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Chelating ion exchange with macroreticular hydroxamic acid resins

Richard James Phillips
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CHELATING ION EXCHANGE WITH MACRORETICULAR HYDROXAMIC ACID RESINS

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Chelating ion exchange with macroreticular hydroxamic acid resins

by

Richard James Phillips

A Dissertation Submitted to the
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DOCTOR OF PHILOSOPHY

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Major: Analytical Chemistry

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Iowa State University
Ames, Iowa

1980

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GENERAL INTRODUCTION

Ion-exchange reactions were first exploited for analytical purposes by Folin and Bell in 1917 (1). Their procedure used a synthetic zeolite for the isolation of ammonia from urine, prior to determination with Nessler's reagent. Since then, applications of ion exchange have become increasingly important in analytical chemistry. These applications generally belong to one of the categories listed below.

1. Determination of total salt concentration
2. Removal of interfering ions prior to analytical determinations
3. Concentration of trace constituents prior to analytical determinations
4. Purification of water and other reagents
5. Chromatographic separations

The most popular ion exchangers are the so-called strong-cation- and strong-anion-exchange resins, which consist of cross-linked polystyrene beads, containing sulfonate and tetramethylammonium groups, respectively. These exchangers operate primarily on the basis of electrostatic forces. As such, they exhibit relatively low selectivity among ions of the same size and charge (2). Chromatographic separations of such ions can be achieved, however, through differential complexation in the mobile phase. The classic example of this approach is the separation of rare earth ions on a strong-cation-exchange resin using citrate (2), 2-hydroxybutyrate (3), or other complexing agents in the eluent.

An alternative approach to separations is to use a stationary phase which contains immobilized chelating groups. A great many of these chelating ion exchangers have been developed, beginning in 1940 (4). Oxygen, nitrogen, and sulfur have been employed as donor atoms (5). The attached ligands are typically bidentate or tridentate, although monodentate (6) and hexadentate (7) groups have also been investigated. Applications of these selective ion exchangers have been developed in the concentration and analysis of trace elements in sea water (7-9), the purification of reagents (10), and chromatographic separations (11-13).

A major disadvantage of most chelating-ion-exchange resins has been the length of time required for equilibration (14,15). Kinetic aspects of chelating ion exchangers have been studied by Nativ _et_ _al_. (16), who demonstrated that sorption takes place by a shell-progressive mechanism. The reaction zone moves inward from the surface of the resin particle as the chelating sites are occupied. The rate-limiting step is diffusion of the ions through the reacted layer. As a result, the reaction kinetics are controlled by the physical properties of the resin matrix.

Chelating resins may be prepared either by polymerization of a chelating monomer or by the preparation of a chelating derivative of an existing polymer. An advantage of the latter approach is that it is possible to choose a starting polymer with known chemical and physical properties. One such substrate which has been used successfully (17) is Amberlite XAD-4, a macroreticular co-polymer of ethylstyrene and divinylbenzene which is manufactured by Rohm and Haas. This resin is chemically and mechanically stable and has good mass-transfer characteristics. The aromatic rings in the resin may be sulfonated, nitrated, alkylated, or acylated, which facilitates the preparation of a variety of chelating derivatives.

The subject of this dissertation is an investigation of three chelating resins prepared by introducing hydroxamic acid groups with different N-substituents into XAD-4. These resins mimic the properties of N-phenylbenzohydroxamic acid by selectively reacting with a small group of metal ions in strongly acidic solution (18). A review of the pertinent chemistry of hydroxamic acids, including previous work on chelating resins with this functional group, is presented in the next section. This is followed by several sections describing the syntheses and characterization of the hydroxamic acid resins. Applications are discussed next, and finally, some conclusions and suggestions for future work.

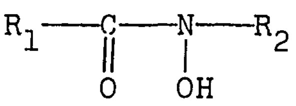
THE CHEMISTRY OF HYDROXAMIC ACIDS

Literature

A number of review articles and at least one book are available to provide an introduction to the literature on hydroxamic acids. Reviews of a general nature have been published by Yale (19), Mathis (20), Coutts (21), and Bauer and Exner (22). Articles dealing specifically with cyclic hydroxamic acids have been written by Coutts (23) and Bapat, Black, and Brown (24). The chemistry of naturally occurring hydroxamic acids has been reviewed by Neilands (25) and Maehr (26). Brandt (27) has reviewed analytical applications of hydroxamic acids up to 1960, and Grossi has reviewed applications involving solvent extraction (28). Majumdar (18) has devoted a book to the analytical applications of hydroxamic acids particularly N-phenylbenzohydroxamic acid.

Structure and Nomenclature

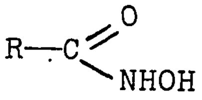
Hydroxamic acids have the general structure shown below.

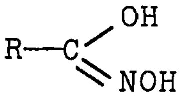


$$R_1-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{N}-R_2$$

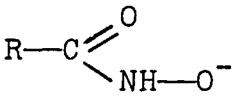
They may be classified as aliphatic or aromatic, depending on the nature of R_1. Compounds in which R_2 is hydrogen are called primary hydroxamic acids and those in which R_2 is an alkyl or aryl group are called secondary hydroxamic acids. The cyclic hydroxamic acids, in which R_1 and R_2 are part of a heterocyclic ring, are an important subgroup. The nomenclature rules developed by the International Union of Pure and Applied Chemistry (29) permit these compounds to be named either as hydroxamic acids, or as N-hydroxy amides. Some typical examples which illustrate the two systems of nomenclature are shown in Table 1.

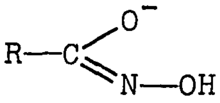
For primary hydroxamic acids, the tautomeric forms A and B, shown below, have been proposed. There is now good

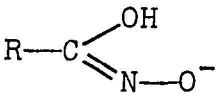

A


B

evidence that structure A is correct both in solution and in the solid state (22). Tautomeric forms C, D, and E have

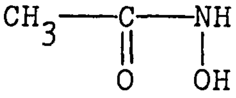
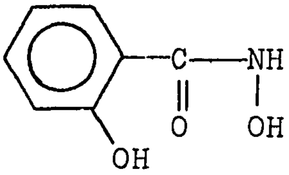
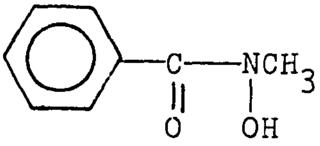
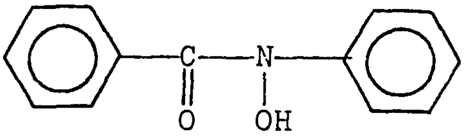
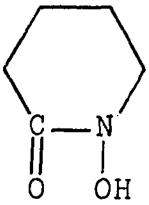
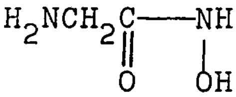

C


D


E

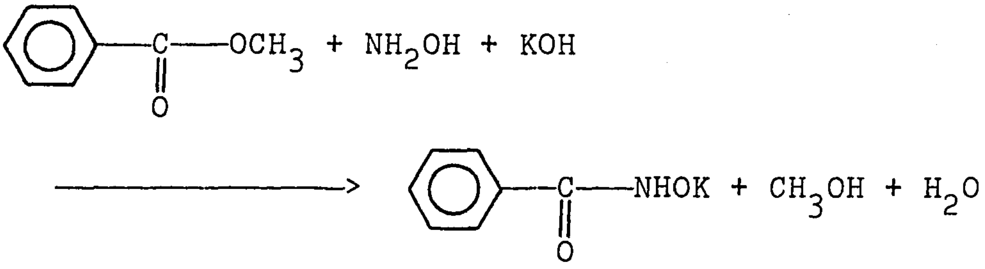
been proposed for the conjugate base. Structure E is now regarded as unlikely, but the relative importance of structures C and D remains controversial. A thorough discussion of this topic appears in reference 22.

Table 1. Representative hydroxamic acids

Structure	Name
 $CH_3-C(=O)-NH-OH$	acetohydroxamic acid or N-hydroxyacetamide
	salicylhydroxamic acid or N-hydroxysalicylamide
	N-methylbenzohydroxamic acid or N-hydroxy-N-methylbenzamide
	N-phenylbenzohydroxamic acid or N-hydroxy-N-phenylbenzamide
	1-hydroxy-2-piperidinone
 $H_2NCH_2-C(=O)-NH-OH$	2-amino-N-hydroxyacetamide

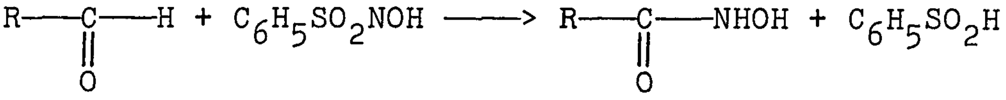
Synthesis

The first hydroxamic acid was discovered by H. Loessen in 1869 from the reaction of hydroxylamine with diethyl oxalate (30). The reaction of hydroxylamine with various derivatives of carboxylic acids remains the most widely applicable synthetic route to primary hydroxamic acids. The acid derivatives commonly used are, in order of increasing reactivity, amides, esters, and acid chlorides. A base is often used to drive the reaction to completion, as in the synthesis of benzohydroxamic acid from methyl benzoate (31).



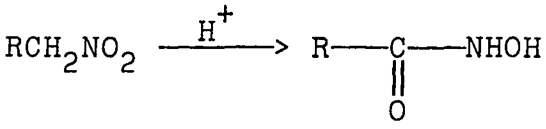
The derivatives of aliphatic acids are more reactive than their aromatic counterparts. For example, hydroxylamine reacts readily with acetamide at room temperature, but the corresponding reaction with benzamide is sluggish and incomplete, even at elevated temperatures (32). Aromatic hydroxamic acids are usually prepared via the ester or acid chloride. Acid chlorides are so reactive that two or even three acyl groups can add to hydroxylamine. The reaction must be carefully controlled to obtain the desired monoacylated product in good yield (33).

Primary hydroxamic acids have also been produced by the oxidation of oximes (34), amines (35), or amides (36) by persulfuric acid or hydrogen peroxide. The oxidations have not found much use because the yields are low. The reaction of aldehydes with N-hydroxybenzenesulfonamide is an interesting method for synthesizing primary hydroxamic acids (37).



$$R-\underset{\displaystyle O}{\overset{\|}{C}}-H + C_6H_5SO_2NOH \longrightarrow R-\underset{\displaystyle O}{\overset{\|}{C}}-NHOH + C_6H_5SO_2H$$

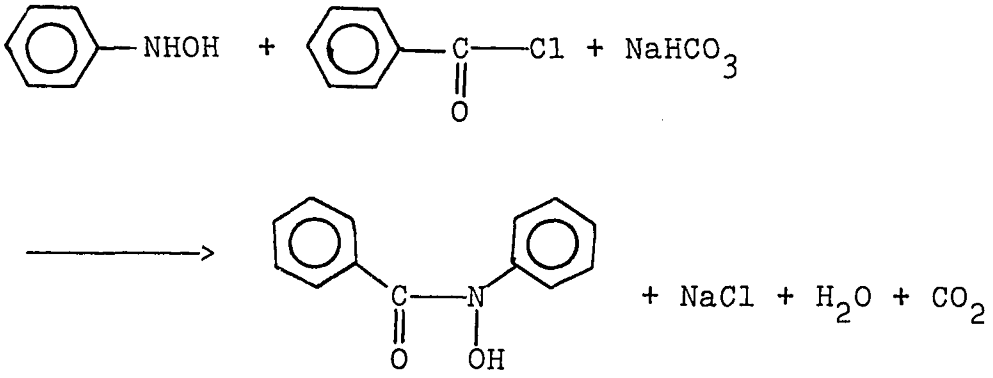
A disadvantage of this reaction is the relatively high cost of the reactants. Another way of obtaining primary hydroxamic acids is the rearrangement of nitroparaffins. This



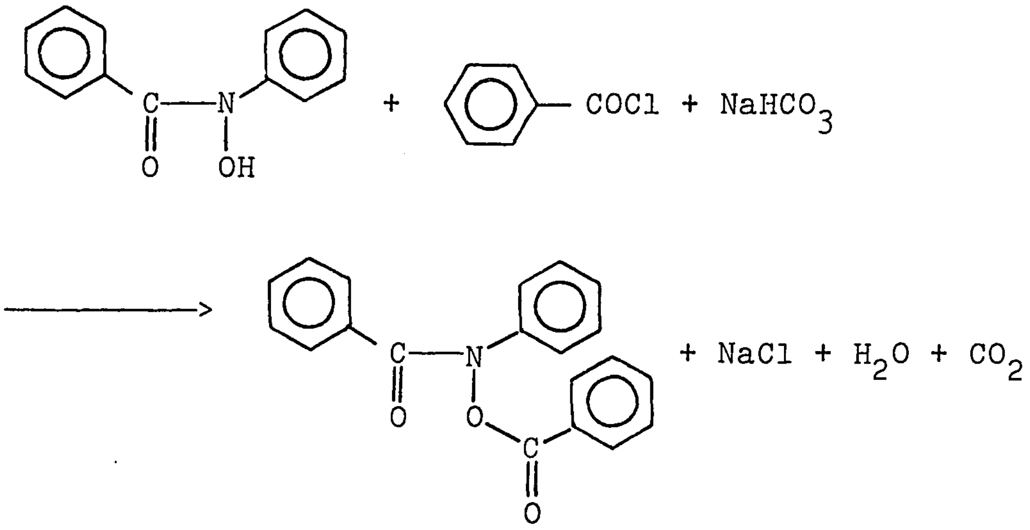
$$RCH_2NO_2 \xrightarrow{H^+} R-\underset{\displaystyle O}{\overset{\|}{C}}-NHOH$$

reaction is the basis for a patented process for propiohydroxamic acid in 50% yield (38).

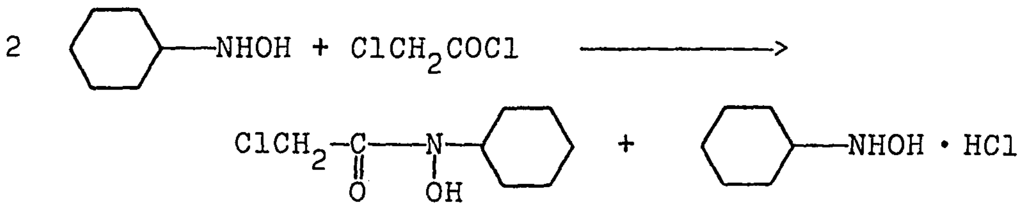
Secondary hydroxamic acids are nearly always prepared by the reaction of an N-alkyl or N-aryl hydroxylamine with an acid chloride. There are two distinct ways of performing the reaction. The first method uses one equivalent of acid chloride per equivalent of hydroxylamine. Base is added to neutralize the liberated hydrochloric acid. An example is the synthesis of N-phenylbenzohydroxamic acid (39), shown on the following page.



Some O-acylation also occurs to form N-phenylbenzohydroxamic benzoic anhydride.

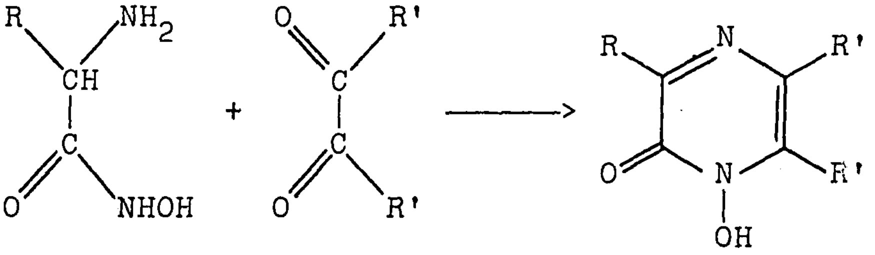


The hydroxamic acid is isolated from the reaction mixture by forming its water-soluble ammonium salt. A variation of this method, in which the hydroxylamine also serves as the base, has been used to prepare N-cyclohexylchloroacetohydroxamic acid in 90% yield (40), as shown on the following page.

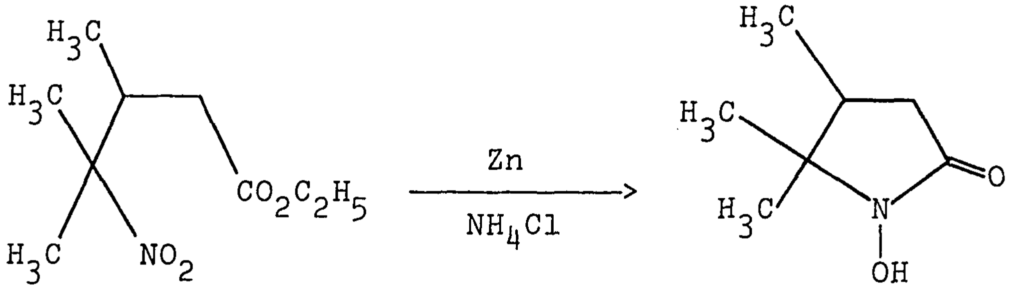


The second method for synthesizing secondary hydroxamic acids employs two equivalents of acid chloride per equivalent of hydroxylamine to form primarily the mixed anhydride. This is isolated, purified, and then converted to the sodium hydroxamate by treatment with sodium ethoxide. The free hydroxamic acid is formed by treatment with a saturated solution of carbon dioxide in water. This method has been used successfully for the synthesis of N-methylbenzohydroxamic acid (41). The choice between the two methods depends upon which component, the acid chloride or the hydroxylamine, is more expensive.

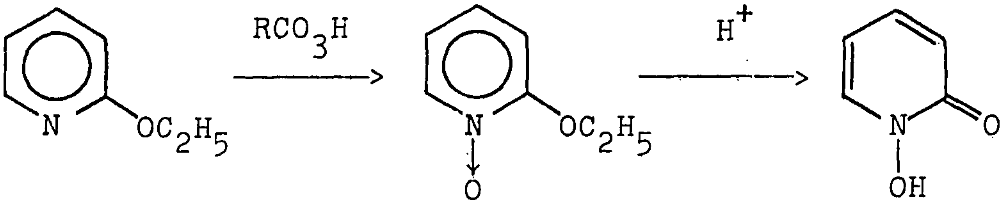
Many cyclic hydroxamic acids exhibit biological activity and this has inspired a great deal of effort toward their synthesis. As a result, a number of interesting reactions and compounds have been discovered. α-Amino hydroxamic acids react with diketones to give 1-hydroxy-2(1H) pyrazinones (42). Cyclic hydroxamic acids are also



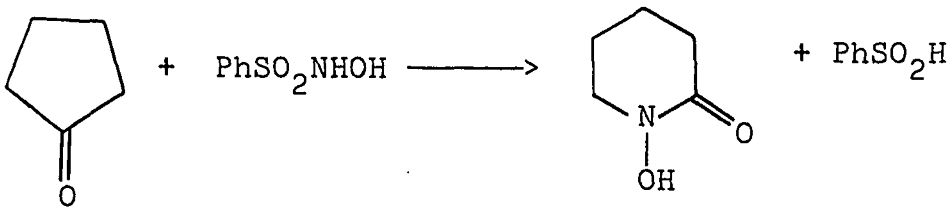
produced by the selective reduction of the nitro group in compounds which also contain a suitably positioned ester group. The intermediate hydroxylamine reacts with the ester to form the desired heterocyclic ring. Zinc dust in aqueous ammonium chloride is often used for the reaction, as in the example shown below (43).



The oxidation of 2-ethoxypyridine with a peracid forms the corresponding N-oxide. Acid hydrolysis of the ethyl group then gives 1-hydroxy-2(1H)-pyridinone, which has the customary properties of a hydroxamic acid (44).



Finally, cyclic hydroxamic acids can be synthesized by ring expansion. Cyclopentanone reacts with N-hydroxybenzenesulfonamide in alkaline solution to give N-hydroxypiperdinone in 22% yield (45), as shown on the following page.



Reactions

A fundamental property of hydroxamic acids is dissociation. Dissociation constants for a number of hydroxamic acids are given in Table 2. Even in this compilation, which does not include all the values which have been reported, there are apparent discrepancies. In most cases, these appear to be caused by differences in ionic strength and the choice of supporting electrolyte. Nevertheless, by comparing values from the same reference, some conclusions can be reached. The effect of structure on the acidity of acyclic hydroxamic acids is similar to what is found for carboxylic acids. For example, aromatic hydroxamic acids are more acidic than their aliphatic counterparts. In addition, N-substitution increases the acidity slightly. A more dramatic difference is found between the two cyclic hydroxamic acids in Table 2. 1-Hydroxy-2-piperidinone is about as acidic as a typical acyclic hydroxamic acid. However, 1-hydroxy-2(1H)-pyridinone, which is partially unsaturated, is more acidic by a factor of 10^3.

Hydroxamic acids are also very weak bases. The protonation of N-methyl hydroxamic acids in sulfuric acid solution

Table 2. Dissociation constants of hydroxamic acids

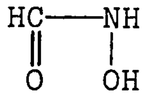
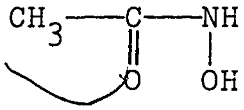
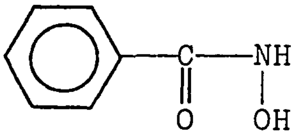
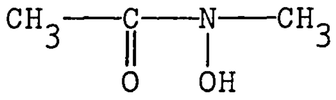
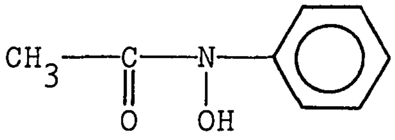
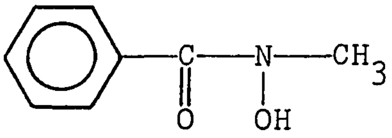
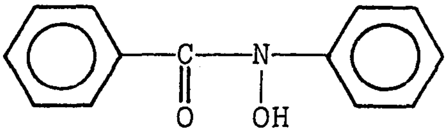
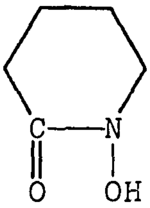
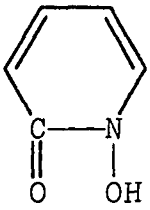
Structure	pK_a	Reference
	8.78	46
	9.37	47
	9.40	48
	8.43	49
	8.79	47
	8.80	50
	8.89	46,48
	8.92	51
	8.85	52
	8.10	49
	8.59	50

Table 2. (Continued)

Structure	pK_a	Reference
	8.14	49
	8.41	46
	8.49	53
	8.55	51
	9.15	54
	5.9	55

has recently been studied by nuclear magnetic resonance and ultraviolet spectroscopy (56). Protonation at nitrogen was observed between 3 and 13 M acid. At higher concentrations of acid, the protonation site shifted from nitrogen to carbonyl oxygen. The pK for deprotonation was estimated to be between -1 and -3. A study of the protonation of substituted benzohydroxamic acids led to similar estimates (57).

