IS-T-770

THE SYNTHESIS AND CHARACTERIZATION OF AN N-(2-HYDROXYETHYL)-ETHYLENEDIAMINETRIACETIC ACID RESIN

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M.S. Thesis Submitted to Iowa State University

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Date Transmitted: October 1977

PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT NO. W-7405-eng-82

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The synthesis and characterization of an N-(2-hydroxyethyl)-ethylenediaminetriacetic acid resin

by

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A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Department: Chemistry
Major: Analytical Chemistry

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For the Graduate College

Iowa State University
Ames, Iowa

1977

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A chelating ion-exchange resin with N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) used as the ligand chemically bonded to XAD-4 by an ester linkage, HEDTA-4, was synthesized. It is stable under normal experimental conditions with the liquid chromatograph. The structure of the resin was confirmed by an infrared spectrum, and by potentiometric titrations. The capacity of the resin was also obtained by potentiometric titration and by a nitrogen analysis. The resin was used to pack a column of 5 mm internal diameter and 5 cm long. The effect of pH on the retention of different metal ions on the resin was studied. It was found that the resin was most selective for chromium(III), copper(II), lead(II), mercury(II), uranium(VI), zirconium(IV) and zinc(II) at a pH of less than 3. Furthermore, the resin proves to be functioning with a chelating mechanism rather than ion-exchange, and it can concentrate trace metal ions in the presence of a large excess of calcium and magnesium. This makes the resin potentially useful for purifying and analyzing drinking water.

INTRODUCTION

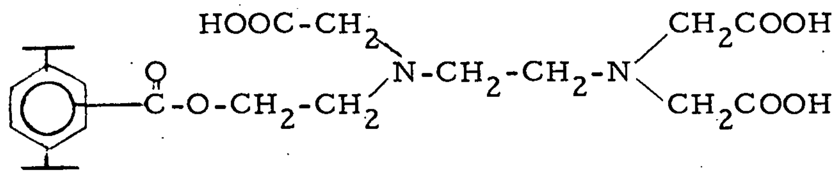
Chelating ion-exchangers are distinguished from ordinary types of ion-exchangers by their high selectivity, bond strength and kinetics (1). Of the chelating ion-exchangers studied, α-amino carboxylic acid resins are becoming more and more important, especially iminodiacetic acid resins (IDAA). For example, Dowex A-1, an iminodiacetic acid resin was found to have a very high adsorption for many metal ions by forming stable 1:1 complexes with the metal ions (2, 3, 4, 5). A wide application of Dowex A-1 has been shown in the determination of trace metals in food, in sea water, ground water as well as industrial waste waters (6, 7). Other IDAA resins synthesized more recently include one containing an iminodiacetate group and one containing an arsonate group. In addition, an iminodiacetic-acid-ethylcellulose (IDE cellulose) has been prepared and found to have an especially high chelating stability for copper(II), nickel(II) and zinc(II) (8, 9, 10).

Resins with multiple IDAA groups have been synthesized. Blasius and Olbrich (11) synthesized one containing two IDAA groups per benzene ring to separate cobalt and nickel. Morris, Mock, Marshall and Howe used vinylbenzyl chloride as the key starting material to synthesize a resin containing N, N, N-benzylamine triacetic acid, which retained both the polymerizability of styrene as well as the capacity to chelate metal ions (12). Blasius and Bock (13) synthesized a N, N, N'-ethylenediamine triacetic acid resin for separating transition metals from the alkaline earths.

EDTA has also been recently used as a ligand for a resin as it has a high complexing ability for many metal ions at high pH and selectivity for a few metal ions at low pH. Moyers (14) synthesized a resin with propylenediamine tetraacetic acid chemically bonded to XAD-4 by an ester linkage and found it useful for separating uranium(VI), thorium(IV), and zirconium(IV) from other metal ions and from each other.

