analysis of river water, although, in this case, slight interference due to competitive sorption of calcium and magnesium was observed.[29] With PAR-loaded Amberlite XAD-2 in the presence of tetren as a competing ligand, differentiation of retention of Ag(I), Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Pb(II), Fe(II), Fe(III), Sb(III), and Zr(IV) occurred. On the basis of these results, Ag(I) was quantitatively isolated from Cu(II) in static conditions, and in dynamic experiments, if tetren was added to the feed solution with the pH in the range 7.2 to 7.7, silver was quantitatively retained in the modified resin, independent of the copper content.[27]

Data from studies with oxine- and 5ClDMPAP-immobilized Amberlite XAD-4 and XAD-7,[45] and glycolate-loaded XAD-4[30] evidenced the utility of these modified resins for preconcentration of rare earth elements and transition metal ions, respectively.

3. Preconcentration and Separation of Metal Ions On-Line

As previously summarized, complex-forming resins have principally been used for off-line preconcentration, selective separations, and matrix elimination before the sample is analyzed by another technique such as UV/vis or atomic absorption spectrometry. However, very little work deals with the use of these resins as stationary phases connected on-line with methods of separation and/or analysis.

a. Chromatographic Techniques

The most direct approach to the use of columns packed with ligand-modified resins for trace metal analysis in complex matrices using high performance liquid chromatography systems (HPLC) is frequently carried out by a hybrid method of conventional ion chromatography and HPLC on reversed columns.[6,36–38] This type of chromatography with ligand-immobilized resins presents the following advantages over the traditional technique:

1. It is possible to overcome the difficulties of conventional ion chromatography with samples of high ionic strength.[36–38]
2. The choice of the modified exchanger used allows improvement of the compatibility with solvents used in the classical technique, stability across a wide pH range, and stability to high back-pressure.[38]
3. Pre-treatment of the sample solution is generally not necessary and simpler mobile phases can be used because selectivity is designed into the stationary phase.[6]
4. A favorable separation can be achieved without using an expensive reagent as an eluent, that is, acid solutions.

As a first approximation to this matter, the chromatographic separations of the Gd(III) and Y(III) pair,[24] La-Pr-Nd and Ho-Er-Tm mixtures,[26] and the selective recovery of Sc(III) from acid-leached solutions of wolframite and tin slag[25] have been carrried out using a PC-88A-Amberlite XAD-7 resin as the stationary phase of chromatographic columns (93.5 x 10 cm i.d.). Yttrium(III) and gadolinium(III) (0.1 mmol) were successfully separated into the components by elution with 0.9 *M* HCl. Moreover, La was favorably separated from Pr and Nd (with mobile phases of 0.9 *M* HCl) while the resolution of the latter remained insufficient. The separation factors of Ho-Er-Tm were mutually rather large, being higher than the concentration of acid in the mobile phase (1.4 M HCl). Last, a selective and effective separation of Sc from Mn(II), Y(III), Sb(III), and Fe(III) was achieved.[40]

In order to produce an efficient column capable of separating groups of metal ions, both the effect of dye type and substrate characteristics needed to use the dye-coated high-performance liquid chromatography resins were studied.[36,37] From the findings of these studies it is encouraging to note that the efficiency of the large particle size dye-coated columns changed markedly with different substrata and chelating dyes. In this way, for a particular dye, the differences found in the pH for complete retention were due to stereochemical effects, because with larger pores there was less steric hindrance for surface chelation.[36,37] It is interesting to note that, for example, a xylenol orange-coated Dowex 1 X8 column has been used successfully as a preconcentration-matrix elimination column coupled to ion chromatography for the determination of trace metals in concentrated brines.[38] Using this preconcentration column and a mobile phase of 0.2 mol/l lactic acid and 0.15 mol/l ethylenediamine at pH 2.8, the chromatography of four alkaline earths (Mg-Ca-Sr-Ba) at the low nanogram per milliliter level was completed within 10 min. Moreover, the methodology was used to monitor on-line feed brines used in the chloro-alkali industry.