Another characteristic reaction of hydroxamic acids is hydrolysis, which is catalyzed by both acid and base. Berndt and Fuller (58) studied the hydrolyses of benzohydroxamic acid in weakly acidic and weakly basic solution. The rate constants for these pseudo-first-order reactions were proportional to the concentration of acid or base. At 88.6°C, the half-lives of benzohydroxamic acid in 0.1 M hydrochloric acid and 0.1 M sodium hydroxide were 3.7 and 16.5 hours, respectively. The hydrolyses of benzohydroxamic acid and several of its derivatives in solutions of higher acidity were studied by Buglas, Hudson, and Tillet (57). In perchloric acid, the reaction rates reached maxima at about 4 M and gradually decreased as the acidity was raised. Similar behavior was found in hydrochloric, hydrobromic, and sulfuric acids.

Berndt and Sharp (59) studied the hydrolyses of several aliphatic hydroxamic acids in 0.25 M p-toluenesulfonic acid. At 50.5°C, the half-lives of acetohydroxamic and propiohydroxamic acids were about 2 hours, and those of isobutyrohydroxamic and phenylacetohydroxamic acids were about 5 hours. For comparison, the rate constant for the hydrolysis of benzohydroxamic acid in 0.25 M hydrochloric acid at 50.5°C was estimated from the data of Berndt and Fuller (58) by interpolation and the use of Arrhenius equation. The corresponding half-life was 44 hours, supporting Grossi's claim that aromatic hydroxamic acids are much more stable to hydrolysis than their aliphatic counterparts (28).

The acid-catalyzed hydrolyses of several N-methylbenzohydroxamic acids were studied by Berndt and Ward (60). The rate constants for the hydrolysis of 4-methyl-N-methylbenzohydroxamic acid in 0.225 M hydrochloric acid at 78.6 and 88.6°C were estimated from their data and compared to the corresponding rate constants for benzohydroxamic acid, as described above. The results indicate that this derivative reacts about four times as fast as the parent compound. Comparative data for the hydrolyses of other N-substituted hydroxamic acids were not available. Cyclic hydroxamic acids are said to be quite resistant to hydrolysis (24).

Little has been written about the oxidation and reduction reactions of hydroxamic acids. They are reportedly reduced by Raney nickel and hydrogen, or hydriodic acid, and oxidized by performic or periodic acids (25). The latter has been used for structural determinations of complex, naturally occurring hydroxamic acids. Primary hydroxamic acids have been oxidized to carboxylic acids and nitrous oxide by bromine (61), nitrous acid (62), and alkaline permanganate (63). N-Phenylbenzohydroxamic acid is reportedly oxidized by acidified permanganate or dichromate, but not by hydrogen peroxide (18).

From an analytical point of view, the most interesting reaction of hydroxamic acids is complexation of metal ions. The stability constants of a number of metal complexes of acetohydroxamic acid were measured by Anderegg, L'Eplattenier, and Schwarzenbach (64). These results are reproduced in Table 3. The most noticeable feature is the relatively high stability of the iron(III) complex. Grossi and co-workers (65,66) obtained the formation constants of several metal complexes of benzohydroxamic acid, shown in Table 4. In this work, the selectivity of benzohydroxamic acid for solvent extraction of zirconium in highly acidic solution was noted. These results also suggest the use of this reagent for separating plutonium from uranium or uranium(IV) from uranium(VI).

The effect of structure on complexation is shown in Table 5, which compares the stability constants for the iron(III) complexes of acetohydroxamic (47), benzohydroxamic (47), and N-phenylbenzohydroxamic (67) acids. By

Table 3. Stability constants of the metal complexes of acetohydroxamic acid at 20° and $\mu = 0.1$ ($NaNO_3$)

Cation	log K_1	log K_2	log K_3
H^+	9.35		
Ca^{+2}	2.4		
Mn^{+2}	4.0	2.9	
Cd^{+2}	4.5	3.3	
Fe^{+2}	4.8	3.7	
Co^{+2}	5.1	3.8	
Ni^{+2}	5.3	4.0	
Zn^{+2}	5.4	4.2	
Pb^{+2}	6.7	4.0	
Cu^{+2}	7.9		
La^{+3}	5.16	4.17	2.55
Ce^{+3}	5.45	4.34	3.0
Sm^{+3}	5.96	4.77	3.68
Gd^{+3}	6.10	4.76	3.07
Dy^{+3}	6.52	5.39	4.04
Yb^{+3}	6.61	5.59	4.29
Al^{+3}	7.95	7.34	6.18
Fe^{+3}	11.42	9.68	7.23

Source: Reference 64

Table 4. Stability constants of some metal complexes of benzohydroxamic acid

Cation	log K_1	log K_2	log K_3	log K_4
UO_2^{+2}	8.72	8.05		
Th^{+4}	9.60	10.21	8.95	
Fe^{+3}	12.18			
Pu^{+4}	12.73			
Zr^{+4}	12.43	11.65		
U^{+4}	9.89	8.11	8.32	6.62

Source: References 65 and 66

Table 5. Stability constants of the iron(III) complexes of some hydroxamic acids

Hydroxamic acid	log K_1	log K_2	log K_3
Aceto[a]	11.42	9.68	7.2
Benzo[a]	11.06	9.37	7.4
N-phenylbenzo[b]	11.39	9.26	8.5

[a] Reference 47.

[b] Reference 67.

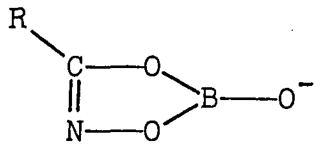
combining these with the dissociation constants from Table 2, the equilibrium constants for the reaction shown below for each of the acids can be determined. The values

$$HA + Fe^{+3} \longrightarrow FeA^{+2} + H^{+}$$

obtained are 2.05, 2.27, and 2.90 for aceto-, benzo-, and N-phenylbenzohydroxamic acids, respectively. The aromatic hydroxamic acid thus exhibits greater selectivity for Fe^{+3} over H^{+} than its aliphatic counterpart. This selectivity is further increased by N-substitution.

Borate complexes of benzohydroxamic acid and some of its derivatives were studied by Christian and co-workers

(68). A 1:1 complex with borate was formed by the primary hydroxamic acids between pH 6 and 11. Secondary, or N-substituted, hydroxamic acids did not give the reaction. These results suggest that complexation occurs with the loss of two protons to give the structure shown below.



A similar mechanism was proposed to explain the formation of an anionic, 3:1 complex of benzohydroxamic acid with Mn(III) (69).

Applications

The first analytical application of hydroxamic acids was in organic analysis by functional groups. Feigl and co-workers (70) developed a spot test for esters based on their reaction with hydroxylamine. The resulting hydroxamic acids were detected as their red to purple iron(III) complexes. Subsequent modifications extended the method to alcohols, aldehydes, ethers, carboxylic acids, sulfonic acids, phenols, nitro compounds, amides, and cyanates. These procedures were reviewed in 1940 by Davidson (71). In 1946, Hill adapted Feigl's method to the quantitative determination of fatty acids and their esters (72). Analysis of the free acids required preliminary methylation. Variations of this method remain important in analysis for trace quantities of carboxylic esters, acid chlorides, and anhydrides (73).

The use of hydroxamic acids as gravimetric reagents appears to have been pioneered by Musante (74). Cobalt, nickel, and copper were determined by precipitation with either benzo-, salicylo-, or anisohydroxamic acid. In each case, the combining ratio was two moles of hydroxamate anion per mole of metal cation. Musante also investigated the reactions of these compounds with bromine, apparently with the aim of developing titrimetric procedures for the analysis of the hydroxamate precipitates.

In 1950, Schome reported the use of N-phenylbenzohydroxamic acid for the gravimetric determination of copper, iron, aluminum, and titanium (39). This reagent was described as similar to cupferron in its reactions, but more stable than that compound. Copper, iron, and aluminum formed precipitates with the formula ML_n, where M is the metal cation, n is its charge, and L is the hydroxamate anion. Titanium formed a precipitate of indefinite composition. It was determined by ignition to the oxide. A number of additional elements have since been determined gravimetrically with N-phenylbenzohydroxamic acid. As shown in Table 6, some selectivity can be obtained by control of pH.

Table 6. Gravimetric determinations with N-phenylbenzohydroxamic acid

pH	Elements Determined
<0	Zr, Hf, Nb, Ta, Ge
0-1	Ti, Sn
1-2	Mo, W
2-4	Al, Cu, Fe, Ga, Hg
4-6	Be, Co, In, Ni, Sc, Th
6-8	Bi, Ce, La

Source: Reference 18

Additional separations may be achieved through the use of masking agents. These procedures have been reviewed in detail by Majumdar (18).

Schome also was the first to describe the use of N-phenylbenzohydroxamic acid as a reagent for the colorimetric determination of vanadium (75). The orange-red complex was formed at pH 2.4 in 50-70% alcohol, and its absorbance was read at 510 nm. The color faded slowly after about five hours. Wise and Brandt developed a colorimetric procedure for vanadium using benzohydroxamic acid (76). The complex was formed at pH 2.0 and extracted into 1-hexanol. A host of similar procedures for determining vanadium with various hydroxamic acids have since been developed, many of which are described by Majumdar (18). Hydroxamic acids have also been used as colorimetric reagents for manganese (69), titanium (77), uranium (78), molybdenum (79), and niobium (80). Bass and Yoe studied thirty-six hydroxamic acids as colorimetric reagents and concluded that color development is a function of pH, solvent, and reagent concentration, and that N-substitution is relatively unimportant (81).

Applications for hydroxamic acids have also been found in the separation of metal ions by solvent extraction and paper chromatography. Forster and Schwabe developed a scheme for group separation of the elements by extraction with N-phenylbenzohydroxamic acid and diethylammonium diethyldithiocarbamate (82). The first group, containing Ti, Zr, Hf, V, Nb, Ta, Mo, W, Sn, Sb, and Re, was extracted from 2 M mineral acid into 0.1 M N-phenylbenzohydroxamic acid in chloroform. Further separations within this group were achieved by selective back-extraction, as shown in Table 7. Villarreal, Krsul, and Barker separated aluminum from uranium, iron, molybdenum, zirconium, vanadium, copper,

Table 7. Back-extraction of metal ions from a chloroform solution of their N-phenylbenzohydroxamates

Wash solutions	Metal ions back-extracted
5 M H_2SO_4	Ti(IV), Zr(IV), Hf(IV)
0.25 M oxalic acid	Sb(III), Sn(IV)
0.5 M HF + 1 M NaF	Nb(V)
10 M HF	Ta(V)
2 M NaOH	Mo(VI), W(VI)

Source: Reference 82

and other elements by extraction with N-phenylbenzohydroxamic acid in the presence of several masking agents (83). Fritz and Sherma evaluated N-phenylbenzohydroxamic acid as a reagent for the paper chromatography of metal ions (84). Thirty-five elements were studied, and a number of selective separations were accomplished.

Vernon and Khorassi compared aromatic and aliphatic hydroxamic acids for solvent extraction of iron, copper, cobalt, and nickel (85). The aliphatic acids were less efficient for the separation of copper and iron, but appeared useful for the extraction of the higher oxidation states of vanadium, chromium, molybdenum, and uranium from acidic solution. On a larger scale, uranium was purified by selective extraction of Pu(IV) and Np(IV) with an aliphatic hydroxamic acid (86). Alkyl hydroxamic acids have also been used in the concentration of rare-metal ores by foam flotation (87), and as a detergent additive to reduce corrosion of copper (88).

Polymeric Hydroxamic Acids

The area of polymeric hydroxamic acids was pioneered by Deuel and co-workers, who prepared hydroxamic acid derivatives of Amberlite IRC-50, and other poly(methacrylic acid) resins. The syntheses of these derivatives involved the conversion of the starting resin to the acid chloride (89,90) or methyl ester (91), followed by hydroxylaminolysis. Some difficulty was experienced in the acid chlorination of high-capacity resins. This was attributed to the formation of anhydride bridges between adjacent carboxy groups. The hydroxamic acid derivatives showed a greater affinity for Fe(III) than their poly(methacrylic acid) precursors. However, little change was seen in their affinity for Cu(II) and Zn(II).

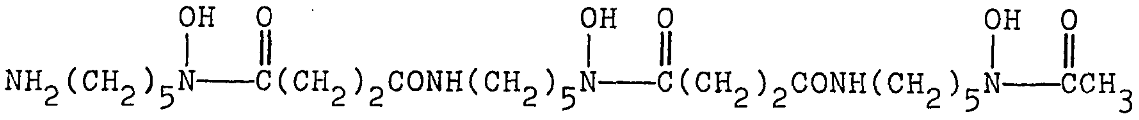
In 1957, Kern and Schulz prepared a linear poly(hydroxamic acid) by hydroxylaminolysis of poly(methyl acrylate) (92). The product was soluble in water and dilute base, but insoluble in dilute acid and organic solvents. It gave precipitates with Cu, Zn, Hg, Al, Ti, Pb, Be, Fe(III), Ce(III), Ce(IV), and U(VI). The iron(III) complex was soluble in dilute solution or in the presence of excess iron(III). For comparison, the iron(III) complex of isobutyrohydroxamic acid was also studied. The polymeric and monomeric hydroxamic acids were each titrated spectrophotometrically with iron(III). The polymer showed a marked tendency toward the formation of a 3:1 (hydroxamic acid:iron(III)) complex which was not observed in the monomer.

In 1958, Schouteden described the conversion of poly(amidoximes) to poly(hydroxamic acids) in about 50% yield by mild hydrolysis (93). Poly(amidoximes) had previously been prepared by the reaction of poly(acrylonitrile) and hydroxylamine in dimethylformamide (94). In 1964, Fetscher obtained a patent for the invention of a radioactive source consisting of a poly(amidoxime) or poly(hydroxamic acid) complexed with a radioactive metal (95). Conditions were described for the immobilization of Pu, U, Co, and Th with these resins.

In 1965, Petrie, Locke, and Meloan described the preparation of a hydroxamic acid derivative of Amberlite IRC-50 via the sequence acid chloride, methyl ester, hydroxamic acid (96). The product showed increased retention of V(V), Fe(II,III), Mo(VI), Ti(IV), Hg(II), Cu(II), U(VI), and Ce(IV). No reference was made to the earlier work of Deuel in this area. A patent was issued in 1974 for a hydroxamic acid resin with 8% cross-linking (97). It was produced by the copolymerization of divinylbenzene and butyl acrylate, followed by hydroxylaminolysis.

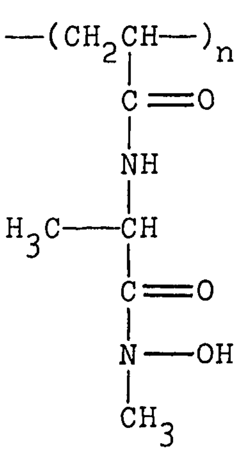
Vernon and Eccles published four papers in 1974 and 1975 dealing with the synthesis, properties, and applications of poly(hydroxamic acids) (98-101). The preferred synthetic route was partial hydrolysis of a macroporous acrylonitrile-divinylbenzene copolymer to a poly(acrylamide), followed by hydroxylaminolysis. The product had a copper(II) capacity of 3.2 mmol/g at pH 6, and an equilibration rate ($t_{\frac{1}{2}}$) of 22 minutes. Vanadium was separated from iron by sorption in 2 M hydrochloric acid, but could not be eluted from the resin. Iron was separated from copper and also from limestone and dolomite samples by sorption at pH 1.5 and 2.0, respectively. Iron could be eluted from the resin by 4 M hydrochloric acid. Copper was separated from nickel and cobalt by sorption at pH 3.5 and elution by 1 M hydrochloric acid. Uranium was concentrated from 1-liter samples of synthetic sea water and eluted by 2 M hydrochloric acid with 95% recovery.

Ramirez and Andrade reacted poly(acrolein) with desferroxamine B, a naturally occurring hydroxamic acid shown below (102). Iron sorption was demonstrated qualitatively for this product, which was proposed for the treatment of severe iron poisoning. In 1975 and 1976, Winston and coworkers developed the polymeric hydroxamic acids shown below (103,104). This work was begun in an attempt to produce a totally synthetic polymer whose chelation of iron(III) would rival that of desferroxamine B. Polymer II was very successful in this regard, while polymer I was less so. Very unsatisfactory results were obtained with polymer III, which reacted more like a monomeric hydroxamic acid. The

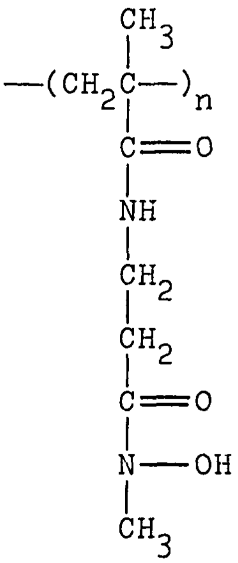


$$NH_2(CH_2)_5\underset{}{\overset{OH}{N}}-\overset{O}{\overset{\|}{C}}(CH_2)_2CONH(CH_2)_5\overset{OH}{N}-\overset{O}{\overset{\|}{C}}(CH_2)_2CONH(CH_2)_5\overset{OH}{N}-\overset{O}{\overset{\|}{C}}CH_3$$

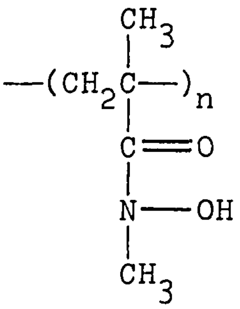
I



II



III



conclusion from this work was that "the spacing of hydroxamic acid units is of fundamental importance in designing a polymer having exceptional affinity for iron" (104).

SYNTHESIS AND CHARACTERIZATION OF AN N-PHENYL HYDROXAMIC ACID RESIN

Introduction

Polymeric hydroxamic acids have been prepared by hydroxylaminolysis of various derivatives of poly(acrylic acid) as described in the previous section. The reactions of these resins with iron, copper, vanadium, and several other elements have been studied qualitatively and a few quantitative separations have been achieved. However, the investigation of polymeric hydroxamic acids is far from complete. Many of the elements which are precipitated or extracted by monomeric hydroxamic acids have not been included in studies of their polymeric analogues. The relationship between the structure of these polymers and the stability of their metal complexes has received relatively little attention.

In this section, the synthesis and characterization of N-hydroxy-N-phenylcarbamoyl XAD-4 are described. This is one of the first aromatic poly(hydroxamic acids) to be reported. Since it contains an N-phenyl group, it is chemically similar to N-phenylbenzohydroxamic acid, the most popular hydroxamic acid for analytical applications (18). The extraction of 20 metal ions from 2 $\underline{M}$ hydrochloric acid by this resin is discussed and conditions for the quantitative extraction and back-extraction of 9 of these are described. These results are compared with the work of Forster and Schwabe on solvent extraction with N-phenylbenzohydroxamic acid (82).

Experimental

Reagents

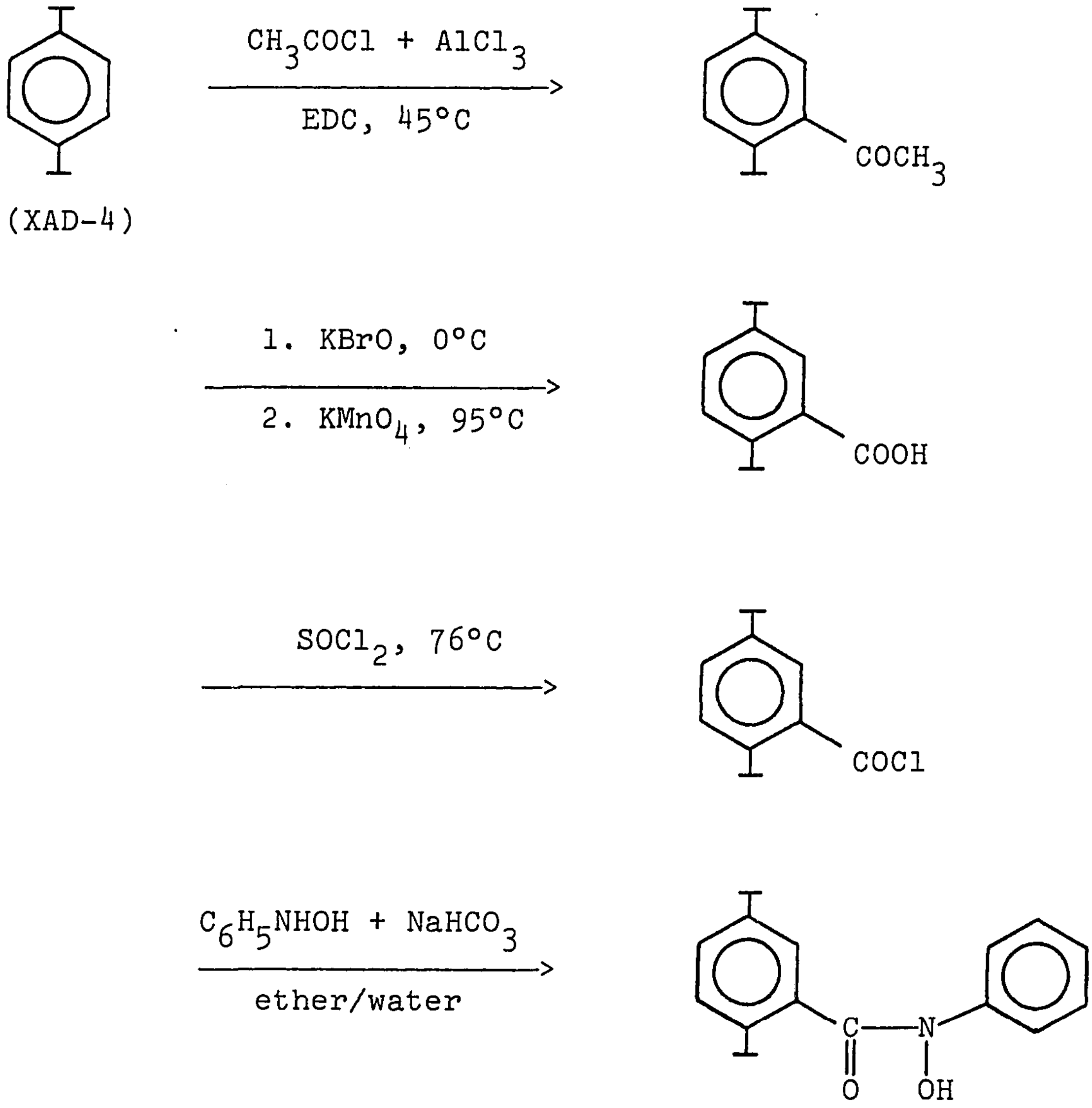
Amberlite XAD-4 resin was supplied by Rohm and Haas Company. The resin was rinsed with methanol and dried by suction filtration. It was ground immediately and sieved into 100-150, 150-200, and 200-325 mesh fractions. Fines were removed by slurrying the resin with methanol, allowing it to settle, and decanting the solvent. This process was repeated several times until all the particles with settling times greater than 5 minutes had been removed. The fractionated resin was stored under methanol until needed. Phenylhydroxylamine was prepared immediately before using by the reduction of nitrobenzene with zinc dust, as described by Vogel (105). All other chemicals used in the resin synthesis, including solvents, were commercially available, reagent-grade materials.

