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Chelation Properties of Highly Selective and Affinity Polymeric Complexing Agents

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Procedures are described to prepare γ-aminobutyrohydroxamate resin and its N-methyl and O-methyl derivatives. With the aid of a chemical method, IR and electronic spectra, and potentiometry, the chelating properties of these resins are compared with each other. The selectivity of resins for various metals is expected to be comparable to complexing properties of a monomer having a structure similar to that of active groups. This correlation was made quantitatively by measurement of metal capacity, fraction of sorption, pH and period for extraction of half the metal ions, stability constants etc. Not only γ-aminobutyrohydroxamate resin but also its N-methyl and O-methyl derivatives exhibit much potential for application in chelation ion chromatography.

INTRODUCTION

Hydroxamic acids have received considerable attention as reagents in analytical chemistry for gravimetric analysis, for solvent extraction and spectrophotometric determination of metals. The reagents are also useful in analysis of trace metals by flow injection analysis and high performance liquid chromatography.[1] Although Schwarzenbach[2] and Melnik[3] suggested that N-substituted hydroxamic acids should be more effective complexing agents than their N-unsubstituted analogues in strongly acidic media, most research on polyhydroxamic acids is concentrated on N-unsubstituted compounds, except work of Vernon and Eccles,[4] Winston and Mazza,[5] and Winston and Mclaughlin.[6] Phillips and Fritz explored extraction of metal ions with N-phenyl, N-methyl and N-unsubstituted hydroxamic acid resins, and compared the chelating properties of these resins.[7]

We prepared previously a γ-aminobutyrohydroxamate resin that simulates siderophore analogues exhibiting large binding efficiencies for transition-metal ions and adopting predominantly intramolecular complexation within a crosslinked polymer chain.[8] Here we apply this strategy of design and modular construction to prepare other siderophore analogues, namely its N-methyl or O-methyl derivatives. The chelating power of this group is modified by varying the inductive effect on the nitrogen atom and hydroxyl group. Steric effects due to substituents near the functional group are considered.

Chelating resins are used to determine trace metals with chromatographic detection. This method is termed chelation ion chromatography that combines analyte concentration and matrix elimination with analytical separations and selective detection for transition metals.[9] For this reason, many works attempt to improve retention of the metal on the chelating concentrator by decreasing the flow rate, adjusting the resin size, decreasing the concentration of the matrix and syntheses of high-capacity chelating resins. The hindrance in this field is that the optimum conditions for elution of concentrated metal ions and those for analytical separation are invariably opposed, as metal complexation depends on pH. This work is expected to provide useful information in chelation-ion chromatography through investigation of chelation properties of these resins.

EXPERIMENTAL SECTION

Apparatus

Elemental analysis was performed on an elemental analyzer (Perkin-Elmer 240C). IR spectra of a resin or a metal-resin complex in KBr pellets were recorded on an infrared spectrophotometer (Perkin-Elmer 983). Diffuse-reflectance spectra were measured with an integrating sphere reflectance attachment (Hitachi). All metal-resin complexes were prepared as lightly packed powder pressed on filter paper. A freshly prepared resin provided the reference signal.

Chemicals

Most chemicals were of analytical reagent grade (E. Merck, Darmstadt, Germany). Purified water (18 MΩ-cm) using a water purification system (Milli-Q Ultrapure Water System, Millipore, USA) was used for all solutions. The metal salts were purchased from Merck. The stock solutions (ca. 0.1 M) of metal ions were prepared by dissolving an appropriate amount of the respective metal salt in nitric acid (0.1 M), diluting with pure water (to 250 mL), adjusting to pH 1.6 and storing in polyethylene bottles. The concentration of metal ion was verified by EDTA complexometric titration.