Investigations on small particle size dye-coated columns such as PLRP-S 8 μm resin revealed that the efficiency of this column approached that of a commercial column that contained similar functional chelating groups (TOSOH column).[36,37] By using the xylenol orange dye-coated column, four alkaline earth metals were separated in 1 mol/l KNO_3, under isocratic conditions, in approximately 8 min (Figure 1) . Moreover, isocratic separation of cadmium and lead was achieved at pH 2.5 (Figure 2). Small particle size coated columns were also used for separating metal ions with gradient elution.[36] In fact, the separation of transition metals such as cadmium, lead, and copper in 1 mol/l KNO_3 and 1000 μg/ml Mg^{2+} was achieved in approximately 20 min by using a gradient from pH 7 to 4 and a chrome azurol S dye-coated column PLRP-S (Figure 3).

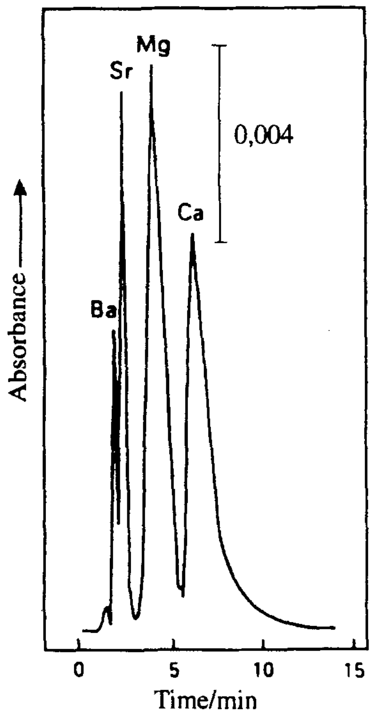


FIGURE 1. Chromatogram showing separation of 10 ppm Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in 1 mol / dm^3 KNO_3 at pH 7.7 using the xylenol orange dye-coated PLRP-S column with PAR-ZnEDTA as the postcolumn reagent. (From Jones, P.; Challenger, O. J.; Hill, S. J.; Barnett, N. W. *Analyst.* **1992**, *117*, 1447 – 1450.

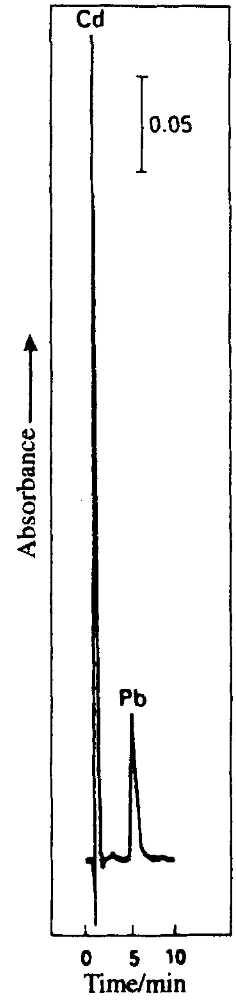


FIGURE 2. Chromatogram showing separation of 5 ppm Cd^{2+} and 10 ppm Pb^{2+} in 1 mol dm^3 KNO_3 at pH 2.5, using the xylenol orange dye-coated PLRP-S column. (From Jones, P.; Challenger, O. J.; Hill, S. J.; Barnett, N. W. *Analyst*, **1992**, *117*, 1447 – 1450.

From these findings, it is obvious that the full potential of dye-coated columns (in particular, small particle size coated columns) for high-performance separation of trace metals should be considered and investigated with special attention in order to improve the efficiency of separations by chromatographic techniques.

b. Flow-Injection Techniques for Sample Preconcentration and Matrix Modification: FIA

On-line column preconcentration methods for trace elements prior to metal-ion analysis by AAS or ICP present numerous and important advantages over conventional off-line procedures either with columns or under static conditions. These benefits are fundamentally a much greater efficiency, higher enrichment factors, and low consumption of sample and eluent. However, the application of on-line column preconcentration may exhibit certain problems such as interference effects.[18] Thus, the range of solid phases used in the on-line preconcentration columns has been extended.[64]