Solutions of metal ions were prepared by dissolving their reagent-grade salts in dilute acid, with the exceptions noted below. Aluminum(III) solutions were prepared by dissolving the reagent-grade metal in 6 M hydrochloric acid. Iron(III) solutions were prepared by dissolving standard-of-reference-grade iron (G. Frederic Smith Co.) in a mixture of hydrochloric and nitric acids. Solutions of 0.01 M titanium(IV) were prepared by fusing 80 mg titanium dioxide with 1 g potassium pyrosulfate, dissolving the melt in hot, 4 M hydrochloric acid, and diluting to 100 mL. Zirconium(IV) solutions were prepared by heating $ZrOCl_2 \cdot 8 H_2O$ in 6 M hydrochloric acid. Solutions of uranium(IV) were prepared by passing solutions of uranium(VI) in 3 M hydrochloric acid through a 5-mm i.d. by 10-cm column containing granular lead (106).

Solutions of arsenic(III) were prepared by dissolving As_2O_3 in a small amount of 6 M sodium hydroxide and acidifying the resulting solution. Solutions of antimony(III) were prepared by dissolving Sb_2O_3 in hot, concentrated sulfuric acid. Ammonium metavanadate was dissolved in a small amount of 1 M sodium hydroxide and acidified with sulfuric acid to give solutions of vanadium(V). Sodium molybdate and sodium tungstate were dissolved in aqueous 0.1 M sodium tartrate and acidified with hydrochloric acid to give solutions of molybdenum(VI) and tungsten(VI), respectively. A 0.001 M niobium(V) solution was prepared by dissolving niobium metal in a mixture of nitric and hydrofluoric acids. Concentrated sulfuric acid was added and the solution was heated to heavy fumes to eliminate fluoride. After cooling, the solution was diluted with aqueous sodium tartrate. It was quantitatively transferred to a 100-mL flask, acidified with hydrochloric acid, and diluted to the mark with water.

Synthesis

The N-phenyl hydroxamic acid resin was prepared by the sequence of reactions shown below.



A slurry of 1.78 g anhydrous aluminum chloride and 4 mL of ethylene dichloride was prepared in a 50-mL flask with a 24/40 ground glass joint. A magnetic stirring bar was introduced and the mixture was stirred until it appeared homogeneous. The flask was cooled in an ice-water bath and 1.55 g of 100-150 mesh XAD-4, which had been dried at 110°C for 2 hours, was slowly added with stirring. The sides of the flask were washed down with an additional 2 mL of ethylene dichloride. The flask was removed from the ice-water bath and connected to a drying tube packed with anhydrous calcium sulfate (Drierite, Hammond). The reaction mixture was heated at 40°C without stirring for 8 hours. It was quenched by pouring it onto a mixture of cracked ice and concentrated hydrochloric acid After several hours, the resin was collected by suction filtration and rinsed with methanol, water, and concentrated hydrochloric acid. After rinsing again with water and methanol, the resin was dried overnight at 60°C. A light orange product weighing 1.78 g was obtained.

A solution of 4.2 g of sodium hydroxide in 35 mL of water was cooled to 0°C in an ice-salt bath. The solution was stirred magnetically while 2 mL of bromine was slowly added. When all the bromine had dissolved, the acetyl XAD-4 was added with stirring. The mixture was allowed to stand at room temperature for 3 hours and then boiled for 10 minutes. The product was isolated by suction filtration, washed with 1 M hydrochloric acid and methanol, and dried at 60°C overnight. The resin was further oxidized by adding it to a solution of 2 g of sodium hydroxide and 1.6 g of potassium permanganate in 100 mL of water. This was heated at 90-100°C for about 2 hours. The product and the precipitated manganese dioxide were collected by suction filtration. The latter was removed by rinsing with concentrated hydrochloric acid. The product, which was light yellow, was rinsed with water and methanol, and dried at 60°C.

The carboxy XAD-4 was treated with thionyl chloride at 60°C for 2.5 hours with intermittent stirring. The chloroformyl XAD-4 was isolated by suction filtration, washed with diethyl ether, and dried by continued suction. It was added to a 100-mL beaker containing 0.5 g of sodium bicarbonate, 1 mL of water, and 10 mL of a solution in diethyl ether of phenylhydroxylamine, freshly prepared from 5 mL of nitrobenzene. This mixture was allowed to stand at room temperature for 90 minutes. The product was collected by suction filtration, washed with water and methanol, and stored under methanol.

Characterization

The hydrogen ion capacity of the carboxy XAD-4 was determined as follows. About 200 mg of dried resin was accurately weighed into a 50-mL beaker and 10 mL of 0.1 M sodium hydroxide was added. A second beaker containing 10 ml of 0.1 M sodium hydroxide was used to determine the blank. The beakers were covered with watch glasses and left for 1 hour. The resin was filtered, and the filtrate and wash were titrated with 0.1 M hydrochloric acid. The amount of acid consumed by the sample was subtracted from that consumed by the blank and the result was divided by the weight of resin in the sample to give its hydrogen ion capacity in millimoles per gram.

The infrared spectra of the starting material, the carboxy intermediate, and the final product were obtained with potassium bromide pellets. A dried sample of the final product was analyzed for nitrogen with a Perkin-Elmer Model 240 Elemental Analyzer. The presence of hydroxamic acid groups in the final product was confirmed by qualitative tests with iron(III) and vanadium(V). A 5-mm i.d. column, packed to a depth of 5 cm with about 250 mg of resin, was used for these tests. Characteristic colored bands were obtained when solutions of the above ions were passed through the column.

Kinetics

The rate of copper(II) uptake was estimated by the following experiment. A solution of 0.518 mmol of $CuSO_4 \cdot 5 H_2O$ in 50 mL of 1 M sodium sulfate was adjusted to pH 4.0

with dilute sulfuric acid. A 0.5-mL aliquot was taken to determine the initial copper concentration. About 1 mL of resin, which had been stored under methanol, was dried by suction filtration and added to the copper(II) solution with stirring. The pH was kept at 4.0 by additions of 0.1 M sodium hydroxide. Additional 0.5-mL aliquots were taken at intervals of 5, 15, 20, 40, and 80 minutes. The stirring was stopped for 90 seconds prior to sampling to allow the resin to settle. The aliquots were analyzed for copper colorimetrically as described in the Appendix. After the experiment, the resin was collected by suction filtration and washed with 1 M hydrochloric acid to remove sorbed copper. The weight after drying at 60°C was 0.224 g.

Column extraction

A 5-mm i.d. by 5-cm gravity column packed with about 250 mg of resin was used to determine the extent of extraction of various ions from 2 M hydrochloric acid. The column was conditioned by passing 5 mL of 2 M HCl through it. A 5-mL aliquot of a 0.001 M solution of the test ion in 2 M HCl was passed through the column at about 1 mL/min, followed by 5 mL of 2 M HCl. The amount of test ion in the effluent was determined spectrophotometrically as described in the Appendix. Similar experiments were performed to test the extraction of selected elements at pH 1-4.

Quantitative recovery of metal ions

The general procedure described above for column extraction was used in these experiments as well. This was followed by elution with 5 mL of back-extracting solution. The overall recovery of the test ion was determined by analysis of the effluent from the back-extraction, as described in the Appendix.

Results and Discussion

The increase in weight of the resin following acetylation was used to estimate a yield of 3.00 millimoles per gram of product for this step. This corresponds to reaction of about half of the aromatic rings in the resin. The hydrogen ion capacity after the hypobromite oxidation was only 0.073 mmol/g. This was surprising since a definite odor of bromoform was noted during the reaction. A capacity of 2.81 mmol/g was obtained after the permanganate oxidation. Omission of the hypobromite oxidation on a second batch of resin led to a capacity of 1.78 mmol/g, indicating that the two-step oxidation was considerably more effective. The nitrogen content of the final product was 1.50% or 1.08 mmol/g. This represents at best a 40% conversion of functional groups from carboxylic to hydroxamic acid. The actual yield may be still lower because of the possible side reaction of O-acylation. The infrared spectrum of the carboxy intermediate shows clear bands at 1720 and 1290 cm^{-1} similar to those found in the spectrum of benzoic acid (107). The spectrum of the final product is consistent with the assumption that at least two types of carbonyl groups are present.

Simple gravity-column experiments were used for qualitative studies of metal complexation. Copper(II) and cadmium(II) were retained from pH 3-5 buffer solutions. Iron(III) was retained from pH 3 tartrate with the formation of a rust-colored band, which could be removed by elution with 3 M hydrochloric or 5 M phosphoric acid. Bismuth(III) was retained from pH 6 tartrate and eluted by 1 M hydrochloric acid. Zirconium(IV) was retained in 0.5 M HCl and remained on the column despite elution with 2.4 and 10 M HCl. Vanadium(V) was retained from 0.2 M sulfuric acid with the formation of a dark band. Successive elution with 0.5, 2.4, and 10 M HCl changed the color of the band to deep purple without moving it. Similar colors have been observed in the solvent extraction of vanadium(V) by N-phenylbenzohydroxamic acid from sulfuric and hydrochloric acids (18). The colored band was removed slowly by continued elution with 6% hydrogen peroxide in dilute sulfuric acid. Elution with 1 M sodium hydroxide removed the colored band quickly, but also caused a permanent change in the color of the resin and, after repeated use, a loss in complexation ability.

The results of the study of the kinetics of copper extraction at pH 4 are shown in Table 8. They indicate an equilibration rate, $t_{\frac{1}{2}}$, less than 5 minutes with a maximum capacity of 0.4 mmol/g. The most successful of the hydroxamic acid resins prepared by Vernon and Eccles had an equilibration rate of 22 minutes with a maximum capacity of 3.2 mmol/g for Cu(II) at pH 6 (101). Direct comparison of these data is impossible since the experimental conditions, especially pH, were not identical. However, the results suggest that our resin exhibits faster kinetics at the price of decreased capacity. This trend has been observed previously in comparing chelating resins derived from XAD-4 with those produced by other techniques (108).

Table 8. Kinetics of copper(II) extraction at pH 4 by N-phenyl hydroxamic acid resin

	Amount of copper extracted	
Time, min	Millimoles per gram of resin	Percentage of final
5	0.29	73
15	0.36	91
20	0.36	91
40	0.39	100
80	0.39	100

The results of column extraction of various ions from 2 M hydrochloric acid are shown in Table 9. Extraction of antimony(III), zirconium(IV), tin(V), molybdenum(VI), and tungsten(VI) is virtually complete, as predicted by the data of Forster and Schwabe on solvent extraction with N-phenylbenzohydroxamic acid (82). Less satisfactory results were obtained with niobium(V) and titanium(IV). The incomplete extraction of niobium may be caused by slow kinetics. Solvent extraction of niobium and tantalum by N-phenylbenzohydroxamic acid is reported to proceed relatively slowly (109). The reason for incomplete extraction of titanium is not understood. Vanadium(V) was not included in this study since it is relatively unstable in hydrochloric acid solution (110). Tantalum(V) was not included because of the difficulty of finding a suitable detection method for this element. The extraction behavior of hafnium(IV) is expected to be very similar to that of zirconium(IV).

The difference in extraction of uranium(IV) and uranium(VI) is gratifying because it is consistent with the published formation constants for uranium(IV) and uranium(VI) benzohydroxamates (66). In addition, it offers a convenient method for the separation of these species. Quantitative experiments were done to find suitable eluents for the

Table 9. Extraction of various ions from 2 M HCl by N-phenyl hydroxamic acid resin

Ion	Percentage extraction
Mg(II)	0
Ca(II)	0
Cu(II)	0
Pb(II)	0
Hg(II)	0
Al(III)	0
Fe(III)	70
As(III)	1
Sb(III)	100
Bi(III)	0
Ti(IV)	57
V(VI)	0
Zr(IV)	100
Sn(IV)	99
Th(IV)	1
U(IV)	99
Nb(V)	94
Mo(VI)	98
W(VI)	100
U(VI)	1

back-extraction of uranium(IV). Acidic solutions of sulfate, phosphate, and oxalate were all effective.

Data for the extraction of several elements from less acidic media are shown in Tables 10-13. Thorium(IV) is quantitatively extracted and can be separated from uranium(VI) at pH 1. The extraction of titanium(IV) at this pH is not quite complete. Copper(II) and uranium(VI) are quantitatively extracted at pH 3 and 4, respectively. At pH 1-4, iron(III) solutions form a distinct colored band at the top of the column. However, the extraction is incomplete below pH 4. These observations imply that the mechanism for iron(III) extraction is complicated and involves a slow step. Aluminum(III) is extracted quantitatively at pH 4. No extraction of calcium is detectable at this pH.

Suitable eluents for quantitative back-extraction were found for most elements, as shown in Table 14. Cu(II), Th(IV) and U(VI) could be eluted by simple changes in eluent pH. The remaining ions required the use of complexing agents for fast, quantitative elution. Forster and Schwabe used 5 M sulfuric acid for the back-extraction of titanium, zirconium, and hafnium N-phenylbenzohydroxamates. However, this was ineffective for the elution of zirconium from the chelating resin. The use of oxalic acid as an eluent for zirconium was suggested by the work of Mazzucotelli and

Table 10. Extraction of selected metal ions from 0.1 M HCl by N-phenyl hydroxamic acid resin

Ion	Percentage extraction
Cu(II)	1
Al(III)	3
Fe(III)	88
Th(IV)	100
U(VI)	0
Ti(IV)	99.7

Table 11. Extraction of selected metal ions from 0.1 M ammonium chloride at pH 2.0 by N-phenyl hydroxamic acid resin

Ion	Percentage extraction
Cu(II)	16
Al(III)	57
Fe(III)	94
U(VI)	99

Table 12. Extraction of selected metal ions from 0.01 M tartrate at pH 3.0 by N-phenyl hydroxamic acid resin

Ion	Percentage extraction
Cu(II)	100
Fe(III)	82
U(VI)	97

Table 13. Extraction of selected metal ions from 0.1 M acetate at pH 4.0 by N-phenyl hydroxamic acid resin

Ion	Percentage extraction
Ca(II)	0
Cu(II)	100
Al(III)	100
Fe(III)	100
U(VI)	100

Table 14. Conditions for quantitative recovery of metal ions by N-phenyl hydroxamic acid resin

Ion	Extraction	Back-extraction
Cu(II)	pH 4 acetate	0.1 M HCl
Al(III)	pH 4 acetate	0.1 M oxalic acid
Fe(III)	pH 4 acetate	0.1 M oxalic acid
Th(IV)	0.1 M HCl	1 M HCl
Zr(IV)	2 M HCl	0.1 M oxalic acid
Ti(IV)	pH 2 lactic acid	0.3 M HF
U(VI)	pH 4 acetate	0.1 M HCl
Mo(VI)	2 M HCl[a]	1 M NH_3[a]
W(VI)	2 M HCl[a]	0.1 M sodium tartrate

[a] Plus 0.1 M tartrate.

others (111). It proved to be effective for the rapid and quantitative elution of iron(III) and aluminum(III) as well as zirconium(IV) from the hydroxamic acid resin. The use of hydrofluoric acid as an eluent for titanium(IV) was suggested by the high formation constants for the fluoro complexes of this element (112). The use of neutral and basic tartrate for the back-extraction of tungsten(VI) and molybdenum(VI), respectively, was suggested by the work of Pyatnitskii and Kravtsova on solvent extraction of these elements from tartrate and citrate media by N-phenylbenzohydroxamic acid (113).

These results demonstrate the feasibility of using an N-phenyl hydroxamic acid resin for a variety of analytical operations. Questions remain, however, about the details of metal complexation. A few ions appear to react slowly, but this has not been shown conclusively. It is not clear whether N-substitution, in this case with a phenyl group, is important in determining the complexation properties of the resin. These questions are addressed in the following section.

COMPARATIVE STUDY OF N-PHENYL, N-METHYL, AND N-UNSUBSTITUTED HYDROXAMIC ACID RESINS

Introduction

The relationship between the structure and complexation properties of hydroxamic acids has received little attention. Bass and Yoe studied thirty-six hydroxamic acids with various structural features for use as colorimetric reagents (81). They concluded that color formation is a function of pH, solvent, and reagent concentration, and that N-substitution is relatively unimportant. The available stability-constant data, however, suggest that the N-substituted hydroxamic acids should be more effective complexing agents than their N-unsubstituted analogues in strongly acidic media (47,67).

Most of the research on poly(hydroxamic acids) has been concentrated on primary, or N-unsubstituted, compounds. Exceptions to this are found in the work of Vernon and Eccles (98,99), Winston and Mazza (103), and Winston and McLaughlin (104). In no case has the relationship between N-substitution and complexation properties been explored systematically. Such a study is reported in this section. It begins with a description of the syntheses of the N-unsubstituted and N-methyl analogues of the N-phenyl hydroxamic acid resin discussed in the preceding section. The three resins are compared with respect to metal-ion complexation, using both batch- and column-extraction methods. Finally, the potential of each resin for analytical separations is evaluated.

Experimental

Apparatus and reagents

A Cheminert CMP-2 metering pump from Chromatronix, Inc. and an automatic fraction collector from Warner-Chilcott Laboratories were used in obtaining the exchange isoplanes. A Burrell automatic shaker was used in the batch-extraction experiments. Hydroxylamine hydrochloride and calcium hypochlorite were obtained from Fisher Scientific. N-methylhydroxylamine hydrochloride was obtained from Aldrich. A commercial laundry bleach was used as 5% sodium hypochlorite. Potassium hypochlorite was prepared as an approximately 1.5 M solution by the reaction of calcium hypochlorite and potassium carbonate (114). The XAD-4 resin, and other reagents used for the syntheses of the chelating resins, are described in the preceding section.

Solutions of iron(II) were prepared by adding 1 g of hydroxylamine hydrochloride to about 30 mL of a solution containing 0.1 mmol of iron(III) and adjusting the pH to 4. After 5 minutes, acid or buffer was added to bring the solution to the desired pH. It was transferred to a 100-mL volumetric flask and diluted to the mark with water. Solutions of other metal ions were prepared as described earlier.

Synthesis

Acetyl XAD-4 was prepared by treating 3.10 g of 100-150 mesh XAD-4 as described in the preceding section. The product was oxidized by a series of hypochlorite reactions, using increasingly rigorous conditions. The hydrogen ion capacity of the product at each stage was determined as described earlier. In the first oxidation, 10 mL of methanol and 90 mL of 5% sodium hypochlorite were added to the resin. The mixture was allowed to stand overnight at room temperature. The resin was filtered, added to 100 mL of fresh 5% sodium hypochlorite, and heated at 70°C for 8 hours. In the second oxidation, the resin was heated at 80°C in 100 mL of 5% sodium hypochlorite for 5 hours. In the third reaction, the resin was heated for 5 hours at 80°C in a solution of 2% sodium hydroxide in 20% ethanol. Finally, the resin was heated for 4 hours at 65°C in 150 mL of approximately 1.5 M potassium hypochlorite.

The acid chlorinations were run as described in the previous section. The N-unsubstituted resin was synthesized by adding approximately 1 g of chloroformyl XAD-4 to a 50-mL beaker containing 2.1 g of sodium carbonate, 1.4 g of hydroxylamine hydrochloride, and 10 mL of diethyl ether. On addition of 2.5 mL of water, the mixture began to effervesce. After about 10 minutes, the product was isolated by suction filtration, washed with water and methanol, and stored under methanol. The N-methyl hydroxamic acid resin was synthesized by substituting 1.68 g of N-methylhydroxylamine hydrochloride for the hydroxylamine hydrochloride in the above procedure. The preparation of the N-phenyl hydroxamic acid resin was described earlier.

Characterization

The hydrogen ion capacity of the carboxy XAD-4 and the nitrogen contents of the final products were determined as described in the preceding section.

Column extraction

These experiments were done as described earlier.

Exchange isoplanes (breakthrough curves)

A slurry of 100 mg of accurately weighed hydroxamic acid resin in methanol was quantitatively transferred to a 2-mm i.d. by 10-cm glass column using a 5-mL syringe. A stock solution of Cu(II) was prepared by adding 2.50 g of $CuSO_4 \cdot 5\ H_2O$ and 2 mL of 0.05 M sulfuric acid to a 100-mL volumetric flask and diluting to the mark with water. A 5-mL aliquot of this solution and 14.2 g of sodium sulfate were added to a 1-liter flask and diluted to the mark with water. The result was a solution of 5×10^{-4} M copper(II) in 0.1 M sodium sulfate with a pH of 6.3. This was pumped through the column of resin at 0.8 mL/min. Fractions were collected automatically at 40-minute intervals. The flow rate was calibrated by dividing the average fraction weight by the density of the solution. The progress of the experiment could be followed by the development of a green zone as the resin absorbed copper. The concentration of copper in the fractions was determined colorimetrically as described in the Appendix.

Stability study

After an initial exchange isoplane had been obtained, each resin was subjected to a series of chemical stresses. The sorbed copper was removed by elution with 0.1 M hydrochloric acid, and 2 M hydrochloric acid was then passed through the column. After 1 hour, the column was eluted with water and a second exchange isoplane was obtained. The copper was removed and 1 M ammonium hydroxide was passed through the column. After 1 hour. the resin was restored to the hydrogen form by elution with 0.1 M hydrochloric acid, followed by water. A third exchange isoplane was obtained. The copper was removed and the resin was transferred from the column to a small, uncovered vial. This was placed on a window sill in diffuse light for 90 days. The resin was returned to the column and a final exchange isoplane was obtained. During the exposure to light and air, the resins were allowed to become completely dry. The N-phenyl resin turned almost black while the

N-methyl resin darkened slightly. No change in the N-unsubstituted resin was observed.