Since 1959 when Meitzner and Oline (15) first discovered the technique of macroreticular synthesis, the Rohm and Haas Company has been studying and developing this interesting and useful concept. Initially, ion exchange resins having discrete physical pores (macroreticular ion-exchange resins) were developed. Further study showed that the pore size and internal surface area can be varied over a very wide range (16) and the concept of using these porous polymers as adsorbents was born. In the XAD series, XAD-4 is the adsorbent with the largest surface area even though it has the smallest pore size so that it has a high capacity for adsorption. In the synthesis of resins, it gives a product of relatively high yield, of definite structure and with fast kinetics. Moyers has used this adsorbent for the synthesis of a hexylthioglycolate resin and a propylenediamine tetraacetic acid resin (14).

To investigate further into resins with EDTA functional groups, N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) was used as the ligand chemically bonded to XAD-4 by an ester linkage. The structure of this resin (HEDTA-4) is



The structure of the resin was supported by an infrared spectrum and a nitrogen analysis. The capacity of the resin was determined by potentiometric titration. The selectivity of the resin for different metal ions at different pH was investigated. A study was also made to determine whether the resin was an ion-exchanging one or a complexing one.

EXPERIMENTAL

Instrumentation

The liquid chromatograph (Figure 1) has been previously described (14, 17, 18). The detector used was a Heath EU-701 for most of the experimental work, but was replaced by a Tracor 970 Variable Wavelength Detector for the analysis of zinc in a large excess of calcium or magnesium. Helium gas pressure was used to maintain a constant flow rate through the resin column.

The resin matrix, Rohm and Haas' XAD-4, was air-dried, Soxhlet extracted with methanol, ground and sieved. After washing with 12 *M* hydrochloric acid, water, and acetone, the 250-325 mesh fraction was used in the synthesis of the HEDTA resin.

A Beckman IR-4250 was used for the infrared spectrum of the resin.

An Orion Research model 701 digital pH meter was used for the potentiometric titration of the resin.

A Perkin-Elmer 303 Atomic Absorption Spectrophotometer was used in the analysis of the study of the selectivity of the resin for zinc in a large excess of calcium or magnesium.

All chemicals used were of reagent grade or better.