Synthesis of γ-Aminobutyrohydroxamate Resin (P13)

γ-aminobutyrohydroxamate resin was prepared according to the procedure described previously.[8] A macroporous cross-linked co-polymer was prepared on reaction of acrylonitrile and divinylbenzene. The hydrolyzed product of the co-polymer was prepared according to the procedure given in Ref. 10. Carboxylic acid resin (20 g) obtained by the above procedure was placed in a flask containing petroleum ether (20 mL) at a temperature below 0 °C. Thionyl chloride (26 mL) was then added dropwise. The temperature was raised to 80 °C and reaction continues for 18 h. The resultant mixture was evaporated under reduced pressure to distill the petroleum ether and excess thionyl chloride away. Dioxane (20 mL) and γ-aminobutyric acid (27 g) were added to the above product, and reacted at 70 °C for 24 h. After the resin turned from yellow to pink, the product was collected on filtration under suction and washed sequentially with water and acetone. The product (20 g) was reacted with hydroxylamine (0.5 M free of hydrochloride) at pH 8-9 at 70 °C for 18 h in methanol. The final product was washed sequentially with sulphuric acid (0.25 M), water and acetone.

Synthesis of N-methyl-γ-aminobutyrohydroxamate Resin (N-methyl-P13)

The syntheses of N-methyl-P13 resin was similar to the above procedure for P13, but N-methyl hydroxylamine hydrochloride (0.5 molar, 43.2g) in methanol (180 mL) was used instead of hydroxylamine hydrochloride, the final product is called N-methyl-P13.

Synthesis of O-methyl-γ-aminobutyrohydroxamate Resin (O-methyl-P13)

The synthesis of O-methyl-P13 resin was similar to the above procedure for N-methyl-P13, but O-methyl hydroxylamine hydrochloride (0.5 molar, 43.2 g) was used instead of N-methyl hydroxylamine hydrochloride, the final product is called O-methyl-P13.

Preparation of Metal-resin Complexes

Dry resin (ca 300 mg) was added to a polyethylene bottle (100 mL) containing metal ion (either 0.04 or 0.0004 M) in deionized water (25 mL). The pH of the solution was adjusted to the required value with perchloric acid or sodium hydroxide. The mixture was stirred for 24 h at 25 ± 0.1 °C. After equilibration, the pH was measured; the solution was then filtered. The metal ion in solution was measured by EDTA titration or spectrophotometry. The wet resin phase was dried in a vacuum oven and subjected to IR and electronic spectral measurements.