Batch extraction

A 50 ± 2 mg portion of resin was accurately weighed into a 60-mL polyethylene bottle and 10 mL of a 10^{-4} M solution of the test ion was added. The bottle was placed in the automatic shaker for 4 hours, except where noted otherwise. After being filtered through glass wool to remove the resin, the solutions were analyzed for the test ion as described in the Appendix.

Results and Discussion

The oxidation procedure used previously was modified in an attempt to improve it. The use of alkaline potassium permanganate is accompanied by the formation of insoluble manganese dioxide. This makes recovery of the resin by suction filtration tedious and difficult. A large amount of concentrated hydrochloric acid is required for the resin cleanup and hazardous chlorine gas is evolved during this process.

Sodium hypochlorite has several advantages as an oxidizing agent in this synthesis. It is selective, which should permit one to oxidize the attached acetyl groups without altering the resin matrix. The reduction products are sodium chloride and chloroform, so that isolation of the oxidized resin is straightforward. Finally, it is relatively inexpensive. However, it was necessary to repeat the reaction several times, with increasingly rigorous conditions, to obtain a reasonable yield.

The capacity after the initial oxidation was only 1.25 mmol/g. This was increased to 1.50 mmol/g by repeating the reaction at a slightly higher temperature. The hypohalite reaction involves chlorination to a trihaloketone followed by hydrolysis. It was felt that the latter step might be rate determining, so the third reaction was a simple hydrolysis in a solution of sodium hydroxide in ethanol/water. This increased the capacity slightly, to 1.81 mmol/g. The final oxidation in 1.5 M potassium hypochlorite raised the capacity to 2.69 mmol/g.

The reaction conditions for hydroxylaminolysis were adapted from the procedure of Jones and Hurd (33). The nitrogen content of the N-unsubstituted product was 2.34% or 1.67 mmol/g, a yield of 64% based on the capacity of the carboxy intermediate. The nitrogen content of the N-methyl resin was 2.44% or 1.74 mmol/g for a yield of 70%. Both resins give the red to purple color with iron(III) characteristic of hydroxamic acids.

The results of column extraction of several ions from 2 M hydrochloric acid by the new resins are shown in Table 15. These should be compared with the results in Table 9.

Table 15. Column extraction (percent) of ions from 2 M HCl by N-unsubstituted and N-methyl hydroxamic acid resins

	Resin	
Ion	N-unsubstituted	N-methyl
Fe(III)	27	98.8
Sb(III)	100	100
Zr(IV)	100	100
Ti(IV)	99.5	99.8
Sn(IV)	99.9	99.9
Mo(VI)	100	100
W(VI)	100	100

Antimony(III), zirconium(IV), tin(IV), molybdenum(VI), and tungsten(VI) are extracted quantitatively by all three resins. Interesting differences are found in the extraction of iron(III) and titanium(IV). The N-methyl hydroxamic acid resin is the most effective of the three for column extraction of both iron and titanium. The N-unsubstituted resin is more effective for titanium but less effective for iron than the N-phenyl resin.

Additional information can be obtained from the exchange isoplanes, or breakthrough curves, for copper(II) extraction by the three resins at pH 6. Exchange isoplanes at two different flow rates are shown in Figure 1. The usable capacity of the column at a given flow rate is calculated from the point at which there is detectable breakthrough. The exchange capacity of the resin can be determined from the point at which 50% breakthrough occurs (2). The steepness of the breakthrough region is a function of the flow rate and the resin kinetics (115). No difference was observed in the shape of the breakthrough curves for the three resins, which suggests that their sorption kinetics are similar.

The exchange capacities for copper of the three hydroxamic acid resins and the carboxy intermediate are shown in Table 16. The carboxy intermediate has some capacity for copper and so, presumably, do the unreacted carboxy groups

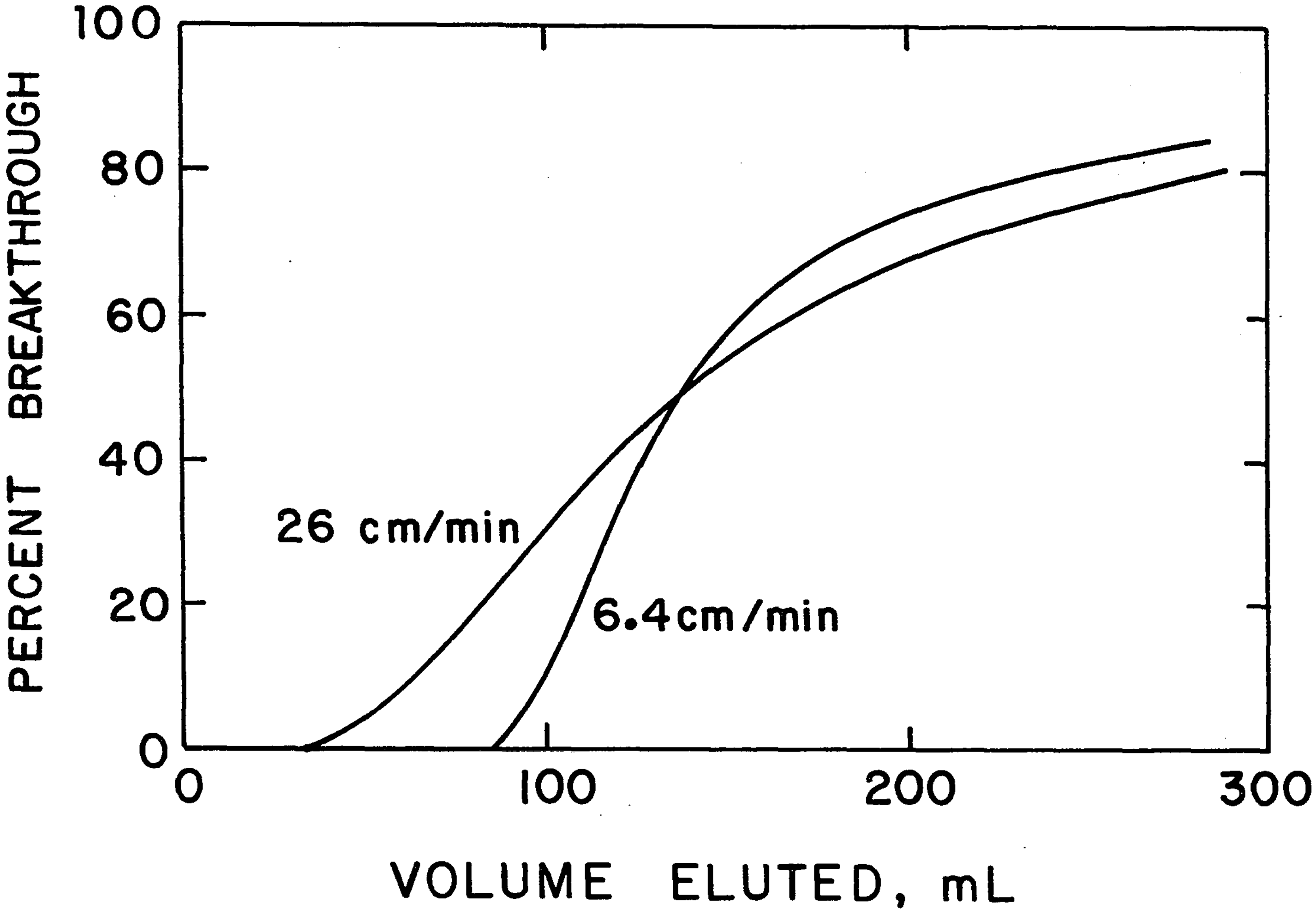


Figure 1. Exchange isoplane (breakthrough curve) for Cu(II) from N-methyl hydroxamic acid resin

Table 16. Copper(II) capacity as determined by breakthrough plots

Functional group	Nitrogen content, mmol/g	Cu(II) capacity mmol/g
-COOH	---[a]	0.15
-CONHOH	1.68	0.48
$-CON(CH_3)OH$	1.78	0.69
$-CON(C_6H_5)OH$	1.08	0.40

[a] Not determined.

in the hydroxamic acid resins. The highest capacity is clearly present in the N-methyl resin. The value of 0.40 mmol/g obtained for the N-phenyl resin agrees with the result reported in the previous section, although the latter was measured at pH 4 by an entirely different technique.

The data in Table 16 can be used to compare the efficiencies of the three types of hydroxamic acid group as follows. The percentage of unreacted carboxy groups in each resin is multiplied by the capacity of the carboxy intermediate. This product is subtracted from the measured capacity to give the contribution of the hydroxamic acid groups. The ratio of the nitrogen content of the resin to this adjusted capacity provides an estimate of the number of hydroxamic acid groups required for complexation. The results of this calculation are 3.9, 2.8, and 3.5 for the N-unsubstituted, N-methyl, and N-phenyl hydroxamic acid resin, respectively.

The acid- and base-catalyzed hydrolyses of hydroxamic acids were discussed in an earlier section. One of the objections to the use of hydroxamic acid resins is that they "are unstable...toward relatively concentrated acids and bases and undergo rearrangements during regeneration" (5). A study of resin stability was done to test this assertion with the results shown in Table 17. Treatment with acid and base actually caused slight increases in the

Table 17. Copper(II) capacities (mmol/g) of hydroxamic acid resins after treatment with acid and base, and after a 90-day exposure to light and air

Functional group	Treatment			
	None	2 <u>M</u> HCl 1 hr	1 <u>M</u> NH_3 1 hr	Light and air 90 days
-CONHOH	0.48	0.51	0.54	0.45
$-CON(CH_3)OH$	0.69	0.69	0.71	0.54
$-CON(C_6H_5)OH$	0.40	0.41	0.40	0.41

capacities of the N-unsubstituted and N-methyl resins and had no measurable effect on the N-phenyl resin. Exposure to light and air, however, had a detrimental effect on the capacities of the first two resins. The dramatic change in the appearance of the N-phenyl resin after exposure to light and air was not accompanied by any loss in capacity.

Column extraction of iron(II) by the three resins was studied in an effort to account for some of the anomalous behavior of iron(III) described in the preceding section. The results, shown in Table 18, are that iron(II) sorption by all three resins is negligible at or below pH 1 but virtually quantitative at pH 4. Reduction of iron(III) to iron(II) on the resin could thus account for the incomplete extraction of iron by the N-phenyl resin at pH 1-3.

In a related experiment, 5-mL aliquots of 10^{-3} $\underline{M}$ iron(III) in 0.1 $\underline{M}$ hydrochloric acid were passed through two gravity columns containing the N-methyl hydroxamic acid resin. A red band developed at the top of each column. The columns were eluted with 5 mL of 0.1 $\underline{M}$ HCl. The effluent from the first column was collected in a buffered (pH 5) solution of 1,10-phenanthroline plus hydroxylamine hydrochloride. The effluent from the second column was collected in a buffered solution of 1,10-phenanthroline alone. Both solutions developed a faint red color, corresponding to 0.8% of the iron added to the columns. Since iron(III)

Table 18. Column extraction (percent) of Fe(II) from different media by hydroxamic acid resins

Functional group	Medium		
	2 M HCl	0.1 M HCl	0.1 M acetate, pH 4
-CONHOH	0.2	0.4	99.9
$-CON(CH_3)OH$	0.0	1.2	99.9
$-CON(C_6H_5)OH$	0.6	0.0	99.9

does not form a colored complex with 1,10-phenanthroline, it is likely that the nonextracted iron was, in fact, iron(II).

Table 19 shows the extraction of aluminum(III) by the three resins in the presence of 0.1 M tartrate. The results demonstrate again the superior complexing ability of the N-methyl resin. Since this is a ligand-exchange reaction, its pH dependence is determined by the ionization constants of the two ligands. The two pKa's of tartaric acid are 3.0 and 4.2, respectively, whereas the pKa for an aromatic hydroxamic acid should be between 8 and 9. It can be shown that the extent of ionization, and thus the complexing power, of the hydroxamic acid will increase relative to that of tartaric acid as the pH is raised from 4 to 5 (112). The data in Table 19 are in qualitative agreement with this prediction.

A disadvantage of column-extraction experiments is that they do not distinguish between thermodynamic and kinetic effects. More fundamental information about the ion-resin interactions can be obtained by batch-extraction experiments. The kinetics of batch extraction were studied using iron(III) as the test ion with the results shown in Table 20. An attempt was made to fit these data to the rate equation for first-order, opposing reactions (116). This was unsuccessful, however, because the observed rate constant decreases as the reaction approaches equilibrium. The

Table 19. Column extraction (percent) of Al(III) from 0.1 M tartrate at pH 4.0 and 5.1 by hydroxamic acid resins

Functional group	pH	
	4.0	5.1
-CONHOH	78.7	94.9
$-CON(CH_3)OH$	90.6	100.0
$-CON(C_6H_5)OH$	54.4	78.3

Table 20. Kinetics of batch extraction of Fe(III) by N-unsubstituted hydroxamic acid resin at pH 1

Time, hours	Percentage extraction
1	96.1
2	97.5
4	98.3
8	98.5
18	98.7

kinetics of several other ions were checked by comparing the results of 1- and 4-hour extractions. Based on these observations, titanium(IV) and thorium(IV) react more slowly than iron(III) while copper(II), aluminum(III), and uranium(VI) react more quickly.

Batch-extraction experiments were used to compare the complexing ability of the three resins. Tables 21-26 show the extraction of copper(II), iron(III), aluminum(III), thorium(IV), uranium(VI), and titanium(IV) as a function of pH. These results were obtained from 4-hour extractions so that they are probably slightly lower than the equilibrium values. They may be used to estimate the distribution coefficients (117) for these systems, however, by the following formula, where E is the percentage extracted.

$$D_g = 200(E)/(100 - E)$$

The factor of 200 is the ratio of solution volume (mL) to resin weight (g) used in the experiments.

Tables 21-26 show again that the most stable complexes are formed by the N-methyl resin. The most dramatic example of this is in the extraction of titanium(IV) from 3 $\underline{M}$ hydrochloric acid. The distribution coefficients in this system are 6200, 360, and 270 for the N-methyl, N-unsubstituted, and N-phenyl resins, respectively. The extraction data for titanium(IV) and iron(III) are plotted as functions

Table 21. Batch extraction (percent) of Cu(II) by hydroxamic acid resins as a function of pH

pH	Functional group		
	-CONHOH	-CON(CH_3)OH	-CON(C_6H_5)OH
1.0	0.0	2.4	0.0
2.0	21.2	42.6	15.2
2.5	63.7	84.6	56.7
3.0	91.4	97.0	88.9
4.0	98.6	100.0	98.6
5.0	99.5	100.0	99.7

Table 22. Batch extraction (percent) of Fe(III) by hydroxamic acid resins as a function of pH

pH	Functional group		
	-CONHOH	-CON(CH_3)OH	-CON(C_6H_5)OH
-0.5	8.5	34.6	4.5
0.0	35.6	83.6	25.8
0.5	87.2	97.8	70.8
1.0	98.2	99.5	85.7
1.5	99.4	99.3	94.5
2.0	100.0	99.7	98.6

Table 23. Batch extraction (percent) of Al(III) by hydroxamic acid resins as a function of pH

pH	Functional group		
	-CONHOH	-CON(CH_3)OH	-CON(C_6H_5)OH
1.0	0.0	1.4	0.0
2.0	44.8	78.6	24.7
2.5	90.0	98.9	74.9
3.0	98.6	99.7	96.4
4.0	99.6	100.0	99.1

Table 24. Batch extraction (percent) of Th(IV) by hydroxamic acids as a function of pH

pH	Functional group		
	-CONHOH	-CON(CH_3)OH	-CON(C_6H_5)OH
0.0	3.8	11.1	1.3
0.5	22.0	51.7	16.8
1.0	77.2	91.2	68.1
1.5	97.4	97.7	94.4
2.0	99.3	97.8	96.9
2.5	99.8	98.6	99.0

Table 25. Batch extraction (percent) of U(VI) by hydroxamic acid resins as a function of pH

pH	Functional group		
	-CONHOH	-CON(CH_3)OH	-CON(C_6H_5)OH
1.0	0.0	0.3	0.0
1.5	5.6	11.4	3.9
2.0	30.5	51.6	23.2
2.5	70.6	87.1	63.8
3.0	90.7	96.9	88.4
4.0	94.0	97.9	94.6

Table 26. Batch extraction (percent) of Ti(IV) by hydroxamic acid resins as a function of pH

pH	Functional group		
	-CONHOH	-CON(CH_3)OH	-CON(C_6H_5)OH
-0.5	64.2	96.9	57.8
0.0	69.0	97.1	53.3
0.5	83.4	98.2	66.1
1.0	94.8	99.0	83.1
1.5	98.8	99.3	96.2

of pH in Figures 2 and 3, respectively. In the latter figure, the extraction curves for the three resins are similar in shape but displaced along the horizontal axis. The effect of the N-methyl group is to shift the extraction curve for this resin toward lower pH.

The extraction of iron(III), copper(II), aluminum(III), thorium(IV), and uranium(VI) by the N-methyl hydroxamic acid resin is plotted vs. pH in Figures 4 and 5. Comparison of these figures shows that complex stability increases in the order $Cu(II) \approx U(VI) < Al(III) < Th(IV) < Fe(III)$. The extraction of thorium is greater than would be expected from solvent-extraction work with N-phenylbenzohydroxamic acid (18). The remaining ions behave about as expected.

The purpose of this section was to explore the relationship between the structure and complexation properties of hydroxamic acid resins. The N-methyl and N-unsubstituted resins cannot be compared directly to the N-phenyl resin reported earlier because they are more highly functionalized. They can be compared to each other, however, because their nitrogen contents indicate a similar degree of functionalization. As noted earlier, the effect of the N-methyl group is to shift the extraction curves of the ions studied toward lower pH. This is most noticeable in the extraction of iron and titanium.

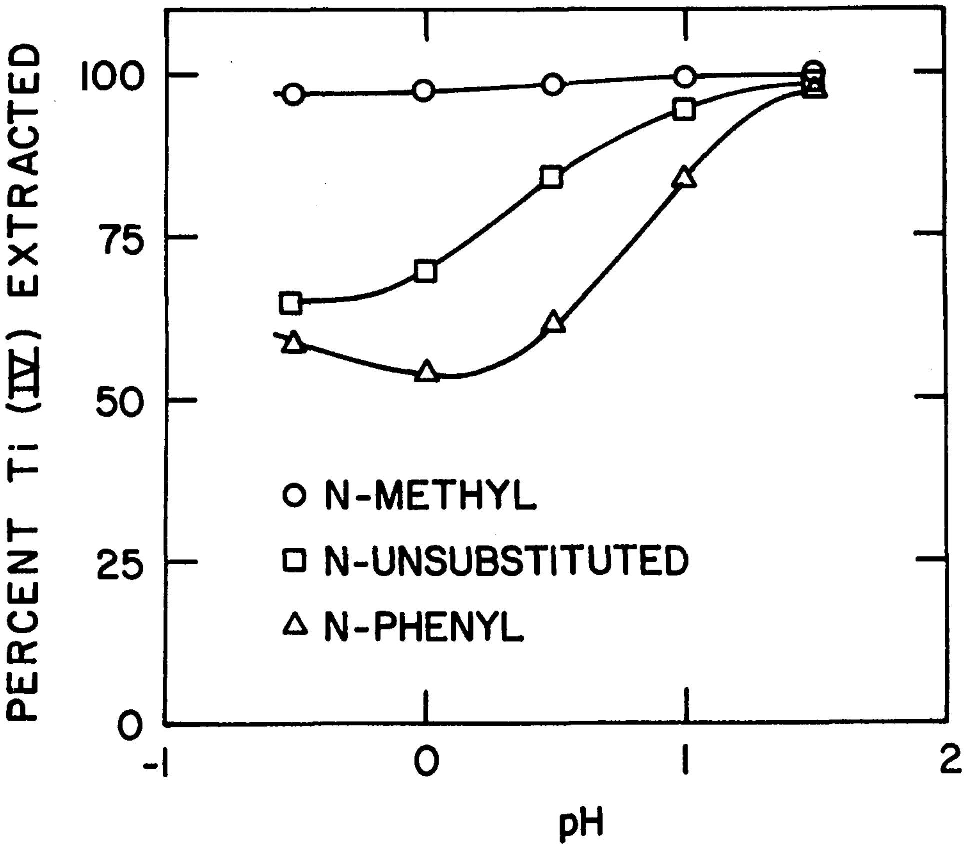


Figure 2. Extraction of Ti(IV) by N-phenyl, N-methyl, and N-unsubstituted hydroxamic acid resins _vs_. pH

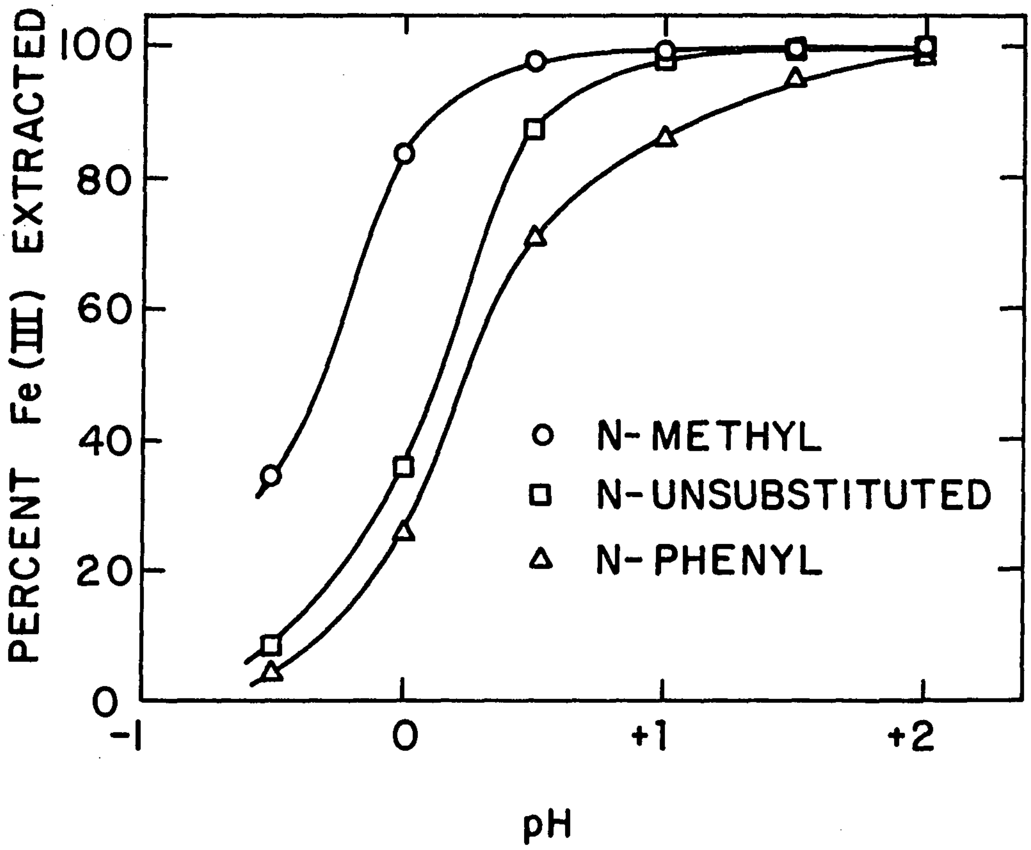


Figure 3. Extraction of Fe(III) by N-phenyl, N-methyl, and N-unsubstituted hydroxamic acid resins *vs*. pH