Numerous papers have reported the use of classic chelating resins for on-line trace metal enrichment and matrix isolation prior to an analysis technique.[6,64] In these resins, the ligand was coupled by chemical reaction, by direct polymerization, or else these substrata were available commercially.[65,66] In fact, large columns of chelex-100 and 8-quinolinol chelating exchanger[67] have been

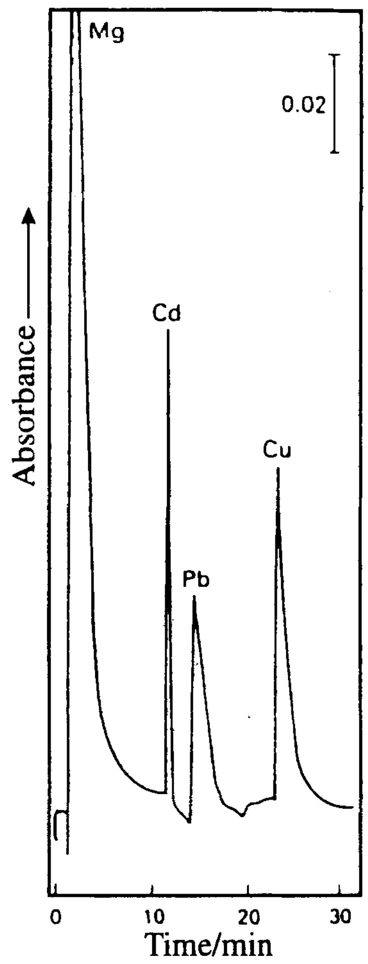


FIGURE 3. Chromatogram showing separation of 5 ppm Cd^{2+} and Cu^{2+} and 10 ppm Pb^{2+} in 1 mol / dm^3 KNO_3, and 1000 ppm Mg^{2+} with the chrome azurol S dye-coated PLRP-S column, using gradient elution from pH 7 to 4 over 10 min, then to pH 1.5 over a further 10 min. (From Jones, P.; Challenger, O. J.; Hill, S. J.; Barnett, N. W. *Analyst*, **1992**, *117*, 1447–1450. With permission.)

used for on-line column preconcentration in flow injection with atomic spectrometric detection systems. Fang et al.[65] described the use of chelex-100 (with an iminodiacetate chelating functional group), the weakly acid Amberlite IRC-50, another weakly acid resin 122 (with salicylic acid functional groups), and azo-immobilized 8-quinolinol exchangers for determination by AAS of trace amounts of Cu, Zn, Pb, and Cd at and below microgram per liter levels in a dual-column flow-injection system with sequential elution/preconcentration.

Although the use of ion-exchange resins and nonpolar sobents modified with chelating ligands in flow-injection systems has not been widely investigated, these modified resins seem promising because of their notable advantages:

1. The possibility of controlling the capacity and selectivity of metal sorption by the appropriate choice of loading organic reagents, thus increasing the efficiency of the process.
2. The capacity to form stable chelates with metal ions even at slightly acid pH.
3. Fast kinetics of the chelating or ion-exchange process, which results in a more ready elution of the analyte from the surface, a smaller volume of eluate, and, thus, an improvement in the enrichment ratio.[6,18,65,66]

A nonpolar sorbent, Amberlite XAD-2, loaded with pyrocatechol violet, PAR, or eriochrome blue-black R was used for the preconcentration and determination of copper[18] and nickel[41] for the rapid and selective separation of silver in copper ores.[27] From FI-AAS measurements of copper performed in 1% borate buffer solution of pH 8 with Amberlite XAD-2 modified with different ligands[18] it can be concluded that under the experimental conditions of this work, a higher efficiency for the sorption of Cu(II) was obtained for PV, probably due to kinetic factors more than to the stability of the chelates formed. With a 70 x 3 mm microcolumn containing the modified resin and using 2 mol/l HNO_3 as the eluent, copper was determined in natural water at the nanogram per milliliter level using a preconcentration time of 20 min.