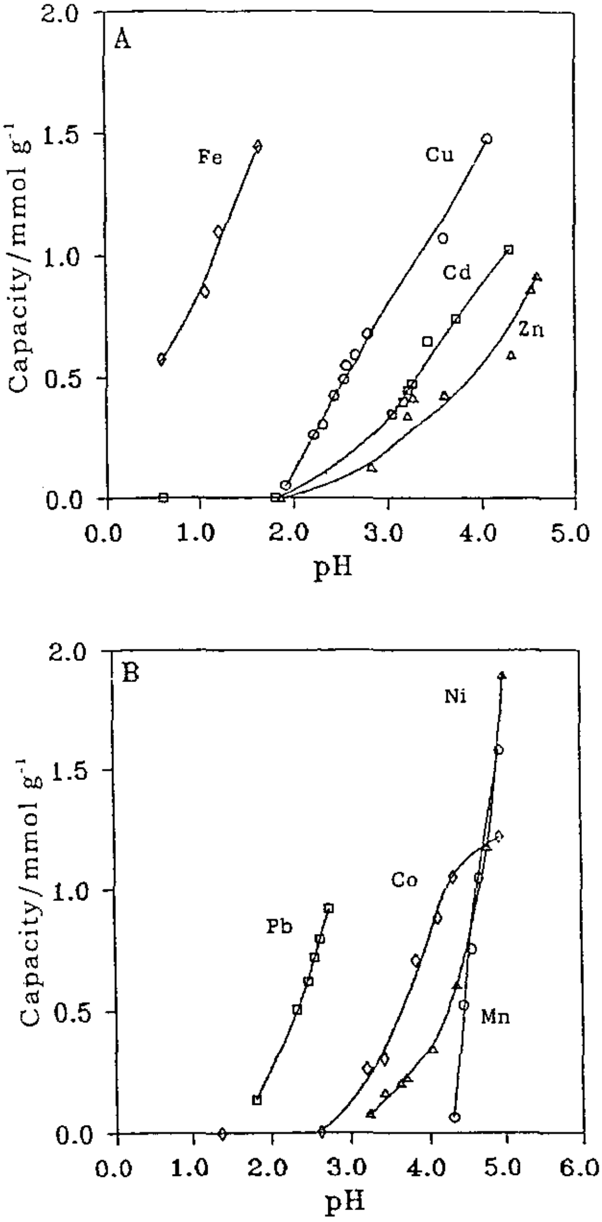


Fig. 1. Metal capacity as a function of pH. Amount of metal ion: 10 mmol.; Amount of P13: 0.3 g; Volume of solution: 25 mL.
A. Cd(□), Cu(o), Fe(◊), Zn(Δ)
B. Co(◊), Mn(o), Ni(Δ), Pb(□)

Table 1. Characteristics of γ-Aminobutyrohydroxamate Resin and Derivatives

	P13	N-M-P13	O-M-P13
Particle size (mesh)	100-140	100-140	100-140
Elemental analysis			
C/%	45.85	56.43	58.34
H/%	6.86	6.93	6.57
N/%	6.83	6.86	7.23
Functionality/mmol g^{-1}			
-CONHOH	2.21	2.45	2.58
-COOH	3.82	2.20	1.77
pK_a^a for -CONHOH	9.36	8.53	
pK_a^a for -COOH	4.75	6.78	
Metal capacity/mmol g^{-1}			
Fe(III) at pH 1.4	1.27	1.34	0.88
Cu(II) at pH 3.5	1.11	1.71	0.87

[a] Ionic strength: 0.1 M; Temp.: 25 ± 0.1 °C

Potentiometric Titrations

Acid dissociation constant

In this investigation, at least 14 samples of resin of each kind (0.2 g) were accurately weighed and placed respectively in each PE bottle (100 mL). Aqueous solutions containing various amounts of sodium hydroxide (0.1 M) were made to ionic strength (0.1 M) with potassium chloride and brought to total volume (25 mL). The solutions were added to a PE bottle containing the resin. The mixture was stirred for 4 h at 25 ± 0.1 °C. After equilibration, the pH was measured.

Stability constant

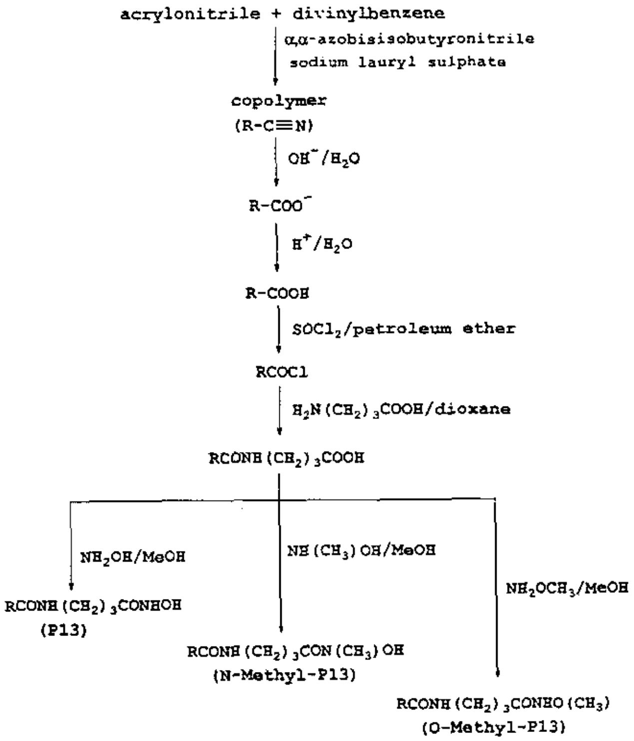
The apparatus and procedures of these experiments were identical to those described in the previous section with the exception that in each case metal salt at a ratio either 3:1 or 1:1 of metal to resin ligand was added to the resin solution. The total volume was 25 mL. After equilibration, the pH was measured.