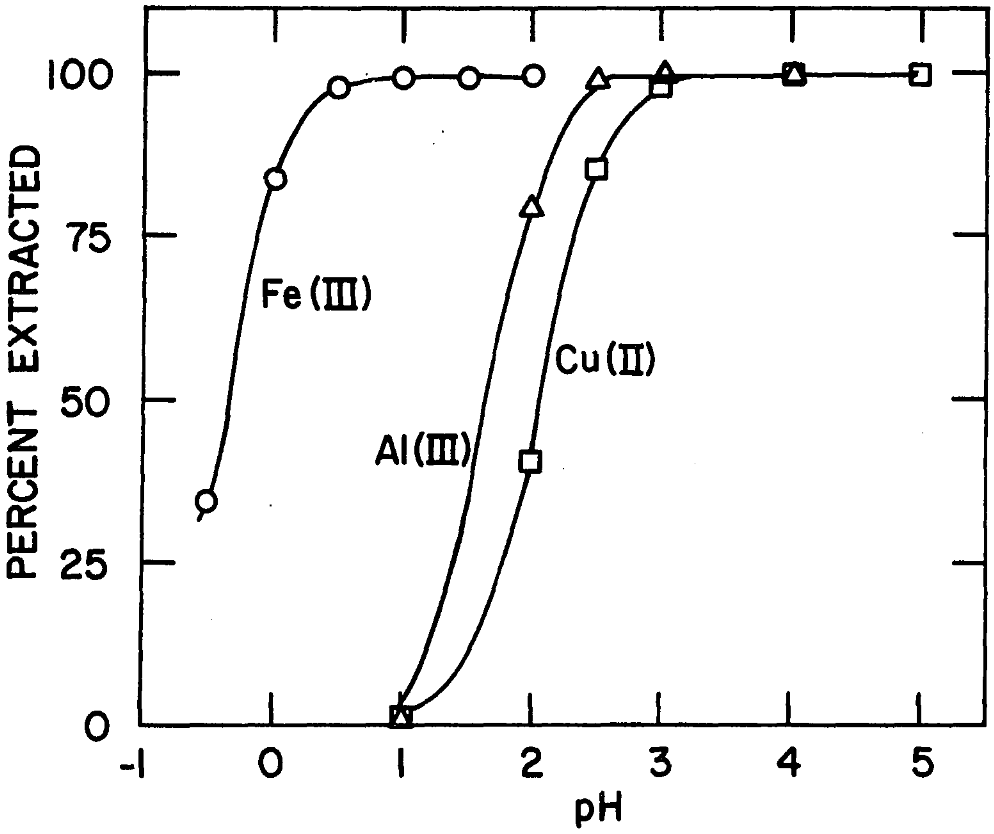


Figure 4. Extraction of Fe(III), Al(III), and Cu(II) by N-methyl hydroxamic acid resin *vs.* pH

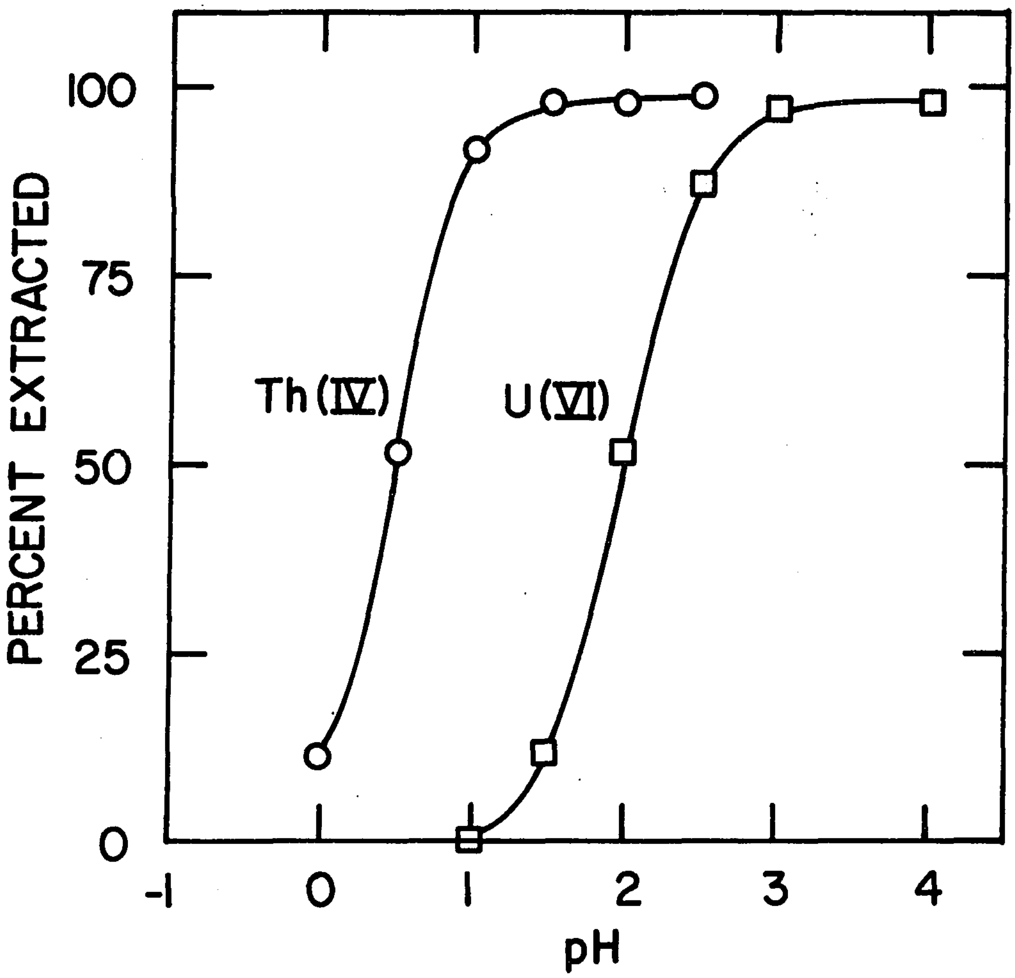


Figure 5. Extraction of U(VI) and Th(IV) by N-methyl hydroxamic acid resin *vs*. pH

The next section will describe additional work on the syntheses, characterization, and applications of the N-methyl and N-unsubstituted hydroxamic acid resins. The former is of interest because it forms the strongest complexes of the resins studied. The unsubstituted resin is also of interest, however, because it is cheaper to produce. In addition, tightly held ions, such as titanium and zirconium, should be more easily eluted from this resin.

EXTRACTION OF METAL IONS BY N-METHYL AND N-UNSUBSTITUTED HYDROXAMIC ACID RESINS

Introduction

The preceding section compared the extraction properties of N-phenyl, N-methyl, and N-unsubstituted hydroxamic acid resins. The latter two show considerable promise for separation and concentration of metal ions. In this section, some work on optimization of the resin syntheses is presented. The extraction of additional ions is examined to more fully characterize the resins. Iron(III) sorption is studied in detail using the Langmuir and Freundlich equations. Finally, several applications of these resins to analytical separations are presented and discussed.

Experimental

Apparatus and reagents

A Burrell automatic shaker was used in the batch-extraction experiments. A liquid chromatograph especially designed for inorganic analysis was used for the separation of thorium(IV) and uranium(IV). The columns, eluent reservoirs, and connecting lines are made of glass or plastic to minimize metallic contamination. Up to three eluent changes may be made during a run by means of a switching valve. The column effluent is automatically mixed with a color-forming reagent and sent to a Tracor Model 970 variable-wavelength spectrophotometric detector. A detailed description of the liquid chromatograph is available in the literature (12). The color-forming reagent in these experiments was a solution of 0.004% Arsenazo III in 3 M hydrochloric acid (118).

Solutions of lanthanum and the rare earths were prepared by heating the oxides in a small amount of 1-6 M hydrochloric acid. Scandium oxide was treated with 7 M nitric acid and evaporated nearly to dryness. This was repeated until a clear solution was obtained. Solutions of vanadium(V) and zirconium(IV) were prepared as described earlier.

Synthesis

The acetylation was done as reported earlier. Several different oxidation procedures were evaluated. In one of these, the resin was just covered with methanol and then treated with excess 1.5 M potassium hypochlorite, prepared as described earlier. This was heated for 4 hours at 60-70°C. The resin was isolated by suction filtration. It was treated with a fresh solution of potassium hypochlorite and heated for 4 hours at 60-70°C. The resin was isolated by suction filtration, washed with water, 1 M hydrochloric acid, and methanol, and dried at 60°C.

In a second procedure, the acetylated resin was boiled for 4 hours in 20% nitric acid, washed with water and methanol, and dried at 60°C. The third procedure was oxidation with potassium permanganate, which was done as follows. A 400-mL beaker containing a magnetic stirring bar and 200 mL of 1 M sodium hydroxide was placed on a stirring hot plate. The solution was heated to boiling and 10 g of acetyl XAD-4 was added. The heat was reduced and 25 g of potassium permanganate was added cautiously in small portions, keeping the temperature between 95 and 100°C and stirring constantly. The mixture was heated again, boiled for 1 hour with stirring, and allowed to cool.

Excess permanganate was reduced by adding 10 mL of ethanol. The solution was carefully decanted, leaving the resin and precipitated manganese dioxide in the beaker. This was washed several times with water, which was decanted each time after allowing the resin to settle. About 100 mL of water was added and adjusted to pH 1 with dilute sulfuric acid. Hydrogen peroxide was added with stirring to reduce and dissolve the manganese dioxide. Additional sulfuric acid was added to keep the pH around 1. When the resin turned from black to pale yellow, it was collected by suction filtration, washed with water, 1 M hydrochloric acid, and methanol, and dried at 60°C.

Several variations of the acid chlorination were also tried. In one, the resin was simply heated at reflux with excess thionyl chloride, as described earlier. In a second, the resin was allowed to stand at room temperature overnight in excess thionyl chloride. In a third, the resin was heated at reflux with a mixture of thionyl chloride and pyridine. In the last variation, the resin was heated at reflux in thionyl chloride containing 10% zinc chloride. The products were isolated by suction filtration and washed with diethyl ether. The yields of the acid chlorinations were determined by adding portions of the chloroformyl XAD-4 to excess diethylamine. These derivatives were washed with water and methanol, dried at 60°C, and analyzed for nitrogen

The reaction with N-methylhydroxylamine was varied as follows. In one procedure, 4 mL of methanol, 1.4 mL of triethylamine, and 0.83 g of N-methylhydroxylamine hydrochloride were placed in a 25-mL beaker. The solution was cooled in an ice-salt bath, which caused a precipitate to form. About 1 g of chloroformyl XAD-4 was added, followed by 2 mL of additional methanol. The resulting slurry was stirred for 1 hour. In a second procedure, a solution of 0.83 g of N-methylhydroxylamine hydrochloride in 4 mL of pyridine was cooled in an ice-salt bath, and 1 g of chloroformyl XAD-4 was added. This mixture was stirred for 1 hour.

In a third procedure, 1.30 g of sodium methoxide and 2.00 g of N-methylhydroxylamine hydrochloride were dissolved in 8 mL of methanol. The solution was filtered and the precipitated sodium chloride was washed with 2 mL of methanol. The combined filtrate and wash were cooled in an ice-salt bath, 2 g of chloroformyl XAD-4 was slowly added, and the mixture was stirred for 1 hour.

In a fourth procedure, 0.53 g of sodium carbonate and 0.83 g of N-methylhydroxylamine hydrochloride were dissolved in 4 mL of water. The solution was cooled in an ice-water bath, 1 g of chloroformyl XAD-4 was added, and the mixture was stirred for 1 hour. A similar procedure was used to prepare the N-unsubstituted resin on a larger scale. A solution of 5.3 g of sodium carbonate and 6.4 g of hydroxylamine hydrochloride in 40 mL of water was cooled in an ice-water bath, 10 g of chloroformyl XAD-4 was added, and the mixture was stirred for 1 hour. The hydroxamic acid resins were isolated by suction filtration, washed with water and methanol, and air-dried overnight.

Characterization

The hydrogen ion capacities of the carboxy XAD-4 and the nitrogen contents of the final products were determined as described earlier.

Batch extraction

These experiments were done as described in the previous section.

Sorption isotherms

Solutions of iron(III) ranging from 2×10^{-4} to 1.5×10^{-2} M were prepared in 0.1 M sulfuric acid A 10-mL aliquot of each solution was shaken with 50 mg of the N-methyl hydroxamic acid resin for 4 hours as in the batch-extraction experiments. The solutions were filtered, diluted where necessary, and analyzed for iron as described in the Appendix. The amount of iron sorption was calculated from the initial and final concentrations of iron in the solution and the weight of the resin used in the experiment.

Purification of reagents

Two solutions of 5% calcium nitrate were prepared. One was spiked with 10^{-5} M aluminum(III) and both were filtered through Whatman #5 paper. About 50 mL of the spiked solution was passed through a 5-mm i.d. gravity column containing 300 mg of the N-methyl hydroxamic acid resin. The first 25 mL of effluent was discarded and the next 25 mL was collected. The aluminum concentration in the blank, the spiked solution, and the column effluent was determined by analyzing 20-mL aliquots colorimetrically as described in the Appendix. Percentage of removal was calculated by the following formula, where R is percentage of removal, A is the absorbance of the solution indicated, s is the spiked solution, e is the column effluent, and b is the blank.

$$R = \frac{100(A_s - A_e)}{(A_s - A_b)}$$

The above experiment was repeated with 5% solutions of sodium chloride and sodium acetate. Similar experiments were done by spiking acidified solutions of 10% aluminum chloride with 4×10^{-5} $\underline{M}$ zirconium(IV) and 5×10^{-5} $\underline{M}$ iron(III). The experiment was also done with 10% solutions of sodium tartrate and 1,2-ethanediammonium dichloride spiked with 5×10^{-5} $\underline{M}$ iron(III) and iron(II), respectively.

Removal of sorbed magnesium and calcium

A 5-mm i.d. gravity column was packed to a depth of 5 cm with the N-methyl hydroxamic acid resin. This was eluted with 5 mL of 1 $\underline{M}$ ammonium acetate, 3 mL of water, 5 mL of 0.100 $\underline{M}$ calcium plus 0.0226 $\underline{M}$ magnesium, and 3 mL of water. It was then eluted with zero to three 5-mL aliquots of 1 $\underline{M}$ ammonium chloride, 3 mL of water, and 5 mL of 0.2 $\underline{M}$ hydrochloric acid. The magnesium and calcium in the acid effluent were determined by atomic absorption spectrometry as described in the Appendix. The experiment was repeated using various combinations of ammonium acetate, acetic acid, and ammonium chloride in place of the 1 M ammonium chloride.

Concentration and recovery of uranium(VI)

Gravity columns and reservoirs for this experiment were constructed by the glass blowing shop. The column consisted of a 15-cm piece of 5-mm i.d. glass tubing. A 5-mm piece of 2-mm i.d. tubing was attached at the bottom and a 24/40 outer joint at the top. Sample reservoirs were made from 250- and 1000-mL round-bottom flasks by attaching 24/40 inner joints to the bottom. The column were packed to a depth of 5 cm with 100-200 mesh N-methyl hydroxamic acid resin.

Synthetic sea water was prepared by a standard procedure (119). Samples were spiked with 120 µg of uranium(VI) dissolved in dilute acid or sodium bicarbonate. The latter was preferable for spiking the sea water samples because it did not decrease the pH. The sample flowed through the column at about 1 mL/min. The column was eluted with about 5 mL of water followed by two 5-mL aliquots of a wash solution containing 0.025 M ammonium acetate, 0.075 M acetic acid, and 0.5 M ammonium chloride. It was rinsed again with water and the sorbed uranium was removed by elution with 5 mL of 0.2 M hydrochloric acid. The uranium content of this solution was determined as described in the Appendix.

Concentration and analysis of aluminum

A 200-mL sample was buffered by adding 1 mL of acetic acid and adjusting the pH to 4 with ammonium hydroxide. This was passed through a gravity column as in the experiment described above. The column was eluted with 5 mL of water followed by two 5-mL aliquots of the wash solution described above. It was rinsed again with water and the sorbed aluminum was removed by elution with 5 mL of 0.1 M oxalic acid. The aluminum content of this solution was determined by atomic absorption spectrometry.

Concentration and analysis of titanium

A gravity column was packed to a depth of 5 cm with the N-unsubstituted hydroxamic acid resin. A small plug of DYNEL (Union Carbide) modacrylic staple fiber, which resists attack by hydrofluoric acid, was used to hold the resin in place. The sample was treated with 1.0 mg of ascorbic acid per milliliter to reduce iron(III). The pH of the sample was adjusted to 1.0 and it was passed through the column. The column was eluted with two 5-mL aliquots of 0.1 M hydrochloric acid followed by 5 mL of 0.3 M hydrofluoric acid. The effluent from the hydrofluoric acid elution was analyzed for titanium as described in the Appendix.

Chromatographic separation of uranium(IV) and thorium(IV)

The liquid chromatograph described earlier was used for this experiment. A 2-mm i.d. by 10-cm column containing 200-325 mesh N-methyl hydroxamic acid resin was used for the separation. The column was eluted with 3 M hydrochloric acid. A sample containing 10^{-4} M each of uranium(IV) and thorium(IV) was injected with a 50-μL sample loop. After 5 minutes, the eluent was switched to 3 M hydrochloric acid plus 0.1 M oxalic acid to elute uranium(IV). The column effluent was automatically mixed with a solution of Arsenazo III, as described earlier, and its absorbance at 665 nm was monitored continuously.

Results and Discussion

One objective of this part of the work was to prepare larger quantities of the N-methyl and N-unsubstituted resins. In order to meet this goal, improved procedures requiring less time and effort were needed. In addition, attempts were made to improve the yields of some of the steps in the reaction sequence. The results obtained with several different oxidation procedures are summarized in Table 27.

Nitric acid was the least expensive and most convenient oxidant employed. The capacity of the oxidized product was independent of the amount of 3 M acid used in the reaction.

A disadvantage of oxidation with nitric acid is the possibility of the side reaction of nitration. The resins oxidized with this reagent developed an orange color during the reaction which darkened to red when the resin was exposed to daylight.

Oxidation with hypochlorite has several advantages, as discussed earlier. However, this was the least reproducible method tested. Several batches of acetylated resin were oxidized by two successive reactions in 1.5 M potassium hypochlorite. As shown in Table 27, the highest capacity obtained with this procedure was 2.4 mmol/g.

The best results were obtained with potassium permanganate. The earlier objections to this reagent were overcome by developing a new method for removing manganese dioxide from the oxidized resin using acidic hydrogen peroxide. The stoichiometry of the permanganate oxidation is shown in the following equation.

$$3\ \mathrm{Res{-\!-}COCH_3} + 8\ \mathrm{MnO_4^-} + \mathrm{OH^-} \longrightarrow 3\ \mathrm{Res{-\!-}COO^-} + 3\ \mathrm{CO_3^{2-}} + 8\ \mathrm{MnO_2} + 5\ \mathrm{H_2O}$$

It should therefore take about 0.4 g of potassium permanganate to produce 1 mmol of carboxy groups. As shown in Table 27, a considerable excess is required, especially when a high capacity is desired. The excess is apparently consumed in attacking the resin matrix. Resins with capacities

Table 27. Oxidation of acetyl XAD-4

Reagents and conditions	-COOH, mmol/g
3 M HNO_3, 100°C	2.5
KOCl, 60-70°C	1.2-2.4
$KMnO_4$, 1:1,[a] 100°C	1.5
$KMnO_4$, 2:1,[a] 100°C	2.8
$KMnO_4$, 3:1,[a] 100°C	3.3

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[a] Weight $KMnO_4$:weight resin.

of more than 3 mmol/g were produced by using a large excess of permanganate. These products lost considerable weight during the reaction. They exhibit shrinking and swelling upon dehydration and rehydration, respectively. The indications are that these high-capacity resins have lost much of their crosslinking, which would make them unsuitable for column work. Resins with a capacity of about 3 mmol/g and good physical properties were obtained consistently by using a 5:2 ratio of potassium permanganate to acetylated resin.

The results of the various acid-chlorination procedures are shown in Table 28. The yields were estimated by reacting the chloroformyl XAD-4 with diethylamine and determining the nitrogen content of the product. The best results were obtained with the original method of heating a mixture of the resin and thionyl chloride at reflux for 1 hour.

Table 29 compares the methods for reacting chloroformyl XAD-4 with N-methylhydroxylamine. The yields obtained in water and methanol were about the same. A lower yield was obtained in pyridine. An advantage of using methanol instead of water is that the side reaction of the acid chloride groups with the solvent will produce methyl ester, rather than carboxylic acid groups. The latter have ion-exchange properties of their own which complicate the study

Table 28. Acid chlorination of carboxy XAD-4

Reagents and conditions	Nitrogen (percent)[a]
$SOCl_2$, reflux, 1 h	3.79
$SOCl_2$, room temperature, 16 h	3.53
$SOCl_2$ + C_5H_5N, reflux, 1 h	3.20
$SOCl_2$ + $ZnCl_2$, reflux, 1 h	3.52

[a] After reaction with diethylamine.