The XAD-2-PAR resin in the presence of 0.05 *M* tetren (pH 7.2 to 7.7) was successfully applied to the on-line isolation of silver.[27] The application of this flow-injection system to selective separation of Ag(I) in copper ores takes less than 1 min and the column can be used several times with the same purpose.

In less than 1 h, flow-injection atomic absorption spectrometry of nickel with preconcentration in a microcolumn of EBBR-modified XAD-2 resin allowed the detectability of flame AAS determination of nickel (0.1 μg/l) to be improved by up to 1000 times.[41]

c. Ion-Exchange Phase Absorptiometry

The technique of ion-exchange absorptiometry, based on direct measurement of the degree of light absorption by an ion-exchange resin phase that has sorbed a sample component, has been widely applied to the determination of numerous metal ions in very diluted sample solution, in particular, water samples.[56,57] A more rapid, simple, and sensitive approach can be obtained when ion-exchanger phase absorptiometry is combined with flow-analysis.[56,58–60,68]

Most of the procedures for color development in the ion-exchanger phase are based on addition of the ion exchanger to the sample solution together with the chromogenic agent, which is highly specific for the analyte. The resultant complex is sorbed onto the ion exchanger[56,58] or else, the analyte is first sorbed onto the ion-exchanger from solution and then the chromogenic agent is added.[55]

However, little work has been done with ligand-immobilized ion exchangers. The main advantages of ligand-loaded resins, namely, the stability of the immobilized reagent on the substrate, fast kinetics of metal-ion retention, and reversibility of the metal-ion sorption process, together with the compatibility of these modified resins and the detection system used, enable the use of these solid phases in the FIA/ion-exchanger phase absorptiometry analysis.[68] This procedure was employed in earlier works when the colored complexes could not be directly sorbed from the sample solution[55] and actually has been employed in the determination of V(V) in natural water[69] and for the determination of Cu(II) at the nanogram per milliliter level.[68] Certainly, Matsuoka et al.[69] used an immobilized organic reagent that exhibits a high selectivity and sensitivity toward V(V), for example, 2-[2-(3, 5-dibromopyridyl)azo]-5-dimethylamino benzoic acid (PAMB), onto anion-exchanger resin AG 1 X2. After passing through a pretreatment column packed with Sephadex G-25 gel, the V(V) was introduced into the carrier solution stream (0.2 mol/l formate buffer solution) in the flow system to reach the flow-through cell packed with the modified resin. The attenuation in the resin was directly measured by visible spectrometry. A detection limit of 0.6 ng V(V) was found, and the vanadium concentration in five or six samples could be determined within 1 h. Similarly, Lazaro et al.[68] used this method for the determination of Cu(II), based on its reaction with PAN immobilized on a Dowex 50 X4-400 cation-exchange resin, by FIA. Later elution of Cu(II) with thioglycolic acid made the system reversible. The determination limit achieved by this system was 1 ng/ml and the sampling frequency, under optimum experimental conditions, was 10 to 110 per hour.

III. FUTURE DEVELOPMENTS

An appropriate choice of the species to be loaded onto the conventional resin allows the use of "new modified resins" for the investigation and analysis of anions and cations as well as the application of these resins to biochemical and clinical purposes. In addition, organic reagent immobilization on other types of supports, such as silica, cellulose, and controlled porosity glass, among others, has proven to be extremely efficient for preconcentration and separation of metal ions mainly in flow-injection systems and chromatographic techniques.

In order to exploit the full potential of these new modified resins and solid sorbents and to examine their future possibilities, we shall discuss the latest findings on these subjects.