RESULTS AND DISCUSSION

Characterization of Resins

The synthesis of chelating resins is indicated in Scheme I. The composition and structure of the product at each step in the synthesis were characterized by spot tests, elemental analysis and infrared spectra. Some chemical and physical properties of these resins are presented in Table 1. Elemental analyses of these resins for carbon, hydrogen and nitrogen confirmed the conversion of the carboxylate resin to the desired hydroxamate resin. The functionality of P13, N-methyl-P13 and O-methyl-P13 calculated from nitrogen content are 2.43, 2.45 and 2.58 mmol g^{-1} respectively.

Scheme I Synthesis of γ-aminobutyrohydroxamate resin and its derivatives



Chelation Behavior of Resins

The uptake of metal ions with either metal ions or resin ligand at large excess as a function of pH are shown in Figs. 1 and 2. The capacity of the resin for each metal ion increased with pH of the solution (Fig. 1). The results are reasonable as an equilibrium involving formation of the metal resin complex is a competition between the metal and hydrogen ions. The more stable was the chelate, the smaller was the pH at which it was capable of existing. The decreasing order of the capacity for P13 is Fe > Cu > Pb > Ni > Co > Cd > Zn. Generally, the factors that govern the relative tendencies of various metals to combine with a given donor are the ionic forces that are related to both charge and radius of the metal ion and the relative tendencies of various metals to form homopolar bonds with electron donors. However, a stereochemical nature also operates and complicates the chelating properties. The effect of pH on sorption of various cations (Fig. 2) was employed to find the conditions necessary for quantitative removal of metal ions from solution with either batch or column methods. All extraction of metal ions attained nearly 100% at pH greater than 3. Additional evidence is furnished by the satisfactory correlation of pH at 50% extraction ($pH_{1/2}$) and the literature values of

β_2 for formation of the various metal-monomeric hydroxamate complexes.[12] In comparison of capacities of P-13, N-methyl-P13 and O-methyl-P13 for metal ions, the $pH_{1/2}$ values decreased in the order of P13 > N-methyl-P13 > O-methyl-P13 (Fig. 3 and Table 2). These results may be explained sterically. The decreased capacity of O-methyl-P13 for metal ion on substitution of a methyl group in the O-position of P13 is rational, whereas that the metal ion capacity of N-methyl-P13 is somewhat smaller than that of P13 may be attributed to blocking of the basic nitrogen atom by the methyl group, thus hindering the approach of metal ions.

The rates of metal ion uptake were measured for Cd(II), Cu(II), Fe(III) and Pb(II) with P13, N-methyl-P13 and O-methyl-P13 in a batch process (Table 2). These metal ions were selected because they represent groups with varying affinities for resins of the three kinds. As expected with P13, copper(II) was extracted in less than one minute,