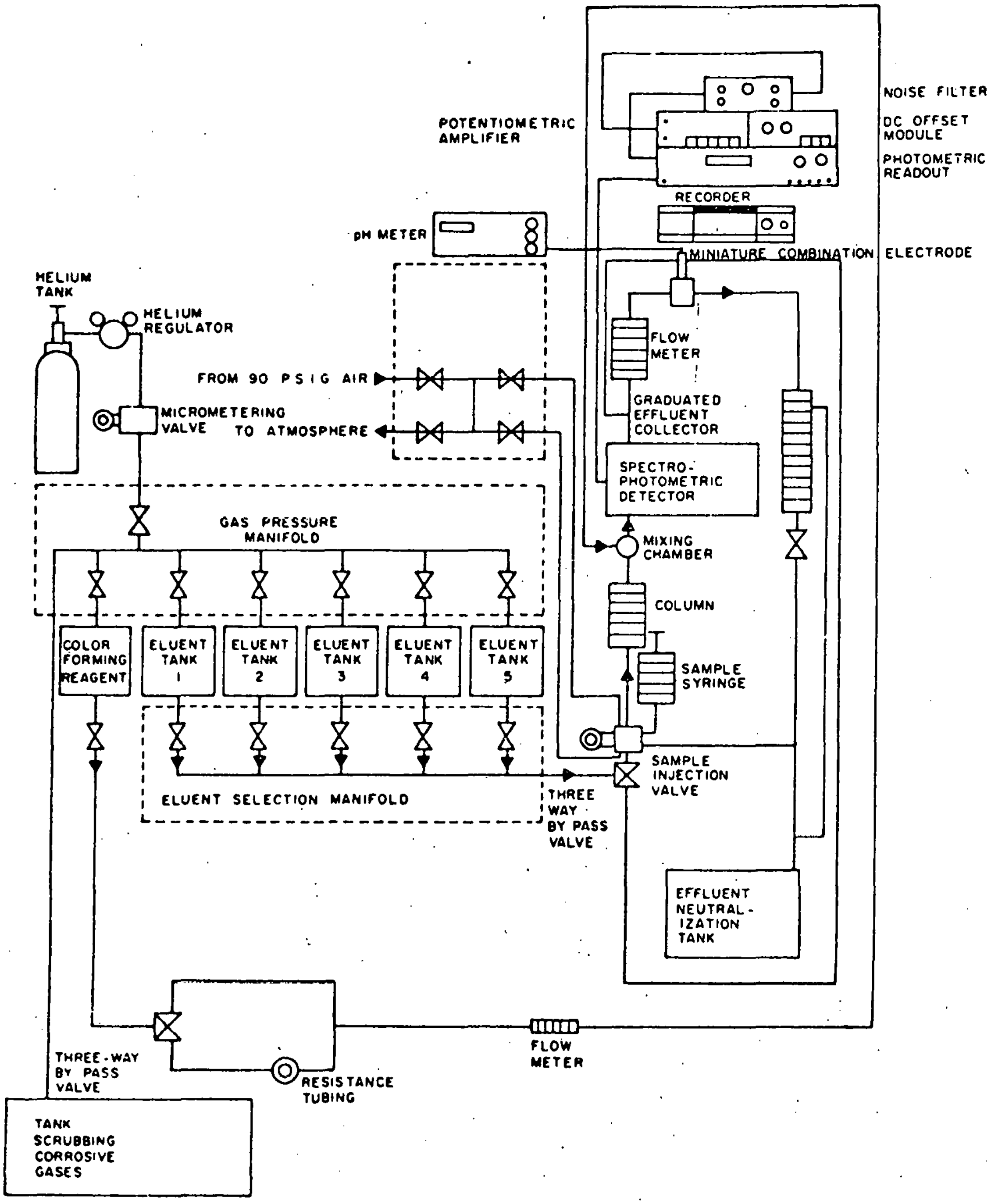
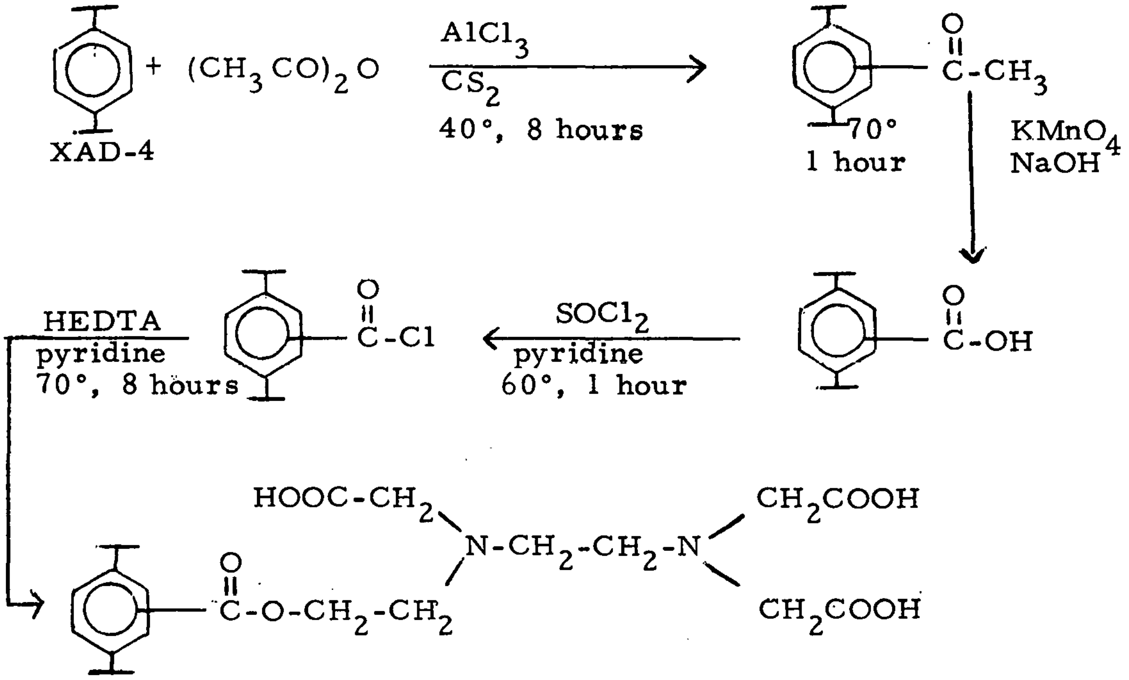