A. Other Applications of Ligand-Loaded Resins

1. Selective Preconcentration and Separation of Anions

In an attempt to develop an effective method for the selective collection and determination of low concentrations of fluoride ions in samples of diverse origin, a new functional resin was prepared from anion-exchange resin loaded with lanthanum complexes of alizarin fluorine blue {3-[*N*,*N*-di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone} (AFB-La)[70] or alizarin fluorine blue sulfonate {3-[*N*,*N*-di (carboxymethyl)aminomethyl]-1,2-dihydroxy-anthraquinone-5-sulfonate} (AFBS-La).[71] From the results obtained by Chikuma et al.,[70] when an anion-exchange resin, Amberlite CG-400 (IRA-400 type, 100 to 200 mesh, 8% divinylbenzene), was loaded with AFB-La complex, it can be stated that this functionalized resin may be satisfactorily used for the selective adsorption of fluoride ions in batch and column operations even at concentrations of this species lower than that which could be determined directly by using ion selective electrodes. Moreover, the interferences caused by common cations and anions was not serious except for Al^{3+} and Fe^{3+}. It is important to emphasize that the amount of total fluoride ion adsorbed on AFB-La-loaded resin was about six times higher than that adsorbed on the anion-exchange resin without AFB-La.

Subsequent investigations carried out by Okabayashi et al.[71] showed that the use of anion-exchange resin CG-400 loaded with AFBS-La complex instead of the resin loaded with AFB-La complex was more effective for the selective preconcentration of fluoride ions, because the sulfonate group in the reagent enhanced the reaction rate of the immobilization of the reagent on the resin and increased both the amount of reagent loaded on the resin and the stability of the new functional resin.

The above-mentioned resins were applied to the preconcentration of fluoride ions in tap water and for the removal of this anion in waste water treatment.

Amberlite IRA-400 loaded with a Pr(III) complex of alizarin fluorine blue was also succesfully employed for selective sorption of fluoride ions in solution.[72]

Recently, inorganic ligands, such as thiocyanate, also have been immobilized in anion-exchange resins for the purpose of determining microquantities of fluoride by ion-exchange spectrophotometry.[73] This method was suitable for the estimation of fluoride in drinking water in the presence of Cl^-, Br^-, I^-, S^{2-}, and SO_4^{2-} when a precolumn in the form of Ag^+ and Ba^{2+} was coupled to the SCN^- column.

2. Electrochemical Analysis

Due to the versatility of ligand-loaded resins, the incorporation of these materials into electrochemical analysis may be considered as a novel sensitive and selective technique in the determination of elements at trace levels.

As a matter of fact, we do not know yet of any study on this subject. However, the potential advantages of the use of ligand-immobilized resins and glassy carbon disk electrodes for the liquid chromatography-electrochemical determination of Fe(III) has been proposed.[74] In this study, a thoron-loaded Amberlyst A-26 resin, which was almost specific for Fe(III) as the counterion,[19] enabled the chromatographic separation of Fe(III) from Cu(II), Ni(II), Co(II), Zn(II), and Pb(II) as well as Ca^{2+} and Mg^{2+}. The Fe(III) eluted from this resin with 1 *M* HCl 1 *M* KCl solution was thus transported to the electrochemical detector cell containing a Ni-CN-Fe coated glassy carbon electrode, which allowed the preconcentration/determination of this metal ion at levels of 0.0001 to 0.005 μg/ml.

An in-depth investigation into the non-electrochemical step of preconcentration or accumulation of the analyte on the surface of carbon electrodes has led to the use of chemically modified electrodes containing highly selective modifiers, such as dimethylglyoxime, 2,9-dimethyl-1,10-phenanthroline, or 1-(2-pyridylazo)-2-naphthol (PAN), for the determination of a wide variety of metal ions[75] and, what is more, the use of carbon paste electrodes modified with conventional ion-exchange resins.[76] This later method was chosen due to the simplicity of the electrode construction and its easy regeneration by differential-pulse voltammetry. In fact, using differential-pulse voltammetry, Hernandez et al.[76] carried out the determination of Cu(II) at levels down to 18 nM with a working electrode made of a mixture of carbon paste and Dowex 50W-X8 cation-exchange resin and a contact of platinum. This method was successfully applied to the determination of copper in pharmaceutical products. A solid electrode modified with a cation-exchange resin also has been employed for simultaneous estimation of Cu(II) and Hg(I) down to nanogram per milliliter levels by voltammetry.[77] Moreover, voltammetric determination of iodide with a carbon paste electrode modified with an anion-exchange resin has been carried out.[78]

More recently, a novel separation electrochemical ion exchange (EIX) has been developed.[79] In this technique, ion-exchange material (a weak acidic exchanger) was incorporated into an electrode by means of a binder. Absorption and subsequent desorption of metal ions was controlled by application of a potential between the EIX electrode and a counter electrode, and, thus, eluant chemicals usually were not required. This versatile technique is currently being developed for nonnuclear applications, for example, removal of heavy metals from industrial effluents, removal of anions from different samples, etc.