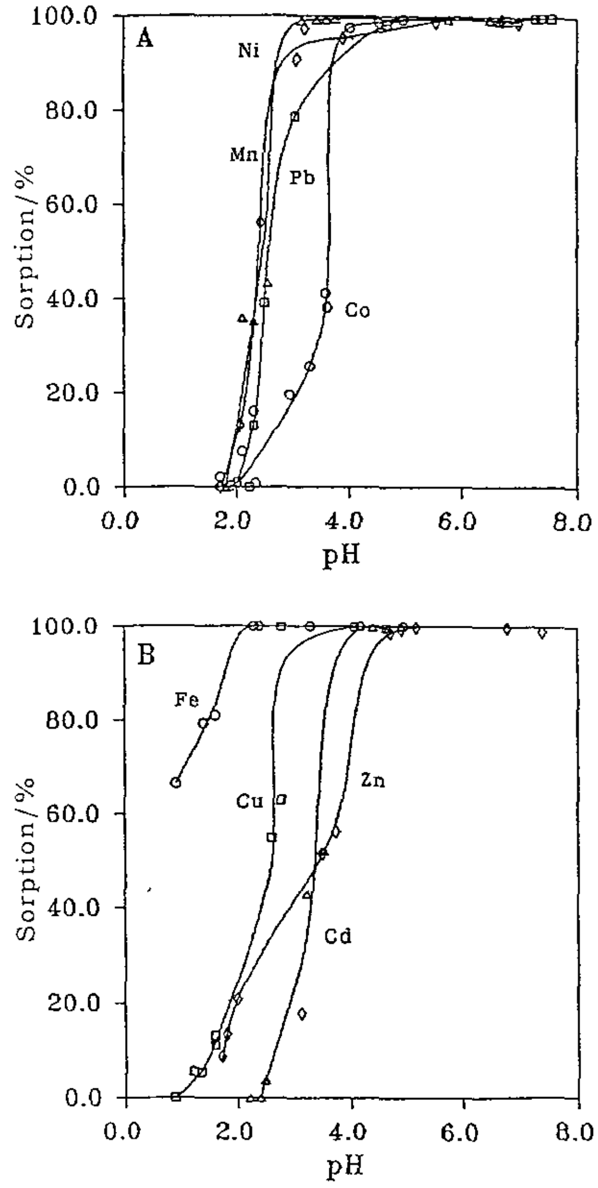


Fig. 2. Metal sorption as a function of pH. Amount of metal ion: 0.1 mmol.; Amount of P13: 0.3 g; Volume of solution: 25 mL.
A. Co(o), Mn(◊), Ni(Δ), Pb(□)
B. Cd(Δ), Cu(□), Fe(o), Zn(◊)

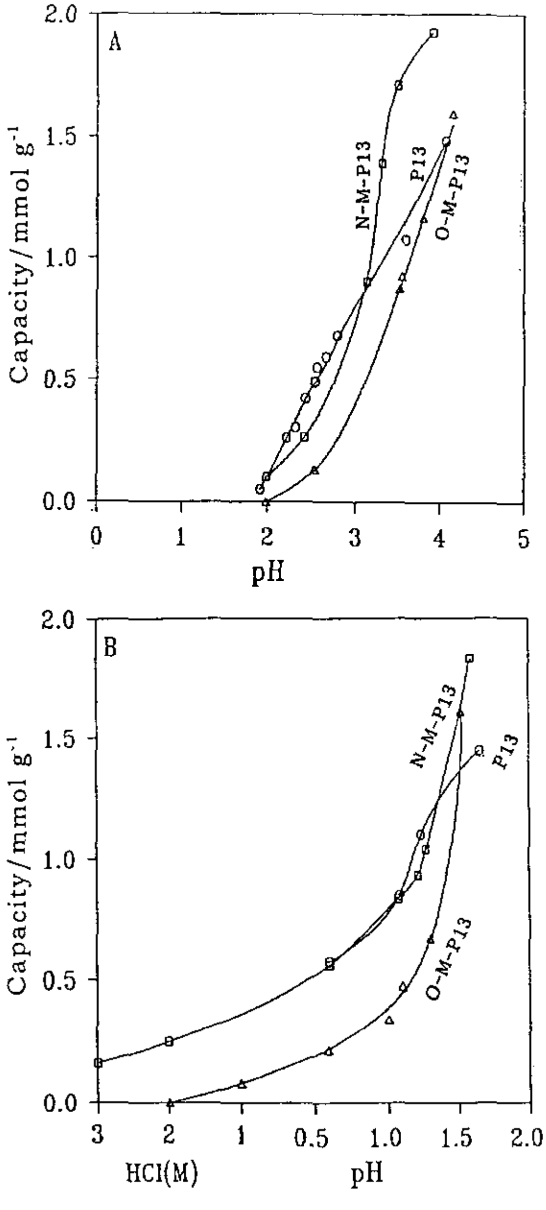


Fig. 3. Comparison of metal capacity as a function of pH among P-13, N-methyl-P13 and O-methyl-P13. Amount of metal ion: 10 mmol.; Amount of resin: 0.3 g; Volume of solution: 25 mL.
A. Cu(II); P13(o), N-M-P13(□), O-M-P13(Δ)
B. Fe(III); P13(o), N-M-P13(□), O-M-P13(Δ)