Figure 1. Schematic diagram of the liquid chromatograph

Synthesis



HEDTA-4

3 g of XAD-4 and 10 g of aluminum chloride were placed in 15 ml of carbon disulfide in a 250-ml standard taper Erlenmeyer flask. A condenser was set up. A mixture of 5 ml of acetic anhydride and 5 ml of carbon disulfide was placed in an addition funnel over the

condenser. The acetic anhydride was added at a rate of about one drop every two seconds while the mixture in the flask was heated with stirring at 40°. The mixture was refluxed for 8 hours.

The product was removed and hydrolyzed with 12 M hydrochloric acid and ice. The substance was then washed with concentrated ammonium hydroxide, concentrated hydrochloric acid, water, and acetone.

The above acetylation and hydrolysis procedure was repeated with the resultant substance to increase the yield.

The product was then oxidized with 0.1 M potassium permanganate in 2% sodium hydroxide at 70° for an hour to give the carboxylic acid which was washed with concentrated ammonium hydroxide, concentrated hydrochloric acid, water, acetone and dried.

1.5 g of the carboxylic acid was mixed with 1 ml of thionyl chloride in 10 ml of pyridine and refluxed at 60° for an hour. The excess thionyl chloride was removed with a vacuum pump. 3 g of HEDTA was then added to the acid chloride and refluxed in about 20 ml of pyridine at 70° for 8 hours. The product was suction filtered, washed with concentrated ammonium hydroxide, concentrated hydrochloric acid, water and acetone.

Characterization

Capacity of the carboxylic acid intermediate and HEDTA-4

The yield of the carboxylic acid intermediate was determined by potentiometric titration. 0.25770 g of the substance was slurried in 10 ml of 0.25 M sodium hydroxide, allowed to equilibrate for two hours and then titrated with 0.0232 M hydrochloric acid. The pH was recorded on every 2-ml increment of the titrant.

The same procedure was followed to determine the capacity of the HEDTA-4.

The titration curve obtained was compared to that obtained for HEDTA alone by a similar procedure.

The capacity of the resin was determined from the amount of titrant used between the first endpoint and the second endpoint.

Spectroscopic characterization

An infrared spectrum of the HEDTA-4 was taken in solid form pressed in a potassium iodide pellet where the proportion of HEDTA-4 to potassium iodide was about 1:8 by weight.

Nitrogen analysis

The nitrogen content of the resin was determined by the Dumas method.

The resin column and conditions of operation

An acetone slurry of 0.2 g of HEDTA-4 from which the fines were decanted was used in packing a glass column with an internal diameter of 5 mm. The resin column was 5 cm long. The packing was done by inserting a plug of glass wool in one end of the column, and then injecting a slurry of the resin in acetone from the other end with a syringe. This column was used for all subsequent experimental work. A pressure of 30 psi and a flow rate of 2 ml/min were used. Detection of the ions eluted was accomplished by means of PAR in THAM at pH 8 and a visible-UV spectrophotometer set at a wavelength of 495 nm.

The effect of pH

The effect of pH on the behavior of the resin was investigated by using solutions of different pH as the eluent.