On the other hand, carbon paste electrodes modified with Dowex A-1 chelating exchange resin (50 to 100 mesh, H^+ form) were used for the determination of very low quantities of lead (4 to 100 ng/ml) in rain water and human urine by cyclic voltammetry.[80] The process can be described according to three stages:

1. Preconcentration of lead in the surface of the protonated form-modified carbon paste electrode.
2. After preconcentration, the electrode is transferred to a voltammetric cell, containing a diluted mineral acid as supporting electrolyte, for the electrochemical measurement. In this step, the elution of the preconcentrated lead is achieved and this metal ion is reduced by applying a cathodic potential for a time.
3. Regeneration of the electrode surface in an acidic solution.

According to these findings, the application of modified resins that exhibit different selectivity toward metal cations depending on the complexing agent immobilized onto the resin should be beneficial for better control of the preconcentration step in the surface of the electrode in which the ligand-loaded resin has been directly incorporated. In fact, these systems combine the stability and sensitivity of glassy carbon electrodes with the high selectivity of resins modified with complexing reagents.

B. New Modified Resins and Their Applications

Reagents other than organic ligands with ion-metal complexing properties can also be immobilized onto anion-exchanger stationary phases with different applications.

1. The Technique of Optical-Fiber Chemical Sensing

In recent years, the technique of optical-fiber chemical sensing has grown steadily in importance. Particular attention has been given to fiber-optic devices for the measurement of pH, gases, and metals for industrial, environmental, and clinical applications. In this sense, several authors have reported the use of ligand-loaded resins for the development of chemically sensitive fiber-optic sensors for measurement of pH.[81-84] In fact, small sensors based on immobilization of acid-base indicators, such as bromothymol blue,[81-84] bromophenol blue,[81,82] bromocresol purple, phenolphthalein,[81] phenol red, chlorophenol red, alizarin,[83] 2,6-dichlorophenol-indophenol,[82] etc., on nonionic resins, that is, Amberlite XAD-2 and XAD-4, have been developed and used for pH measurements.

The technique of dye immobilization on a polymeric matrix seems to be promising for the development of fiber-optic pH sensors. These fiber-optic probes present advantages over a conventional electrode in safety, reliability, applicability, and cost.[81] However, care must be taken because the adsorption on the polymeric matrix can affect the acid-base properties of the indicator[82,83] and some adventitious organic matter may be co-adsorbed in the nonselective substrate, thus influencing the response of the reagent.[84]

2. Biochemistry and Pharmaceutical Industry

Jacobson and Guiochon[85] described a fast and simple method for the immobilization of a biopolymer, namely, bovine serum albumin (BSA), on a quaternary ammonium anion-exchange stationary phase. The immobilization of the albumin was carried out *in situ* by frontal chromatography on a column packed with the anion-exchange material at a pH above the isoelectric point of BSA (pI 4.7). The BSA-loaded anion-exchanger stationary phase separated the following racemic mixtures in a liquid chromatograph (UV detector, mobile phases varied in phosphate concentration or in percent added 1-propanol): triptophan, mandelic acid, *N*-benzoylalanine, 2-phenylpropionic acid, and 2-phenylbutyric acid.

Moreover, an on-line infrared analyzer system to monitor cephamycin C loading on a cation-exchange resin (Dowex 50W X4)[86] was developed in order to improve productivity, avoid product losses, minimize raw material cost, and reduce off-line laboratory testing in the isolation and purification of cephamycin C, which was used in the pharmaceutical-chemical industry.