Table 2. pH and Period for Extraction of half the Metal Ions on γ-Aminobutyrohydroxamate Resin and Derivatives

metal ion	P13		N-M-P13		O-M-P13	
	$t_{1/2}$/min	$pH_{1/2}$	$t_{1/2}$/min	$pH_{1/2}$	$t_{1/2}$/min	$pH_{1/2}$
Cd(II)	0.7	3.34				
Co(II)		3.65				
Cu(II)	0.5	2.60	0.6	2.71	0.9	2.85
Fe(III)	1.2	0.94	1.4	2.74	2.7	1.41
Mn(II)		2.38				
Ni(II)		2.44				
Pb(II)	0.3	2.59				
Zn(II)		3.40				

Table 3. Formation Constants for Metal-Resin Complexes[a]

Equilibrium	log K_f				
	AHA	N-M-AHA	P13	N-M-P13	O-M-P13
H^+	HL/H.L	9.4		9.4	8.3
		9.0[b]	8.6[b]		
Cd^{2+}	ML/M.L	4.5		7.8	
	$ML_2/M.L^2$	7.8		15.5	
Co^{2+}	ML/M.L	5.1		8.8	
	$ML_2/M.L^2$	8.9		16.2	
Cu^{2+}	ML/M.L	7.9		8.9	7.4
	$ML_2/M.L^2$			17.1	14.3
Fe^{3+}	ML/M.L	11.4	2.5[c]	9.7	8.3
	$ML_2/M.L^2$	21.1		19.1	16.0
	$ML_3/M.L^3$	28.3			22.4
Mn^{2+}	ML/M.L	4.0		7.4	
	$ML_2/M.L^2$	6.9		14.7	
Ni^{2+}	ML/M.L	5.3		7.4	
	$ML_2/M.L^2$	9.3		14.2	
Pb^{2+}	ML/M.L	6.7		8.8	
	$ML_2/M.L^2$	10.7		17.3	
Zn^{2+}	ML/M.L	5.4		7.9	
	$ML_2/M.L^2$	9.6		15.8	

[a] Temp.: 25 ± 0.1 °C; Ionic strength: 0.1 M

[b] Ionic strength: 2.0 M

[c] Ionic strength: 1.1 M

Abbreviations:

AHA: acetohydroxamic acid
N-M-AHA: N-methylacetohydroxamic acid
P13: γ-aminobutyrohydroxamate resin
N-M-P13: γ-aminobutyro(N-methyl)hydroxamate resin
O-M-P13: γ-aminobutyro(O-methyl)hydroxamate resin

whereas both N-methyl-P13 and O-methyl-P13 were also satisfactory for chromatographic usage.

The functionality and coordination behavior of the resin are confirmed by infrared spectra. The line near 3300 cm^{-1} is assigned to the N-H and O-H stretching mode, whereas lines observed in the region 3080-3060 cm^{-1} were attributed to the overtone of amide II band. Specific evidence of covalently bound hydroxamate, N-methyl hydroxamate and O-methyl hydroxamate is provided by infrared absorption due to ketonic carbonyl and intramolecular hydrogen bonding of hydroxamate groups about 1650-1585 cm^{-1}. Coordination of hydroxamate caused the absorption to shift towards smaller wavenumbers and the peak intensity decreased. Lines in the region near 1445 cm^{-1} are assigned qualitatively to the N-C stretching vibration with contributions from C-O and C-R modes, those about 1300 cm^{-1} to C-R stretches, and those about 1100 cm^{-1} to a practically pure N-O stretching mode. The ν(NO) stretch moves from 900 cm^{-1} for the free ligand to ~920 cm^{-1} for the complexes, indicating some delocalization of the ketone double bond into the chelating ring. Some possible M-O stretches are observed in the region < 600 cm^{-1}, but assignment is difficult.

The colours of metal complexes are important properties in relation to the chelation behavior of a ligand. γ-Aminobutyrohydroxamate resin and its derivative interacted with some metal ions tested (Co, Cu, Ni and Fe) to produce variously coloured solutions as pH increased. The maximum wavelengths varied little as pH increased for each species, but the intensity increased obviously. Electronic spectra show a broad absorption with λ_{max} at 714-743 nm for all copper-resin complexes, and at 453-473 nm for all iron-resin complexes. The large intensity of these features indicates ligand-to-metal charge-transfer phenomena. The results also indicate formation of one-to-one metal-resin complexes[13] and the color variation with P13 is most evident among these resins, whereas that with O-methyl-P13 is less than that with N-methyl-P13.