Table 29. Optimization of N-methyl hydroxamic acid resin synthesis

Solvent	Base	Nitrogen (percent)
Methanol	triethylamine	3.1
Pyridine	pyridine	2.5
Water	sodium carbonate	3.3
Methanol	sodium methoxide	3.4

and use of the hydroxamic acid resin. A slightly higher yield was obtained when sodium methoxide, rather than triethylamine, was used as the base.

Table 30 shows the yields obtained on larger batches of resin. About 10 g of carboxy XAD-4 was treated with thionyl chloride, followed by methylhydroxylamine (from the hydrochloride and sodium methoxide) in methanol. The yield of 75% was calculated from the nitrogen content of the product and the capacity of the carboxy XAD-4. In a second reaction, 10 g of the same batch of carboxy XAD-4 was treated with thionyl chloride. A small portion of the chloroformyl XAD-4 was added to diethylamine to estimate the yield of the acid chlorination. The remainder was stirred with aqueous hydroxylamine. The yield in the latter reaction was nearly 90%, even higher than that obtained with diethylamine.

A series of batch-extraction experiments was done with the N-methyl resin to examine its behavior with additional ions. The results of these experiments are shown in Tables 31-37. Extraction of magnesium and calcium begins at a surprisingly low pH. Zinc(II), cobalt(II), nickel(II), and manganese(II) are extracted more strongly than the alkaline earths but less strongly than copper(II) and aluminum(III), in agreement with the stability constant data in Table 3. The extraction of chromium(III) is nearly complete at

Table 30. Conversion of carboxy XAD-4 to amide derivatives

Functional group	Nitrogen		Yield (percent)[a]
	percent	millimoles per gram	
$-CON(CH_3)OH$	2.94	2.10	75
$-CONHOH$	3.44	2.46	89
$-CON(C_2H_5)_2$	3.16	2.26	87

[a] Assuming 2.97 mmol/g $-COOH$ in the starting material.

Table 31. Batch extraction (percent) of Ca(II) and Mg(II) by N-methyl hydroxamic acid resin as a function of pH

pH	Metal Ion	
	Mg(II)	Ca(II)
2.0	0	0
3.0	31	0
4.0	30	22
5.0	31	39
6.0	46	57
7.0	54	65
8.0	94	91
9.0	100	97

Table 32. Batch extraction (percent) of Zn(II), Co(II), and Ni(II) by N-methyl hydroxamic acid resin as a function of pH

pH	Metal Ion		
	Zn(II)	Co(II)	Ni(II)
1.0	0.0	0.0	0.0
2.0	2.8	2.0	3.1
3.0	24.5	27.0	35.6
4.0	55.6	49.3	58.8
5.0	81.2	68.3	77.8
6.0	96.8	91.4	94.7

Table 33. Batch extraction (percent) of Mn(II), Cr(III), and V(V) by N-methyl hydroxamic acid resin as a function of pH

pH	Metal Ion		
	Mn(II)	Cr(III)	V(V)
1.0	0.0	0.0	---[a]
2.0	0.0	5.1	99.8
3.0	24.6	49.8	100.0
4.0	38.0	91.6	61.4
5.0	47.4	98.5	40.2
6.0	72.4	99.2	35.0

[a] See Table 34.

Table 34. Batch extraction (percent) of V(V) from hydrochloric and perchloric acids by N-methyl hydroxamic acid resin

Molarity	Acid	
	HCl	$HClO_4$
0.1	78.9	88.2
0.3	63.5	80.8
1.0	44.8	74.8
3.0	35.2	79.8
6.0	33.7	94.4

Table 35. Batch extraction of Zr(IV) from hydrochloric acid by N-methyl hydroxamic acid resin

Molarity	Percentage extraction
0.1	100.0
0.4	99.7
1.0	100.0
4.0	99.6

Table 36. Batch extraction of Sc(III) by N-methyl hydroxamic acid resin as a function of pH

pH	Percentage extraction
0.0	6.2
0.5	10.7
1.0	51.5
1.5	90.8
2.0	100.0
3.0	100.0

Table 37. Batch extraction (percent) of rare earths by N-methyl hydroxamic acid resin as a function of pH

pH	Metal Ion		
	La(III)	Eu(III)	Lu(III)
1.0	0.6	0.0	0.6
2.0	11.2	21.0	17.6
2.5	57.5	64.8	59.0
3.0	91.6	88.5	92.9
4.0	97.6	99.0	99.2
5.0	99.0	100.0	99.2

pH 5-6, which is surprising because chromium(III) is not efficiently extracted by N-phenylbenzohydroxamic acid (18).

The extraction curves for copper(II), nickel(II), and calcium(II) are shown in Figure 6. These ions are 50% extracted at pH 2.1, 3.6, and 5.6, respectively. At pH 5.6, the residual carboxy groups in the resin are probably ionized and the mechanism for calcium(II) extraction may be simple ion exchange rather than chelation. This might account for the difference in the shapes of the extraction curves for copper(II) and calcium(II). At pH 3.6, some ionization of the carboxy groups might be expected and the extraction of nickel may involve either chelation, simple ion exchange, or both. An experiment for distinguishing between simple ion exchange and chelation has been described by Moyers and Fritz (7). This will be discussed in the section on future work.

Vanadium(V) extraction was studied in both weakly and strongly acidic solutions. It reaches a maximum at pH 3. Extraction from solutions of hydrochloric acid may be complicated by reduction to vanadium(IV) (110). Vanadium(V) is extracted more efficiently from perchloric than from hydrochloric acid. Vanadium(IV) extraction was also studied at pH 1-3. The results, not shown in the tables, were nearly identical to those found with vanadium(V) in this pH range. Here it appears that vanadium(IV) was oxidized

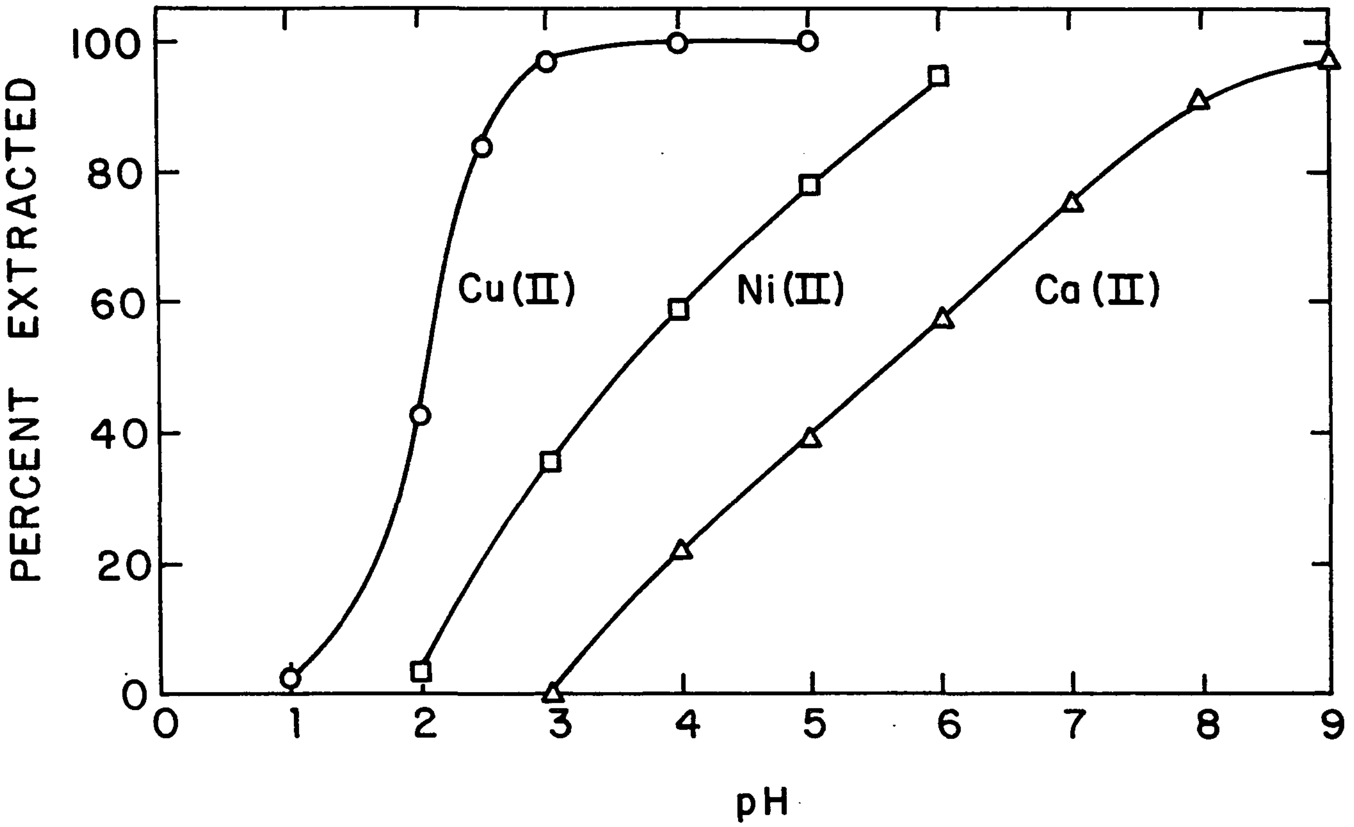


Figure 6. Extraction of Cu(II), Ni(II), and Ca(II) by N-methyl hydroxamic acid resin *vs*. pH

to vanadium(V). Brandt has reported that vanadium(IV) reacts only extremely slowly with benzohydroxamic acid when exposed to air (27). The vigorous shaking used in the batch-extraction experiments may have accelerated this process. The data for vanadium extraction is plotted as a function of pH in Figure 7.

The extraction of zirconium(IV) can only be described as remarkable. The distribution coefficients for this system exceed 2×10^4, even in 4 M acid. Scandium(III) is extracted quantitatively at pH 2 while lanthanum and the rare earths are strongly complexed at pH 4-5. The data for the extraction of lanthanum and scandium, which are compared in Figure 8, indicate a possible separation of these elements. The distribution coefficients of the rare earths are quite similar. There appears to be little possibility of using the hydroxamic acid resins to achieve separations within this group.

The pH for 50% extraction by the N-methyl hydroxamic acid resin of most of the ions studied is shown in Table 38. This is a convenient way of comparing the relative affinity of various ions for the resin. In general, the results correlate well with the stability-constant data in Table 3. As noted earlier, the alkaline earths are extracted at lower pH than expected. Vanadium(V) is not included in this table because, unlike the other ions, its extraction does not

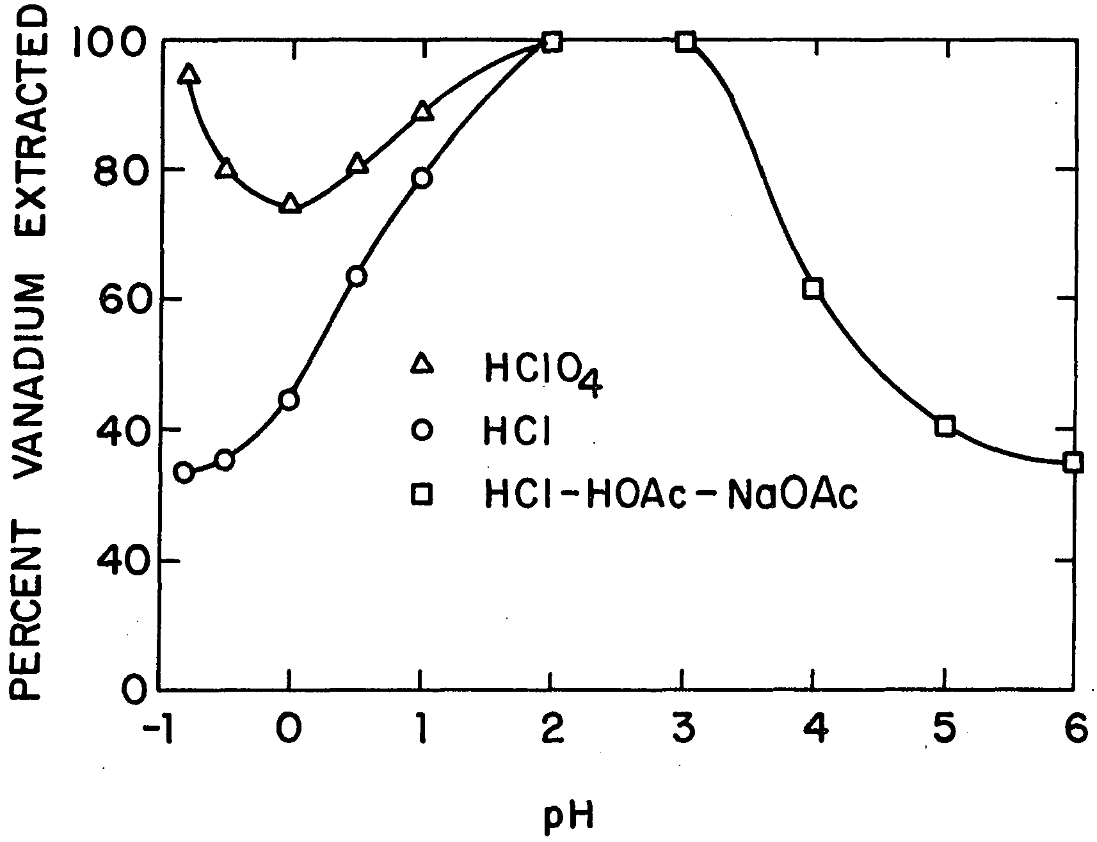


Figure 7. Extraction of vanadium by N-methyl hydroxamic acid resin vs. pH

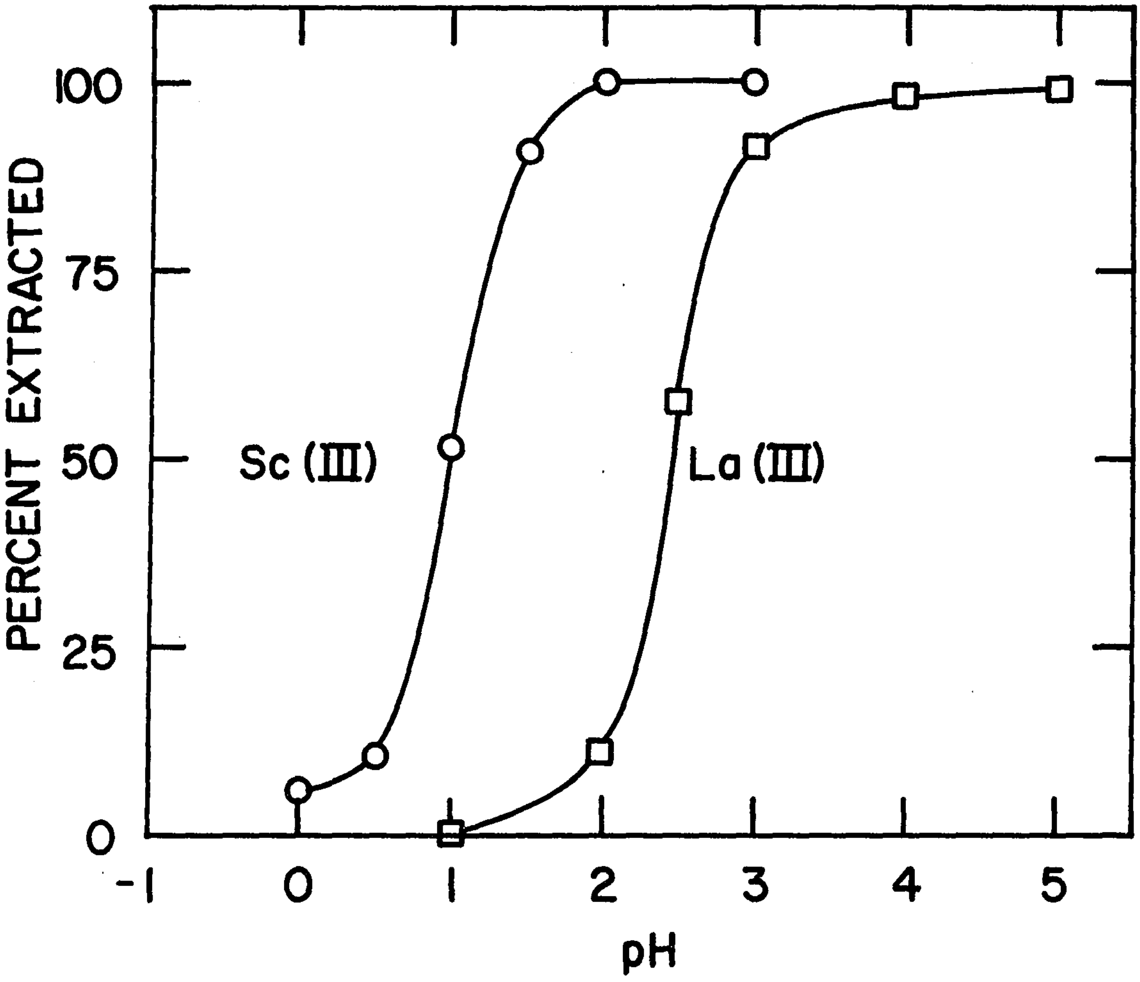


Figure 8. Extraction of La(III) and Sc(III) by N-methyl hydroxamic acid resin vs. pH

Table 38. pH for 50% extraction of ions by N-methyl hydroxamic acid resin

Ion	pH for 50% extraction
Mg(II)	6.4
Ca(II)	5.6
Mn(II)	5.2
Co(II)	4.0
Ni(II)	3.6
Zn(II)	3.6
Cr(III)	3.0
La(III)	2.5
Lu(III)	2.4
Eu(III)	2.3
Cu(II)	2.1
U(VI)	2.0
Al(III)	1.8
Sc(III)	1.0
Th(IV)	0.5
Fe(III)	-0.4

increase continuously as the pH is raised. Titanium(IV) and zirconium(IV) are not included since their extraction exceeds 95% even in 3-4 M acid.

In studies on solvent extraction of metal complexes, the formula of the extracted complex can often be obtained from the dependence of the distribution ratio on reagent concentration and acidity (117). A plot of the logarithm of the distribution ratio *vs*. the logarithm of reagent concentration at constant pH gives a straight line whose slope is equal to the number of reagent molecules required for complexation. Similarly, a plot of log D_c *vs*. pH at constant reagent concentration gives a straight line whose slope is equal to the number of protons involved in the reaction.

With a chelating resin, it is not convenient to vary the concentration of the functional groups on the resin. However, it is easy to obtain log D_g *vs*. pH from batch-extraction data. If only a small fraction of the resin capacity is used, the concentration of available functional groups is essentially constant. Figures 9 and 10 show the results of plotting some of the batch-extraction data as log D_g *vs*. pH. Iron(III), thorium(IV), and scandium(III) give linear plots whose slopes are 1.98, 1.98, and 1.95, respectively. Copper(II) gives a linear plot with a slope of 1.46. The plots for lanthanum(III), uranium(VI), and

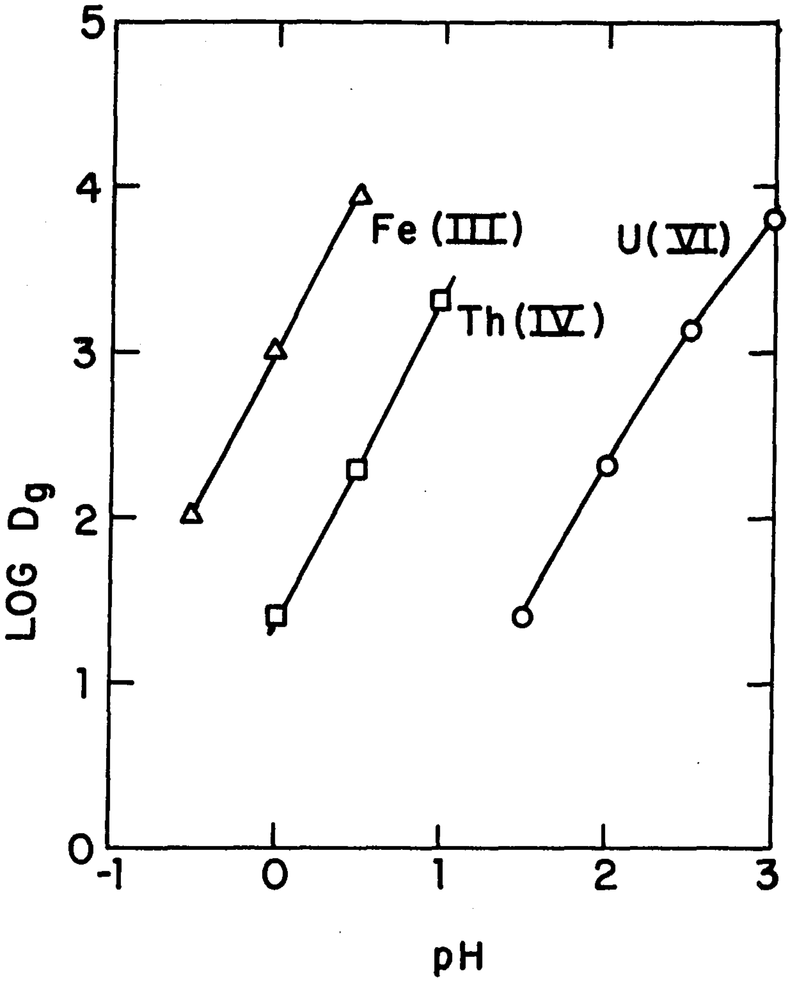


Figure 9. Log D_g *vs*. pH for extraction of Fe(III), Th(IV), and U(VI) by N-methyl hydroxamic acid resin

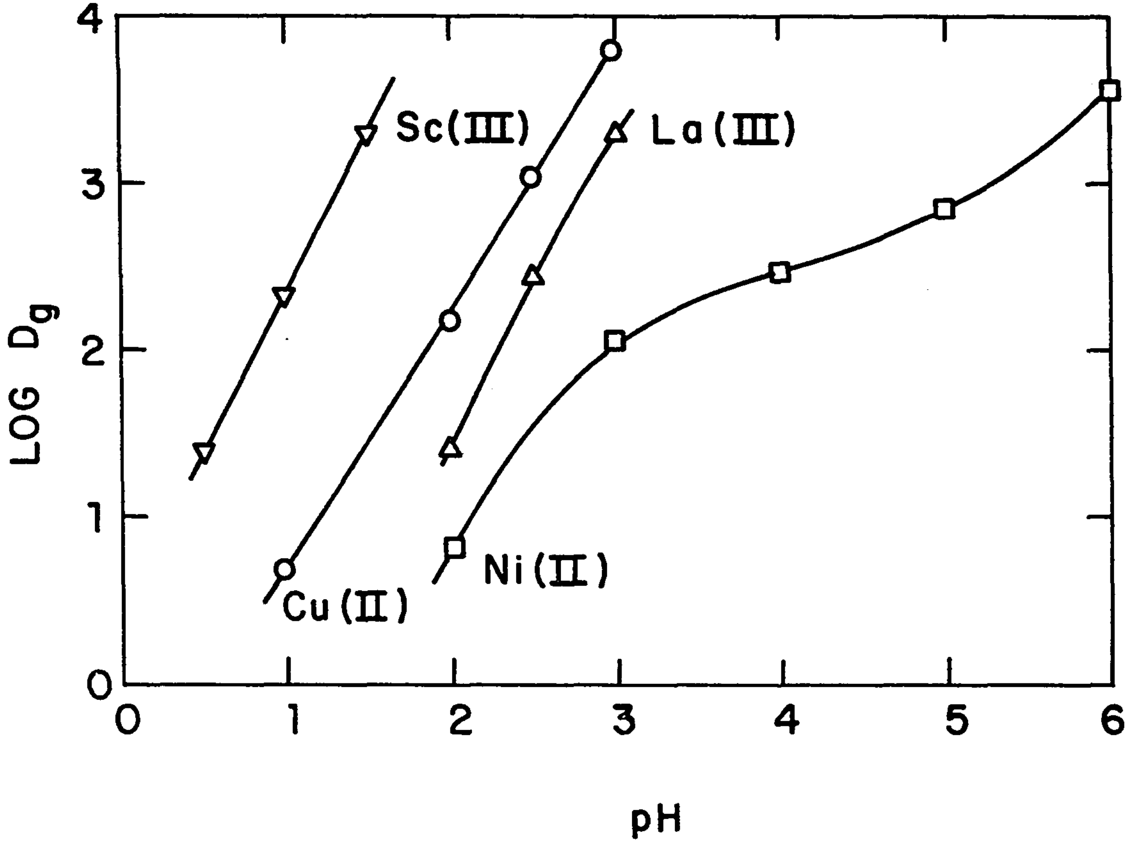


Figure 10. Log D_g vs. pH for extraction of Sc(III), Cu(II), La(III), and Ni(II) by N-methyl hydroxamic acid resin

nickel(II) are nonlinear. For the first two ions, however, the first derivatives of the curves approach the value of 2 at lower pH.