The immobilization of organometallic aluminum compounds on conventional ion-exchange resins was useful for preparation of highly active and stable immobilized lipid — or polysaccharide — degradation enzymes.[87] In addition, a novel weak anion exchanger modified with tosylated cyclodextrin was used for the separation of biological compounds, that is, proteins, nucleotides and nucleic acids.[88]

On the other hand, Saito et al.[89-93] reported that some ion-exchange resins modified with metalloporphins as terfunctional reagents behave as good artificial mimeses of catalase and peroxidase. Both enzymes have been used widely for the determination of hydrogen peroxide released from some substances that are the subject of clinical analyses; however, these enzymes are not stable enough and frequently present a low reproducibility of their activity. In this sense, the catalase-[89,90] and peroxidase-like[91,92] activities of an ion-exchange resin (Amberlite IRA-900, 24 to 42 mesh, NO_3^- form) modified with metalloporphyrins, such as metallo-tetrakis(sulfophenyl)porphine, metallo-tetra(*p*-carboxyphenyl)porphine, metalloprotoporphyrin, metallo-chlorophyllin, and metallo-tetrasulfophthalocyanine, were tested. These functional resins were easily prepared because the metalloporphyrins, which in solution are structural analogues of the active centers of catalase and peroxidase, are retained firmly on the anion exchanger due to strong physical adsorption. Moreover, the activities of the resins were retained even after repeated use (ten times), and interference by common foreign substances, that is, heparin, EDTA, ascorbic acid, Ca^{2+}, Mg^{2+}, PO_4^{3-}, Cl^-, etc., was found to be negligible. Evaluation of the enzymic activity by using the tested resins found that the Amberlite IRA-900 modified with manganese-tetrakis(sulfophenyl)porphine was the best resin. In fact, the presence of manganese or cobalt as a central metal ion was found to be essential for the activity.[90]

Recently, Mifune et al.[94] reported that the anion-exchange resin Amberlite IRA-900 modified with Mn^{3+}-tetrakis(sulfophenyl) porphine and a cation-exchange resin (Dowex MSC-1, 20 to 50 mesh) modified with Mn^{3+}-tetrakis(1-methylpyridinium-4-yl)porphine exhibited uricase-like activity, and thus both resins are useful for the determination of uric acid.

3. Removal of Toxic Organic and Inorganic Species

Few applications have been found for the new modified resins in the qualitative and quantitative analysis of organic and inorganic toxic species. Nevertheless, Hiraide et al.[95] developed a method for the quantitative separation and analysis of humic and fulvic acids from cations in samples such as river water. In fact, they used the nonionic XAD-2 resin (pulverized to 1 to 10 μm particles to achieve effective sorption) in which the cation-binding sites were saturated with indium ions to sorb, under dynamic conditions, both humic and fulvic acids through complex formation. The recoveries were determined from the decrease in absorbance of the effluent at 400 nm. Under optimum experimental conditions, the sorption was quantitative and the interferences caused by metal anions such as Cr(VI), EDTA complexes of cadmium, Cu(II) and Pb, and colloidal hydrated Fe(III) oxide, were negligible.

On the other hand, Hogarth[96] developed an ion-exchange resin bead test for the cyanide anions. According to this procedure, the strongly basic Amberlite IRA-400 resin (Cl^- form) was loaded with a Pd(II) complex of 4-(2-pyridylazo)-resorcinol, and the resulting modified resin (with a dark rose/violet color) was allowed to react with a cyanide-containing solution. The formation of a more stable cyanide complex caused a color change in the resin that was indicative of the presence of cyanide ions in solution. This qualitative procedure has the advantages of being quick, economical, requiring only small samples of solution, and being accurate enough to detect 10 μg/ml or even lower levels of cyanide.

All of these investigations indicate that these new functional resins have a quite attractive and promising field of application in biochemistry, the pharmaceutical-chemical industry, and the clinical field.

C. Organic Reagent Immobilization on Supports Other Than Resins

The incorporation of chelating reagents in various column-packing materials different from conventional anionic or nonionic resins with the aim of separating metal ions has also been reported.[66,97–105]. It should be noted that, in most cases, the complex-forming reagent is covalently attached to these supports and the mechanisms of ion-exchange or adsorption are not involved.