Acidic and basic properties of chelating resins are generally characterized by determining the content of chelating groups and the dissociation constants. The data of potentiometric titration are typically used for this purpose. The stability of complexes formed in the phase of chelating resins is characterized by means of calculated stability constants. Various methods can be used for this purpose. The values of stability constants are approximate, but they are highly useful to estimate the selectivity of chelating resins and their analytical potentialities. In this investigation, the dissociation constants of the resin and the stability constants of metal-resin complexes were determined under conditions different from those in homogeneous solution.[8] Titration curves for the ligand and metal-complex formation appear in Figs. 4. The ligand titration curves show two buffer regions, one for the unreacted carboxylic acid and the other for the hydroxamic acid functional group. All formation curves of the metal complexes occur at a smaller pH than that of ligand titration in the absence of metal ion, indicating competition between metal ions and protons to bind with the ligand. The complexation reactions for these metal ions are described according to the following equilibrium processes and the corresponding equilibrium constants

$$M^{n+} + HL = ML^{(n-1)+} + H^{+} \qquad K_{f1} = \frac{[ML]\,[H]}{[M]\,[HL]}$$

$$ML^{(n-1)} + HL = ML_2^{(n-2)+} + H^{+} \qquad K_{f2} = \frac{[ML_2]\,[H]}{[ML]\,[HL]}$$

Bjerrum[14] introduced the concept of the average ligand number to characterize the extent of complex formation-the average number of ligands coordinated to one metal ion in a system containing the series of complexes ML, and ML_2. Accordingly, the defining equation is

$$\bar{n} = \frac{T_L - [L]}{T_M} = \frac{[ML] + 2\,[ML_2]}{[M] + [ML] + [ML_2]}$$

in which T_L and T_M are the total concentrations of ligand and metal ion, respectively, and [L] is the equilibrium concentration of the ligand. The difference between T_L and [L] is therefore the concentration of the bound ligand.

By ploting $\bar{n}$ against pL, we read approximate values of log K_{f1} and log K_{f2} directly from the graph. Table 3 lists the dissociation constants of hydroxamate groups for P-13 and N-methyl-P13. As expected, pK_a of P-13 is larger than that of N-methyl-P13 in a manner similar to the monomeric acetohydroxamic acid with respect to N-methyl-acetohydroxamic acid.[12] The transition-metal ions Mn(II), Fe(III), Co(II), Ni(II), Zn(II) and Cd(II) and the post-transition-metal ion Pb(II) all form strong complexes with P13, N-methyl-P13 and O-methyl-P13 (Table 3). The results show that stability constants vary little among the metal ions for P13, except those of Fe(III) and Cu(II). The stability constants are notably larger than those of monomeric hydroxamate metal complexes. In general, stability constants of chelating resins are smaller than those of monomeric ligands because of steric limitations imposed by the polymeric structure of the resin or large energy expenditures needed to complex chelating resins. This enhancement might be due to the ap-