These results indicate that extraction of several of the ions is accompanied by the release of two protons. It seems likely that in these cases, two adjacent hydroxamic acid groups are involved in complexation. Precipitation or extraction with monomeric hydroxamic acids usually involves complexes with the formula ML_n, where M is the metal cation, n is its charge, and L is the hydroxamate anion (18). In the resin, however, there are obvious limitations to the number of immobilized groups which can approach the same metal ion closely enough for chelation. In addition, while the formation of a neutral complex is necessary for solvent extraction or precipitation, it does not follow that this is also the case for a chelating resin. Excess charge at the chelation site could be balanced by counter ions from the solution.

The sorption process at higher loading was studied by obtaining an isotherm for iron(III) extraction by the N-methyl hydroxamic acid resin at pH 1. The data are shown in Figures 11 and 12, plotted according to the Langmuir and Freundlich equations, respectively (120). The latter approach gives a better fit to the data, although, as noted by Samuelson, it has no sound theoretical interpretation (2).

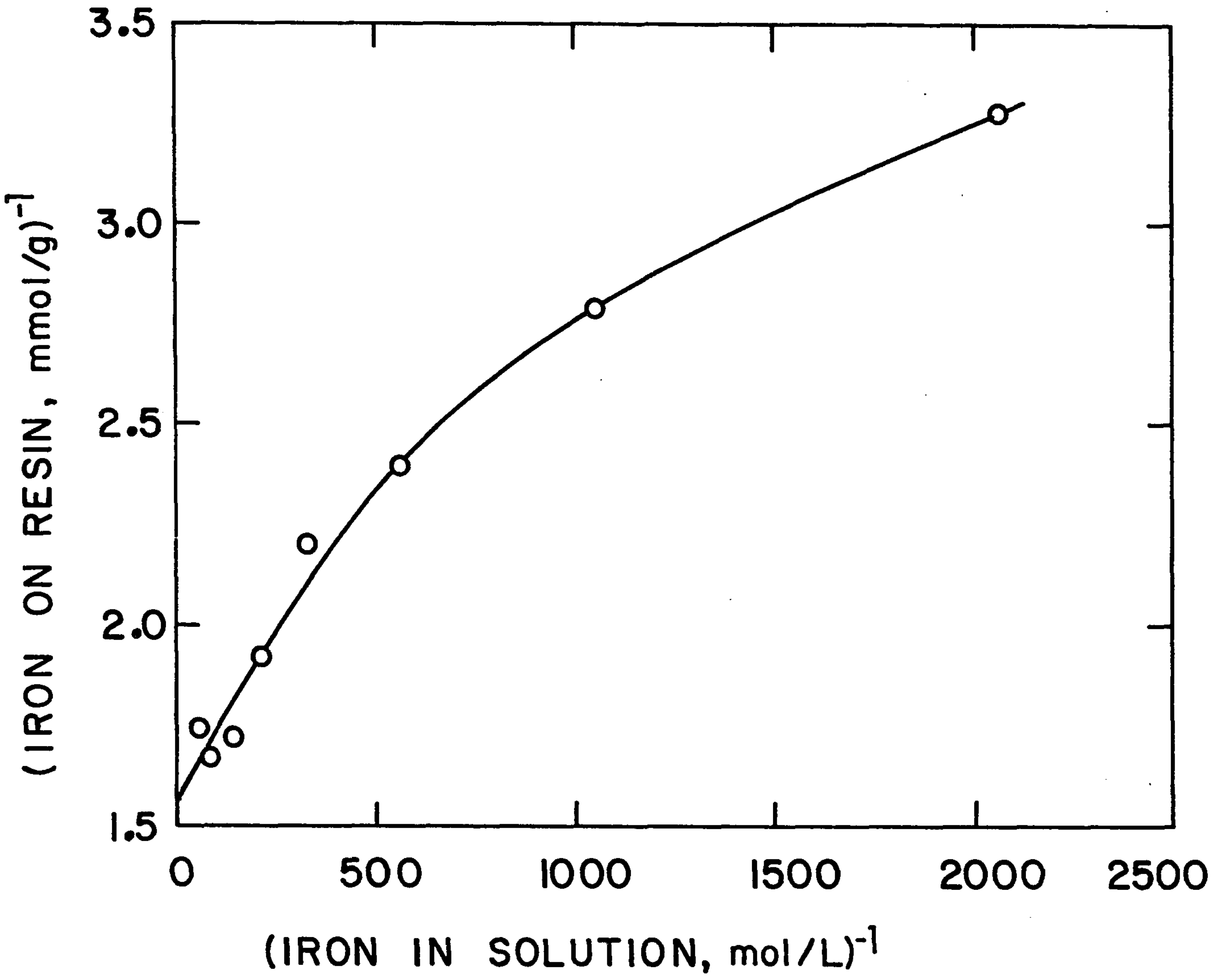


Figure 11. Langmuir plot of iron(III) sorption by N-methyl hydroxamic acid resin

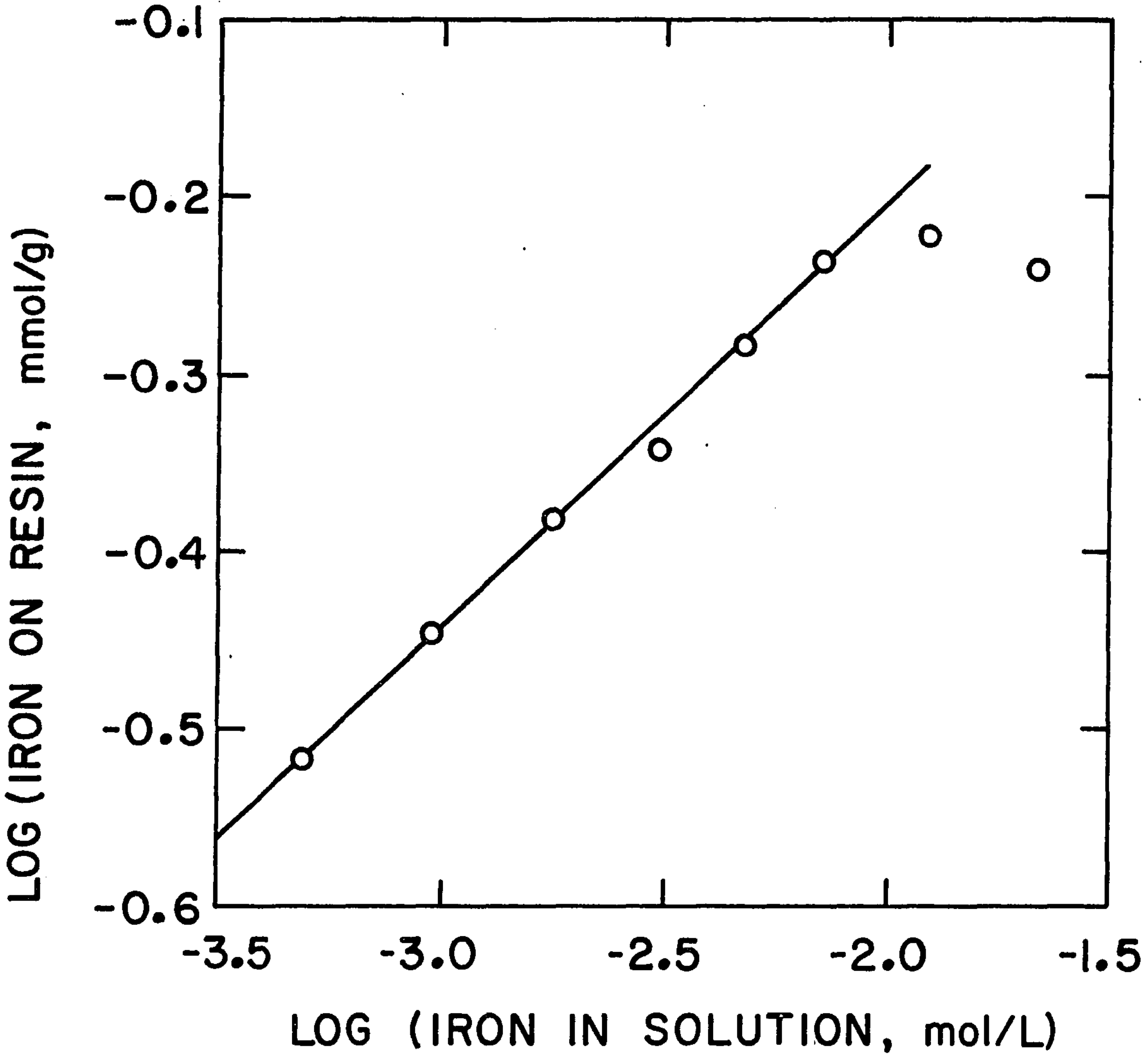


Figure 12. Freundlich plot of iron(III) sorption by N-methyl hydroxamic acid resin

The maximum capacity for iron(III) at this pH appears to be about 0.6 mmol/g.

One of the proposed uses for these resins is the purification of reagents by selective extraction of metallic impurities. The results of several experiments of this type are shown in Table 39. In most cases, the technique was quite successful although the separation of iron(III) from aluminum(III) was incomplete. The removal of iron(II) from 1,2-ethanediammonium dichloride seems especially noteworthy. This selectivity for inorganic versus organic cations is a unique feature of chelating ion exchangers.

Another proposed use for these resins is the separation of elements such as aluminum, uranium, and rare earths from large excesses of magnesium and calcium. As shown earlier, the alkaline earths are partially extracted by the resin at pH 3-5. A study was done to find a suitable eluent for selectively removing sorbed magnesium and calcium from the resin. Figure 13 shows the results obtained using several combinations of ammonium chloride, ammonium acetate, and acetic acid. The ammonium ion presumably works by mass action while the acetate buffer controls the pH at the optimum value. Over 99.9% of the sorbed calcium was removed by washing the resin with 0.5 M ammonium chloride buffered at pH 4. Increasing the ammonium ion concentration to 2 M added little improvement. Magnesium was also removed by this procedure.

Table 39. Removal of aluminum, zirconium, and iron from concentrated reagent solutions

Solution	Ion added	Concentration	Percentage of removal
5% $Ca(NO_3)_2 \cdot 4\ H_2O$	Al(III)	1×10^{-5} $\underline{M}$	97
5% NaCl	Al(III)	1×10^{-5} $\underline{M}$	103
5% $NaC_2H_3O_2 \cdot 3\ H_2O$	Al(III)	1×10^{-5} $\underline{M}$	105
10% $AlCl_3 \cdot 6\ H_2O$	Zr(IV)	4×10^{-5} $\underline{M}$	100[a]
10% $AlCl_3 \cdot 6\ H_2O$	Fe(III)	5×10^{-5} $\underline{M}$	90[b]
10% $Na_2C_4H_4O_6 \cdot 2\ H_2O$	Fe(III)	5×10^{-5} $\underline{M}$	102
10% $C_2H_{10}N_2Cl_2$	Fe(II)	5×10^{-5} $\underline{M}$	101[c]

[a] Solution in 1 $\underline{M}$ hydrochloric acid.

[b] Solution in 0.1 $\underline{M}$ hydrochloric acid.

[c] Solution at pH 3.5.

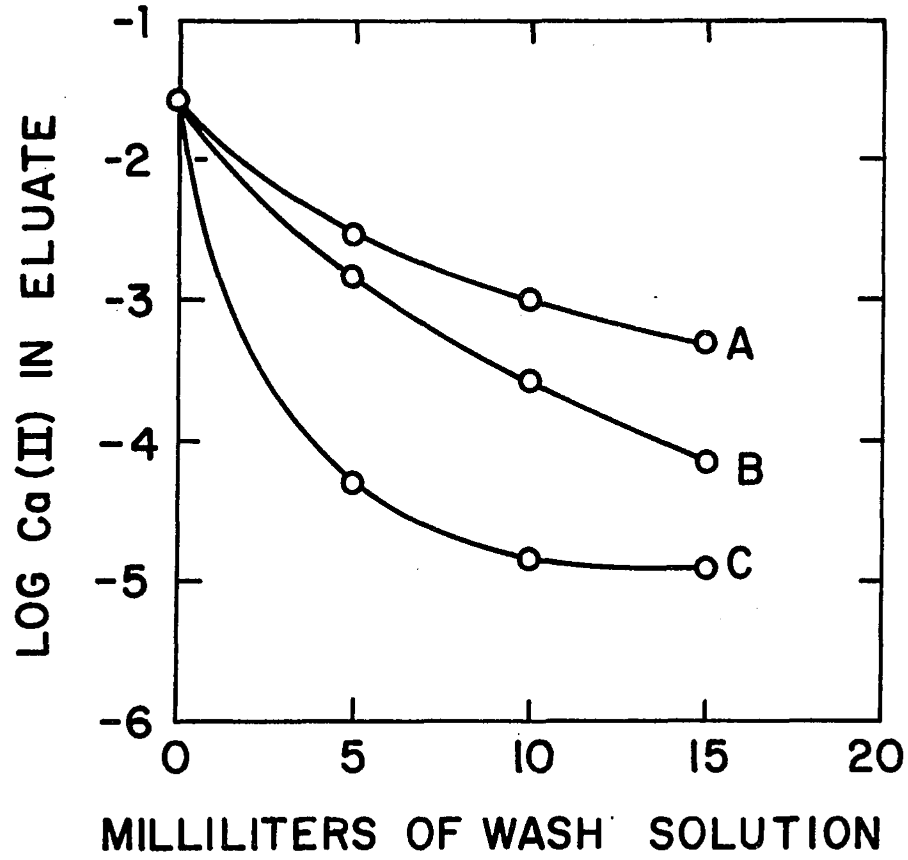


Figure 13. Removal of sorbed Ca(II) from N-methyl hydroxamic acid resin. (A) 1 M NH_4Cl. (B) 0.025 M NH_4OAc, 0.075 M HOAc, 0.1 M NH_4Cl. (C) 0.025 M NH_4OAc, 0.075 M HOAc, 0.5 M NH_4Cl

Tables 40-42 show the effectiveness of the hydroxamic acid resins for the selective concentration of metal ions. Uranium(VI) was extracted by the N-methyl resin from synthetic sea water and dilute bicarbonate at pH 7-8 with recoveries of 99-101%. A concentration of 200 fold was achieved in one of the extractions from sea water. Extraction of uranium(VI) from a pH 10 carbonate buffer was incomplete. Aluminum (III) was efficiently concentrated by the N-methyl resin at pH 4 in the presence of either calcium or phosphate. This procedure should be applicable to the analysis of trace aluminum in biological samples (121). Titanium(IV) was efficiently complexed by both resins. It was more readily eluted from the N-unsubstituted resin, however, using 0.3 M hydrofluoric acid. The recovery of titanium from concentrated aluminum chloride solutions was slightly low, ranging from 97 to 99%.

Additional experiments on selective concentration of ions were done with the following results. Europium(III) was quantitatively extracted by the N-methyl resin from pH 4 acetate buffer. Elution with 0.1 M hydrochloric acid gave 100% recovery. A 100-mL sample of 0.1 M sodium chloride plus 0.025 M calcium nitrate was spiked with 500 nmol of europium. The sample was buffered by adding 1 mL of acetic acid and adjusting the pH to 4.0. The solution was passed through a column of the chelating resin,

Table 40. Recoveries of uranium from various media by N-methyl hydroxamic acid resin

Medium	Volume extracted, mL	Percentage of U(VI) recovered
0.1 M acetate pH 4	5	100
0.01 M CO_3^{-2} + 0.01 M HCO_3^- pH 10.1	5	68
Synthetic sea water pH 7	100	101
Synthetic sea water pH 8.1	1000	99
0.005 M HCO_3^- pH 8.3	5	101

Table 41. Concentration and analysis of aluminum

Solution	Al added, ppm	Al found, ppm[a]
Tap water	0.00	0.00
Tap water	0.34	0.34
Distilled water	0.00	0.00
1000 ppm Ca^{+2}	1.05	1.05[b]
1000 ppm PO_4^{-3}	1.05	1.05

[a] Corrected for concentration from 200 to 5 mL.

[b] Concentrate also contained 0.0019% of the original Ca^{+2}.

Table 42. Recoveries of titanium from solutions at pH 1

Sample[a]	Volume, mL	Ti added, µg	Ti found, µg
Distilled water	5	47.9	47.9
5% $AlCl_3 \cdot 6\ H_2O$	5	0.0	0.4
5% $AlCl_3 \cdot 6\ H_2O$	5	47.9	47.8
5% $AlCl_3 \cdot 6\ H_2O$	200	0.0	1.7
5% $AlCl_3 \cdot 6\ H_2O$	200	47.9	48.2

[a] All solutions were 0.1 M in hydrochloric acid and contained 0.1% ascorbic acid to mask iron.

which was then washed with buffered ammonium chloride as in the concentration and analysis of aluminum. The recovery of europium following elution with 0.1 M hydrochloric acid was 96%.

Zirconium(IV) was extracted from 1 M hydrochloric acid by the N-methyl resin. The column was eluted with 5 mL of 0.1 M oxalic acid. No zirconium was found in the effluent, however, in contrast to the results reported earlier using the N-phenyl resin. A solution of chromium(III) in pH 5 acetate buffer was passed through a column of the N-methyl resin, resulting in 99% extraction. Elution with 5 mL of 0.1 M hydrochloric acid recovered 22% of the sorbed chromium.

Figure 14 shows the chromatographic separation of uranium(IV) from thorium(IV). Based on the results from batch and column extraction experiments, it should be possible to separate uranium(IV) from many other ions, including uranium(VI), iron(II), zirconium(IV), and vanadium(IV). The possibility of extending the use of these resins from analytical separations to larger scale processing of nuclear fuels should certainly be considered. As noted earlier, such applications have already been found for solvent extraction with hydroxamic acids (86).

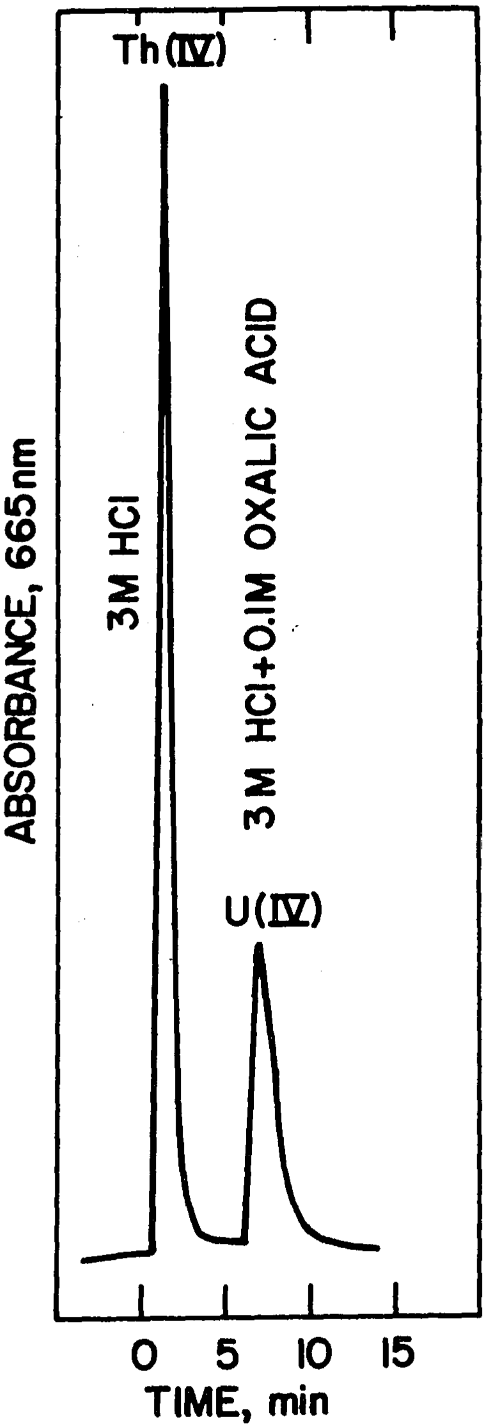


Figure 14. Chromatographic separation of Th(IV) and U(IV) with N-methyl hydroxamic acid resin

CONCLUSIONS

The preparation of hydroxamic acid resins from XAD-4 has been shown to be feasible. The N-phenyl resin cannot be produced in high yield, presumably because of steric hindrance in the highly crosslinked resin. However, the N-methyl and N-unsubstituted resins can be produced with yields approaching 2.5 millimoles of hydroxamic acid groups per gram of resin. The latter two resins deserve further study. The N-methyl resin forms the strongest complexes of the three resins studied. The N-unsubstituted resin is easier to prepare, however, and should be more suitable for use with ions which are difficult to elute.