The column was first washed with water for about 10 minutes and then with the eluent to be used. Samples containing 10^{-4} $\underline{M}$ solutions of different ions were injected separately onto the column with a syringe through a 50-μl sample loop. The ions used were: Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Hg(II), Mn(II), Mo(VI), U(VI), Zr(IV), Cr(III), and Th(IV). After each injection, the column was washed with 10^{-2} $\underline{M}$ nitric acid. The ions eluted were detected with PAR in THAM-HCl and the elution peaks were recorded. In the case of thorium(IV), 10^{-2} $\underline{M}$ perchloric acid had to be used to elute the ions.

The same procedure was carried out for eluents of higher pH including pH3 nitric acid, pH 4 hydrochloric acid-potassium hydrogen phthalate buffer, pH 5 acetate buffer, and pH 8 ammonium buffer.

When the ions were still retained on the column for 5 minutes, the eluent was switched to one of lower pH until the elution was complete as indicated by the tracing of the peaks on the recorder.

Complexing character

To determine whether the resin was functioning as an ion-exchanger or as a complexer, the effect of 2 M sodium chloride at pH 5.7 being used as the eluent was observed. Samples of 10^{-4} M uranium(VI), thorium(IV), zirconium(IV) and lead(II) were injected separately onto the column through a 50-μl sample loop after washing the column with 2 M sodium hydroxide. The column was then washed with the same eluent for about 5 minutes, and subsequently with pH 2 nitric acid or perchloric acid to elute the ions retained.

The retention on the column was also investigated for calcium and magnesium which should have a comparatively lower formation constant than those of the other ions already tried. 50-μl samples of 10^{-4} M calcium and magnesium were injected, and pH 8 ammonium buffer and pH 5 acetate buffer were used as eluents separately.

To confirm that the resin was complexing, the effect of the presence of a large excess of calcium on the retention of zinc on the column was studied. The original column and a second column with the amount of resin on the column reduced to 0.1 g and hence the column length to 2.5 cm. were used. A sample of 0.987 M calcium(II) and 2×10^{-5} $\underline{M}$ zinc(II) was injected onto the column through a 214-µl sample loop so that the amount of calcium(II) in the sample was equivalent to twice the capacity of the resin and was 50,000 : 1 in excess of the zinc(II). Solutions of pH 8 ammonium buffer and pH 5 acetate buffer were used as the eluent separately. The eluate was collected in a 25-ml volumetric flask and then analyzed for calcium and zinc with the atomic absorption spectrophotometer. Following the collection of the eluate, the eluent was switched to 0.1 $\underline{M}$ hydrochloric acid to elute any calcium and zinc retained on the column and the elution peaks were recorded.

The same procedure was followed for a sample mixture of 0.987 $\underline{M}$ Mg(II) and 2×10^{-5} $\underline{M}$ Zn(II).

RESULTS AND DISCUSSION

Physical properties

The product of the synthesis, HEDTA-4, a chelating resin with N-(2-hydroxyethyl)ethylenediaminetriacetic acid chemically bonded onto XAD-4 by an ester linkage, is tan in color when dry and brown when wet. The particle size is similar to that of the starting XAD-4. It is stable under normal experimental conditions with the liquid chromatograph.

Capacity

The capacity of the carboxylic acid intermediate was found by potentiometric titration to be 1.17 millimole/g, which meant there was a relatively good yield in the first part of the synthesis. (Figure 2). The titration curve of the HEDTA-4 is very similar to that of HEDTA, which has pK values of $pK_1 = 3.5$, $pK_2 = 5.6$, $pK_3 = 9.9$ (Figures 3 and 4). The capacity of the HEDTA-4 resin was found to be 0.93 millimole/g. At the same time, the nitrogen analysis gave 2.71% by weight of nitrogen. Since the nitrogen must have come from the HEDTA bonded onto the resin matrix, this result corresponds to a capacity of 0.97 millimole/g. This is rather consistent with the result of the potentiometric titration.