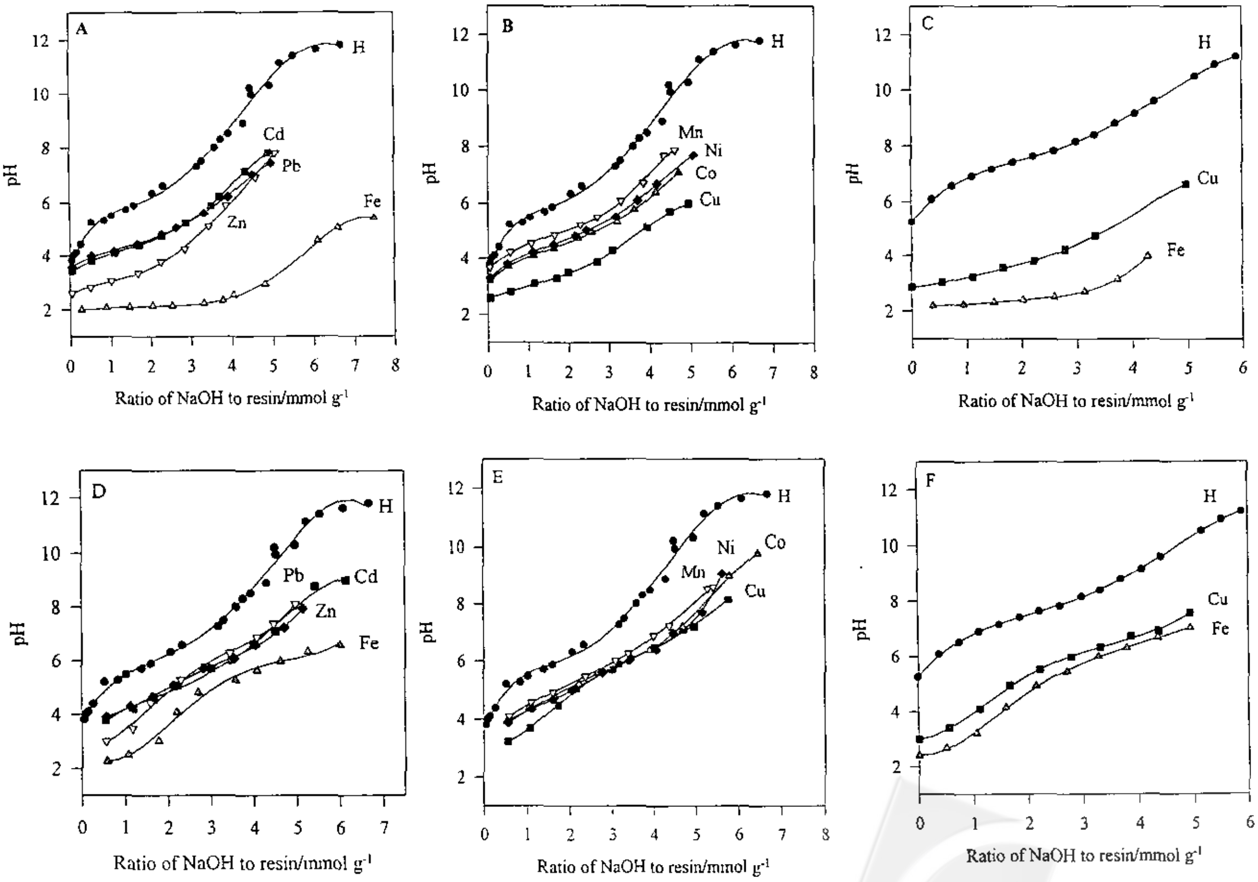


Fig. 4. Titration curves of γ-aminobutyrohydroxamate resin (P-13), N-methyl-P13 and its metal complexes. Amount of resin: 0.2 g; Volume of solution: 25 mL; Ionic strength: 0.1 M; Temperature: 25 ± 0.1 °C; A, B and C. $C_L/C_M = 1$; D, E and F. $C_L/C_M = 3$.

propriate design of the molecules described previously.[8] As interaction of metal ions with a nonionic resin (O-methyl-P13) cannot be determined with the proton-metal ion competition method, the formation constants of O-methyl-P13 metal complexes cannot be discussed here.

The varied stability of complexes formed in the resin phase during sorption is reflected in their selectivity for individual elements. This features serves as the basis for selective concentration and separation of elements. The selectivity series are the same as that from sorption and metal capacity and are consistent with Irving-William's series for the monomeric hydroxamic acids.[12]

In conclusion, all resins synthesized exhibited properties of large capacity for metals, rapid kinetics and high selectivity for transition-metal ions, and are expected to be highly promising as both concentrator and separator in chelation-ion chromatography for determination of trace metal ions in complex matrix samples, such as environmental or biological samples.

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Key Words

γ-Aminobutyrohydroxamate resin; Chelation properties; Transition-metal ions.

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