These hydroxamic acid resins behave like N-phenylbenzohydroxamic acid in selectively extracting a small group of metal ions from strongly acidic solution (18). Additional ions are extracted as the pH is raised. Several ions, including titanium(IV), zirconium(IV), and vanadium(V), form such strong complexes that they are difficult to elute quantitatively from the resin. For others, such as aluminum(III) and chromium(III), slow desorption kinetics present special problems. These observations underscore the need for gathering basic, quantitative information about the complexation process in chelating resins. Both thermodynamic and kinetic aspects are important and require study.

Despite the problems encountered, several interesting applications have been developed. The resins are an efficient means of purifying reagents by selective removal of strongly complexed ions. The procedures for concentrating aluminum and titanium should extend the detection limits for these elements in difficult matrices. The affinity of uranium(IV) for the hydroxamic acid resins may have applications in the processing of nuclear fuel. We can look forward to additional applications as some of the more basic questions about the thermodynamics and kinetics of these chelating resins are answered.

FUTURE WORK

One of the conclusions of this work was that basic thermodynamic and kinetic information is essential for the proper evaluation of a chelating resin and for the development of applications. As mentioned earlier, both the N-methyl and N-unsubstituted resins are worth further study. The first objective of future work should be to obtain data on extraction vs. pH for additional ions. These should include molybdenum(VI), tungsten(VI), niobium(V), tantalum(V), tin(IV), antimony(III), bismuth(III), and the platinum group.

As noted earlier, the unexpected extraction of magnesium and calcium at pH 3-5 may be caused by a simple ion-exchange process involving unreacted carboxy groups. This question should be investigated by studying the effect of sodium ion concentration on extraction, as described by Moyers and Fritz (7). If the extraction of calcium is by simple ion exchange, it should decrease in the presence of another exchangeable cation. If extraction involves a chelation process, it should not be affected.

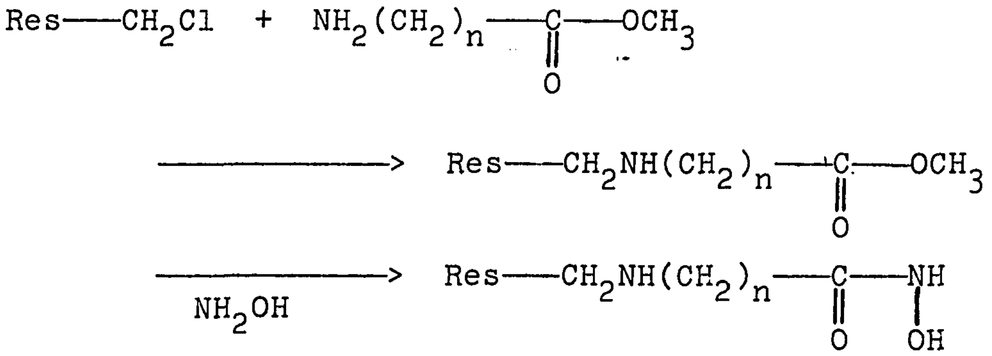
Alternatively, the extraction of calcium by the carboxy intermediate could be studied. Since this intermediate has been used in the preparation of other chelating resins (7,122), such data would be of general interest. Carboxy XAD-4 should extract more calcium than the hydroxamic acid resins at pH 3-5 if a simple ion-exchange process is involved because it has a higher concentration of ionizable groups.

The assumption that the distribution coefficient, D_g, is independent of concentration at low loading is essential to the application of chromatographic theory to ion-exchange processes (117). This assumption should be tested for the case of the hydroxamic acid resins by obtaining sorption isotherms at low loading. If the data can be fit by the Langmuir equation, the procedure used for obtaining D_g from the batch-extraction experiments will be validated. Valid distribution coefficients would allow the selection of eluents for the removal of sorbed ions to be made on a rational basis, using available formation constants, rather than by trial and error (112,117).

The effect of capacity on distribution coefficients should be studied by preparing hydroxamic acid resins with a lower density of functional groups. Such resins might be useful in applications with elements like zirconium and vanadium which are difficult to elute. The dependence of distribution coefficients on capacity should provide greater insight into the mechanism of complexation. It might be possible to determine the number of groups involved in complexation with this approach. Lower capacity resins might prove to be superior for chromatographic applications. As the capacity is decreased, it should be possible to reach the point where only 1:1 interactions between metal ions and chelating groups can occur. Hopefully, such resins will exhibit more uniformity and faster kinetics.

Experiments for measuring sorption and desorption kinetics should be designed. Such experiments would be used for comparing the reaction rates of different ions and the effects of pH, auxiliary complexing agents, temperature, and resin structure. The overall goal would be to enlarge the scope of separations using chelating resins by increasing the rates of the sorption and desorption reactions.

One structural feature of the hydroxamic acid resins which could be varied is the distance between the chelating group and the resin matrix. Winston and co-workers found that this was an important variable in determining the stability of poly(hydroxamic acid) complexes (103,104). The same observation was made by Orf in a study of chelating resins with amide functional groups (108). A series of hydroxamic acid resins could be prepared readily from chloromethylated polystyrene via the following reaction sequence.



$$\mathrm{Res{-}CH_2Cl} + \mathrm{NH_2(CH_2)_n{-}\underset{\substack{\| \\ O}}{C}{-}OCH_3}$$

$$\longrightarrow \mathrm{Res{-}CH_2NH(CH_2)_n{-}\underset{\substack{\| \\ O}}{C}{-}OCH_3}$$

$$\xrightarrow[\mathrm{NH_2OH}]{} \mathrm{Res{-}CH_2NH(CH_2)_n{-}\underset{\substack{\| \\ O}}{C}{-}\underset{\substack{| \\ OH}}{NH}}$$

The reaction of amino acid methyl esters with hydroxylamine to give amino hydroxamic acids is described in the literature (123). It would be interesting to compare such polymers with the hydroxamic acid resins described in this work.

Although this dissertation is concerned with polymeric hydroxamic acids, it seems appropriate to mention that there are opportunities for research with the monomeric acids as well. N-methylbenzohydroxamic acid forms water-soluble complexes with titanium (77) and other metal ions. Initial work shows that these complexes are efficiently adsorbed by Amberlite XAD-2 resin from aqueous solution. They are readily desorbed by elution with organic solvents. This suggests a simple method for preconcentration of metal ions, similar to the work of Knapp and co-workers on preconcentration by adsorption of metal diethyldithiocarbamates (124).

The cyclic hydroxamic acids are unusually stable and more acidic than the acyclic compounds. It does not appear that any work has been done in utilizing these properties of cyclic hydroxamic acids for analytical applications. This appears to be an excellent opportunity for an analyst who is interested in the development of new organic reagents for inorganic analysis.

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APPENDIX

Methods for the Determination of Ions in Column Effluents

Aluminum(III)

Atomic absorption spectrometry   Determine aluminum(III) in the 10^{-4} to 10^{-3} M range by atomic absorption spectrometry in a nitrous oxide-acetylene flame.

Colorimetry   Pipette 5 mL of 2-6 x 10^{-5} M aluminum(III) into a 50-mL beaker. Add 5 mL of 0.1% cetyltrimethylammonium bromide, 5 mL of 0.05% chromazurol S, and 2 mL of 1 M acetate buffer. Adjust the pH to 5.6, quantitatively transfer to a 50-mL volumetric flask, and dilute to the mark. Let stand for 15-20 minutes and read the absorbance at 615 nm. The molar absorptivity is about 10^5 (125).

Arsenic(III)

Combine 1 mL of 1-5 x 10^{-4} M arsenic(III) in 2 M hydrochloric acid with 1 mL of 0.07% potassium bromate in a 30-mL beaker. Heat at 50°C for five minutes to oxidize As(III) to As(V). Add 3 mL of 0.5 M sulfuric acid and 1 mL of 5% $NH_4MoO_3 \cdot 4\ H_2O$ in 6 M sulfuric acid and mix. Add 1 mL of 1% hydrazine sulfate, quantitatively transfer to a 25-mL volumetric flask, and dilute to the mark. After two hours, read the absorbance at 660 nm. The molar absorptivity is about 7 x 10^3 (126).

Bismuth(III)

Dilute with 2.4 M hydrochloric acid to 1-5 x 10^{-5} M bismuth(III) and read the absorbance at 327 nm. The molar absorptivity is about 1.1 x 10^4 (13,127).

Calcium(II)

Dilute standards and samples with 0.6% sodium chloride in 0.02 M hydrochloric acid to 2-10 x 10^{-5} M Ca(II). Determine by atomic absorption spectrometry in an air-acetylene flame.

Chromium(III)

Add 5 mL of 2-10 x 10^{-5} M chromium(III) to a 30-mL beaker. Acidify the sample with 6 M hydrochloric acid, add 2 mL of 30% hydrogen peroxide, and evaporate to dryness. Dissolve the residue in 2 mL of 1:9 sulfuric acid, add 2 mL of 1% ceric ammonium nitrate in 0.5 M sulfuric acid, and boil for 15 minutes. Cool, and destroy excess Ce(IV) by dropwise addition of 1% sodium azide. Add 1 mL of 1% diphenylcarbazide in acetone, quantitatively transfer to a 25-mL volumetric flask, and dilute to the mark with water. After 15 minutes, read the absorbance at 540 nm. The molar absorptivity is about 3.7 x 10^4 (128,129).

Cobalt(II)

Add 5 mL of 1-10 x 10^{-5} M cobalt(II) to a 30-mL beaker. Evaporate almost to dryness, add 1 mL of concentrated nitric acid, and evaporate just to dryness. Dissolve in 5 mL of 0.3 M hydrochloric acid plus 0.07 M nitric acid. Add 0.5 mL of 0.2% nitroso R solution and 1.0 g of sodium acetate trihydrate. Check the pH and adjust to 5.5 if necessary. Boil for 1 minute, add 1 mL of concentrated nitric acid, and boil again for 1 minute. Cool, quantitatively transfer to a 10-mL volumetric flask, and dilute to the mark. Read the absorbance at 500 nm. The molar absorptivity is 1.6×10^4 (130).

Copper(II)

Prepare stock solutions of 1% v/v carbon disulfide in methanol, 35 mg/mL diethanolamine in methanol and 1 M tris(hydroxy)aminomethane buffer, adjusted to pH 8.0 with hydrochloric acid. Just before using, prepare copper reagent solution by mixing 1 mL each of the carbon disulfide and diethanolamine solutions and diluting the mixture with 40 mL of buffer solution. Add 5 mL of $1\text{-}10 \times 10^{-5}$ M copper(II) to a 30-mL beaker. Neutralize any excess acid with ammonium hydroxide and add 2 mL of copper reagent solution. Check the pH and adjust to 8.0, if necessary. Quantitatively transfer to a 10-mL volumetric flask and dilute to the mark. Read the absorbance at 432 nm. The molar absorptivity is about 1.3×10^4 (131).

Europium(III)

See Rare earths.

Iron(II,III)

Combine 5 mL of 1-5 x 10^{-5} M iron with 0.5 mL of 5% hydroxylamine hydrochloride, 1 mL of 0.1% ferrozine, and 1 mL of 1 M sodium acetate in a 30-mL beaker. Check the pH and adjust to 5 if necessary. Quantitatively transfer to a 10-mL volumetric flask and dilute to the mark. Read the absorbance at 562 nm. The molar absorptivity is about 2.8 x 10^4 (132).

Lanthanum(III)

See Rare earths.

Lead(II)

Dilute the sample to 1-5 x 10^{-5} M with water and hydrochloric acid so that the final solution is in 6 M HCl. Read the absorbance at 271 nm. The molar absorptivity is 1.1 x 10^4 (127).

Lutetium(III)

See Rare earths.

Magnesium(II)

Dilute standards and samples with 0.6% sodium chloride in 0.02 M hydrochloric acid to 5-25 x 10^{-6} M magnesium(II). Determine by atomic absorption spectrometry in an air-acetylene flame.

Manganese(II)

Prepare manganese reagent by dissolving 4 g of hydroxylamine hydrochloride in 50 mL of water, adding 2 mL of 37% formaldehyde, and diluting to 100 mL. Add 5 mL of 1-10 x 10^{-5} $\underline{M}$ manganese(II) to a 10-mL volumetric flask. Add 1 mL of manganese reagent and 1 mL of 6 $\underline{M}$ ammonium hydroxide. Dilute to the mark with water. After a few minutes, read the absorbance at 450 nm. The molar absorptivity is about 10^4 (128,133).

Mercury(II)

Dilute sample to 1-3 x 10^{-5} $\underline{M}$ in 2 $\underline{M}$ hydrochloric acid and read the absorbance at 229 nm. The molar absorptivity is about 2.9 x 10^4 (13,127).

Molybdenum(VI)

Prepare a solution of masking agents and buffer containing 0.01 $\underline{M}$ sodium tartrate, 0.01 $\underline{M}$ 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, and 10% sodium acetate. Combine 5 mL of 5-20 x 10^{-5} $\underline{M}$ molybdenum(VI), 1 mL of the masking and buffer solution, 5 mL of 10% hydroxylamine sulfate, and 5 mL of 0.001 $\underline{M}$ 4-(2-pyridylazo)resorcinol in a 50-mL beaker. Adjust the pH to 6.0 with sodium hydroxide and boil for 10 minutes. After the solution has cooled, quantitatively transfer it to a 50-mL volumetric flask and dilute to the mark. Read the absorbance at 530 nm. The molar absorptivity is about 3 x 10^4 (134).

Nickel(II)

Combine 5 mL of 2-10 x 10^{-5} M nickel(II), 10 mL of 0.05 M borate buffer (pH 9), 1 mL of 0.5 M sodium citrate, and 1 mL of 0.1% 4-(2-pyridylazo)resorcinol in a 50-mL beaker. Adjust the pH to 9.3, quantitatively transfer to a 50-mL volumetric flask, and dilute to the mark. After 10 minutes, read the absorbance at 494 nm. The molar absorptivity is about 8 x 10^4 (128,135).

Niobium(V)

Combine 5 mL of 2-10 x 10^{-5} M niobium(V), 4 mL of 0.025 M ethylenediaminetetraacetic acid, 5 mL of 0.001 M 4-(2-pyridylazo)resorcinol, and 5 mL of 1 M ammonium acetate in a 50-mL beaker. Adjust the pH to 6.0, quantitatively transfer to a 50-mL volumetric flask and dilute to the mark. After 1 hour, read the absorbance at 550 nm in a 2-cm cell. The molar absorptivity is 3.5 x 10^4 (136).

Rare earths

Combine 8 mL of 2-10 x 10^{-5} M lanthanum or rare earth, 2 mL of 10^{-3} M arsenazo I, and 3 mL of 1 M triethanolamine buffer (pH 8) in a 50-mL beaker. Adjust the pH to 8.0, quantitatively transfer to a 25-mL volumetric flask, and dilute to the mark. Measure the absorbance at 570 nm. The molar absorptivity is about 2.5 x 10^4 (137).

Scandium(III)

Combine 8 mL of 2-10^{-5} M scandium(III), 3 mL of 0.05% bromopyrogallol red, and 5 mL of 1 M sodium acetate in a 30-mL beaker. Adjust the pH to 6.1, quantitatively transfer to a 25-mL volumetric flask, and dilute to the mark. Read the absorbance at 610 nm. The molar absorptivity is about 2.6 x 10^4 (138).

Thorium(IV)

Pipette 8 mL of 1-10 x 10^{-5} M thorium(IV) into a 25-mL volumetric flask. Add enough hydrochloric acid to make the final concentration 0.24 M. Add 10 mL of 0.02% thorin and dilute to the mark. Read the absorbance at 545 nm. The molar absorptivity is about 1.6 x 10^4 (139).

Tin(IV)

Combine 2 mL of 1-10 x 10^{-6} M tin(IV) in 2 M hydrochloric acid, 3 mL of water, and 2 mL of 0.05% pyrocatechol violet in a 30-mL beaker. Add 5 mL of a saturated solution of potassium acid phthalate in 0.1 M hydrochloric acid. Adjust the pH to 2.5, quantitatively transfer to a 25-mL volumetric flask, and dilute to the mark. Read the absorbance at 555 nm. The molar absorptivity is about 7.5 x 10^4 (140).

Titanium(IV)

Colorimetry Pipette 5 mL of 1-5 x 10^{-4} M titanium(IV) into a 50-mL beaker. Add 10 mL of 0.2% tiron and 2 mL of 1 M sodium acetate. Adjust the pH to 5.0, quantitatively transfer to a 50-mL volumetric flask, and dilute to the mark. Read the absorbance at 410 nm. The molar absorptivity is about 1.3 x 10^4 (141).

Removal of fluoride For samples in 0.3 M hydrofluoric acid, pipette 5 mL into a 10-mL Teflon beaker. Add 1 mL of 6 M sulfuric acid and 0.5 mL each of perchloric and nitric acids. Heat to heavy fumes of sulfuric acid in a suitable hood. Cool, quantitatively transfer to a 50-mL beaker, and proceed as above.

Tungsten(VI)

Pipette 2 mL of 1-5 x 10^{-5} M tungsten(VI) in 0.1 M tartrate into a 30-mL beaker and evaporate to dryness. Add 2 mL of 10% stannous chloride in concentrated hydrochloric acid. After 30 minutes, add 5 mL of 3 M ammonium thiocyanate. Quantitatively transfer to a 25-mL volumetric flask and dilute to the mark with water. Read the absorbance at 398 nm. The molar absorptivity is about 1.2 x 10^4. No interference from tartrate, citrate, oxalate, or sulfate is reported with this method (142).

Uranium(IV)

Pipette 5 mL of 1-6 x 10^{-5} M uranium(VI) into a 50-mL volumetric flask. Add 2 mL of 0.05% arsenazo III and dilute to the mark with 4 M hydrochloric acid. Read the absorbance at 665 nm. The molar absorptivity is about 10^5. Negative deviations from Beer's law have been observed with this method (118).

Uranium(VI)

Prepare a complexing solution containing 5 g of 1,2-diaminocyclohexane-N,N',N'-tetraacetic acid, 0.5 g of sodium fluoride, and 13.0 g of sulfosalicylic acid per 100 mL. Pipette 1 mL of 1-6 x 10^{-4} M uranium(VI) into a 50-mL beaker. Add 5 mL of complexing solution and 4 mL of 1 M triethanolamine buffer (pH 8). Check the pH and adjust to 8.0 if necessary. Add 2 mL of 0.2% 4-(2-pyridylazo)-resorcinol, quantitatively transfer to a 50-mL volumetric flask, and dilute to the mark. Read the absorbance at 530 nm. The molar absorptivity is about 4 x 10^4 (143).

Vanadium(IV,V)

Pipette 5 mL of 1-10 x 10^{-5} M vanadium into a 30-mL beaker. Add 100 mg of sodium sulfate and 1 mL of 60% perchloric acid. Evaporate to dryness in a suitable hood. Dissolve the residue in 5 mL of 0.2 M perchloric acid and 1 mL of 1% ammonium persulfate. After 10 minutes, cover the beaker with a watch glass and boil for about 20 minutes, replacing water as necessary. Cool and add 1 mL of 0.02% ammonium persulfate. After 10 minutes, adjust the pH to 6-7 with dilute ammonium hydroxide. Add 5 mL of 0.01 M 1,2-diaminocyclohexane-N,N',N'-tetraacetic acid, 2 mL of 1 M ammonium acetate, and 2 mL of 0.05% 4-(2-pyridylazo)-resorcinol. Check the pH and adjust to 6.5 if necessary. Quantitatively transfer to a 25-mL volumetric flask and dilute to the mark. After 30 minutes, read the absorbance at 545 nm. The molar absorptivity is about 2.7×10^4 (144).

Zinc(II)

Add 10 mL of 0.05 M borate buffer (pH 8) to a 50-mL volumetric flask. Add 5 mL of $2\text{-}10 \times 10^{-5}$ zinc(II) followed by 1 mL of 0.1% 4-(2-pyridylazo)resorcinol. Dilute to the mark and measure the absorbance at 495 nm. The molar absorptivity is about 7.8×10^4 (128,145).

Zirconium(IV)

Colorimetric method 1   Add 4 mL of $1\text{-}5 \times 10^{-5}$ M Zr(IV) in 2 M hydrochloric or perchloric acid to a 10-mL volumetric flask. Add 2 mL of 0.02% xylenol orange and dilute to the mark with water. After 1 hour, read the absorbance at 535 nm. The molar absorptivity is about 3×10^4. Sulfate and nitrate interfere (146).

Colorimetric method 2 Add 1 mL of 0.03% arsenazo III in 0.024% sodium bicarbonate and 1 mL of concentrated hydrochloric acid to a 10-mL volumetric flask. Add 3 mL of 3-20 x 10^{-6} M Zr(IV) in 6 M hydrochloric acid and dilute to the mark with concentrated hydrochloric acid for a final concentration of 9 M HCl. Read the absorbance at 665 nm. The molar absorptivity is about 1.2 x 10^{5} (118).

Removal of oxalic acid For samples in 0.1 M oxalic acid, pipette 5 mL of 2-10 x 10^{-5} M Zr(IV) into a 30-mL beaker. Add 1 mL each of 1:1 nitric acid and 5% sodium bromate. Cover the beaker with a watch glass and let stand overnight. Add 8 mL of concentrated hydrochloric acid and boil for 5 minutes. After the solution has cooled, add 1 mL of 5% hydroxylamine hydrochloride. Quantitatively transfer to a 25-mL volumetric flask and dilute to the mark with 6 M hydrochloric acid (147). Analyze a 3-mL aliquot of this solution for Zr(IV) as in colorimetric method 2.