This capacity is somewhat higher than that of BPDTA-4, synthesized by Moyers (14). This is probably due to the fact that carbon disulfide is a more effective solvent than petroleum ether in

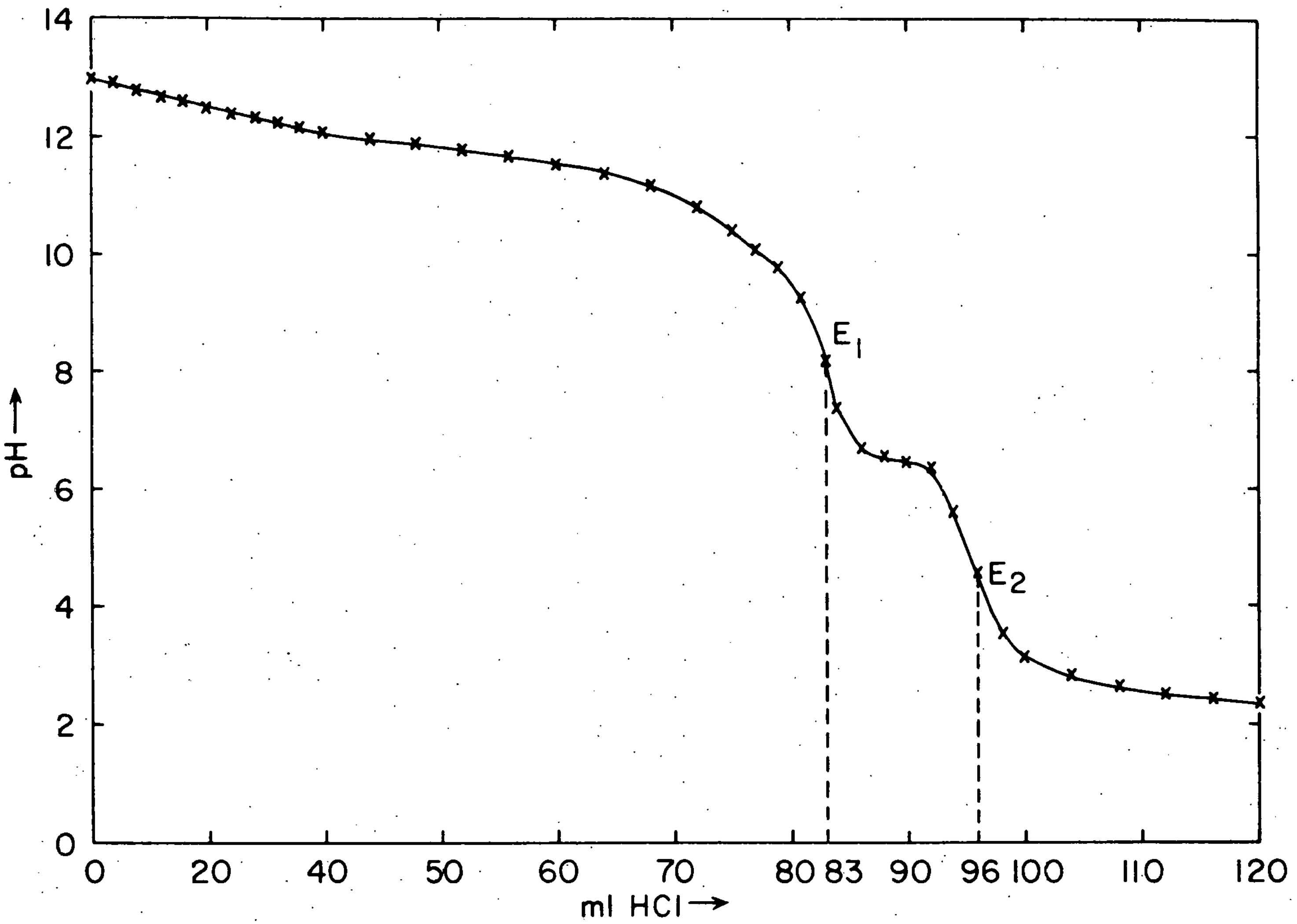


Figure 2. Titration curve of carboxylic acid intermediate + excess NaOH
E_1 = first endpoint, E_2 = second endpoint