Silica[97–99] is one of the most extensively used inorganic supports because it is characterized by high mechanical strength, high thermal stability, resistance to high pressure, and stability toward organic solvents and mineral acids.[6] In addition, ligand-loaded silica supports have, in many cases, given more efficient and selective separations of metal ions, and they exhibit a high versatility.[97,99] However, they are unstable at high pH, leading to cleavage of the immobilized reagent.[15] One of the most convenient ways to attach an organic reagent to a silica support is by means of silylation reactions.[97,98] According to this procedure, a silica support modified with 2-pyridinecarboxyaldehyde phenylhydrazone (PAPH) was prepared and applied to the separation of mixtures of Fe(II), Co(II), Ni(II), and Cu(II).[105] In addition, silica immobilized PAPH was used as the stationary phase for effective separation and quantitative analysis of aqueous solutions containing Mn(II), Cu(II), Cd(II), Zn(II), Co(II), Pb(II) and Cu(II) by HPLC.[97] Verweij et al.[99] presented details of grafting two novel ligands, 2-(3, 5-dimethyl-1-pyrazolyl)ethylamine (Naed) and bis[2-(3, 5-dimethyl-1-pyrazolyl)ethyl]amine (ddaH) to silica by means of the bifunctional spacer (3-glycidyloxypropyl)trimethoxysilane (GLYMO). These new ion-exchange materials, under static conditions, selectively adsorbed Cu(II) from aqueous solutions containing a mixture of Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}.

The azo-immobilization of 8-hydroxyquinoline on controlled porosity glass (CPG) has also been reported.[66,103] CPG also has been used as a support for the immobilization of 8-hydroxyquinoline-5-sulfonic acid for the preconcentration of Cu(II).[105]

Cellulose is among the naturally occurring organic matrices used as a sorbent for the formation of ligand-loaded ion exchangers.[6,101] In fact, Beinrohr et al.[101] carried out the on-line preconcentration of copper for flame atomic absorption spectrometry using a spherical cellulose sorbent with chemically bound quinolin-8-ol.

On the other hand, synthetic organic compounds such as naphthalene also have been applied to prepare modified sorbents for the determination of several metal ions. Satake et al.[100] described the analytical potential for the preconcentration of nickel with 2,3-butanedione dioxime (DMG), acenaphthenequinone dioxime (ANDO), and their mixed ligands (DMG-ANDO). At a given pH range, nickel formed chelates with all of these ligands supported on microcrystalline naphthalene packed in a column. The metal complexes and naphthalene were then dissolved out from the column using a mixture of dimethylformamide and nitric acid, and nickel was then analyzed by atomic absorption spectrometry. This method was successfully applied for the determination of nickel in samples of different sources such as water, alloys of nickel, tea leaves, and pepperbush.

The method involving solid-liquid separation after the adsorption of metal ions on organic reagent-loaded sorbents such as thiol cotton, C_{18}-bonded silica gel, and a few metal oxides and hydroxides may also be successfully used for the determination of several metal ions.[100]

IV. SUMMARY AND CONCLUSIONS

The studies summarized in this review show the full potential of conventional anion-exchange resins and nonionic sorbents modified with chelating reagents for highly selective separation and preconcentration of trace metal ions in solution. Compared to the classical chelating resins prepared by synthesis, these new complexing resins, which can be used in both off- and on-line techniques (chromatography, flow-injection systems, and ion-exchange phase absorptiometry), appear to be a promising and sure alternative for highly selective separation and preconcentration of trace metal ions and inorganic anions as well.

Recently, attempts have been made to immobilize proteins, metalloporphins, acid-base indicators, and other reagents in conventional resins and other supports in order to use these modified resins in the pharmaceutical industry, clinical analysis, biochemistry, etc. Although the findings of these studies are satisfactory, further research is needed in this new field to exploit the possibilities and the great capacity of these modified resins by means of optimum selection of the reagent immobilized, the support, and the reaction medium.

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