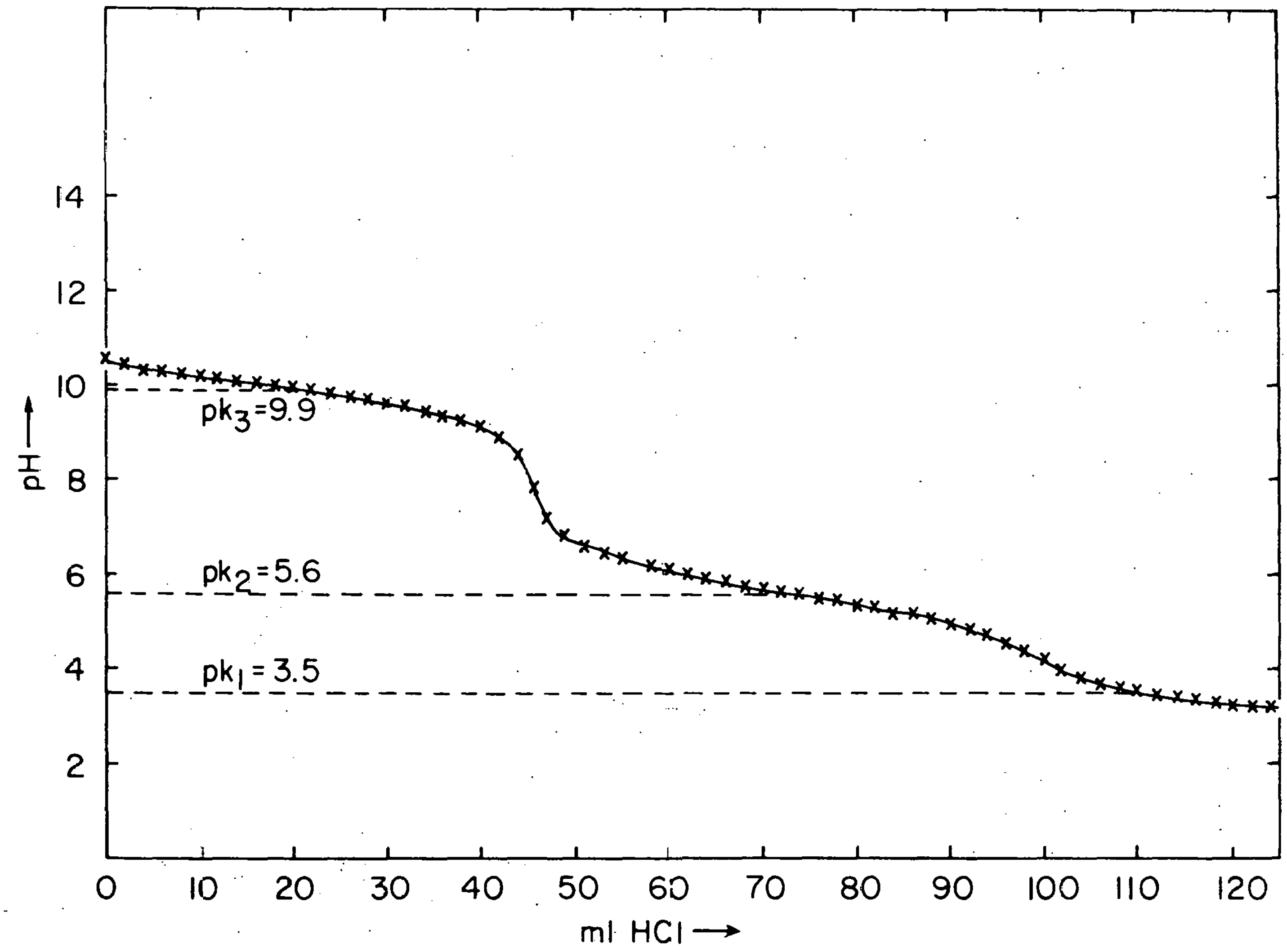


Figure 3. Titration curve of HEDTA + excess NaOH

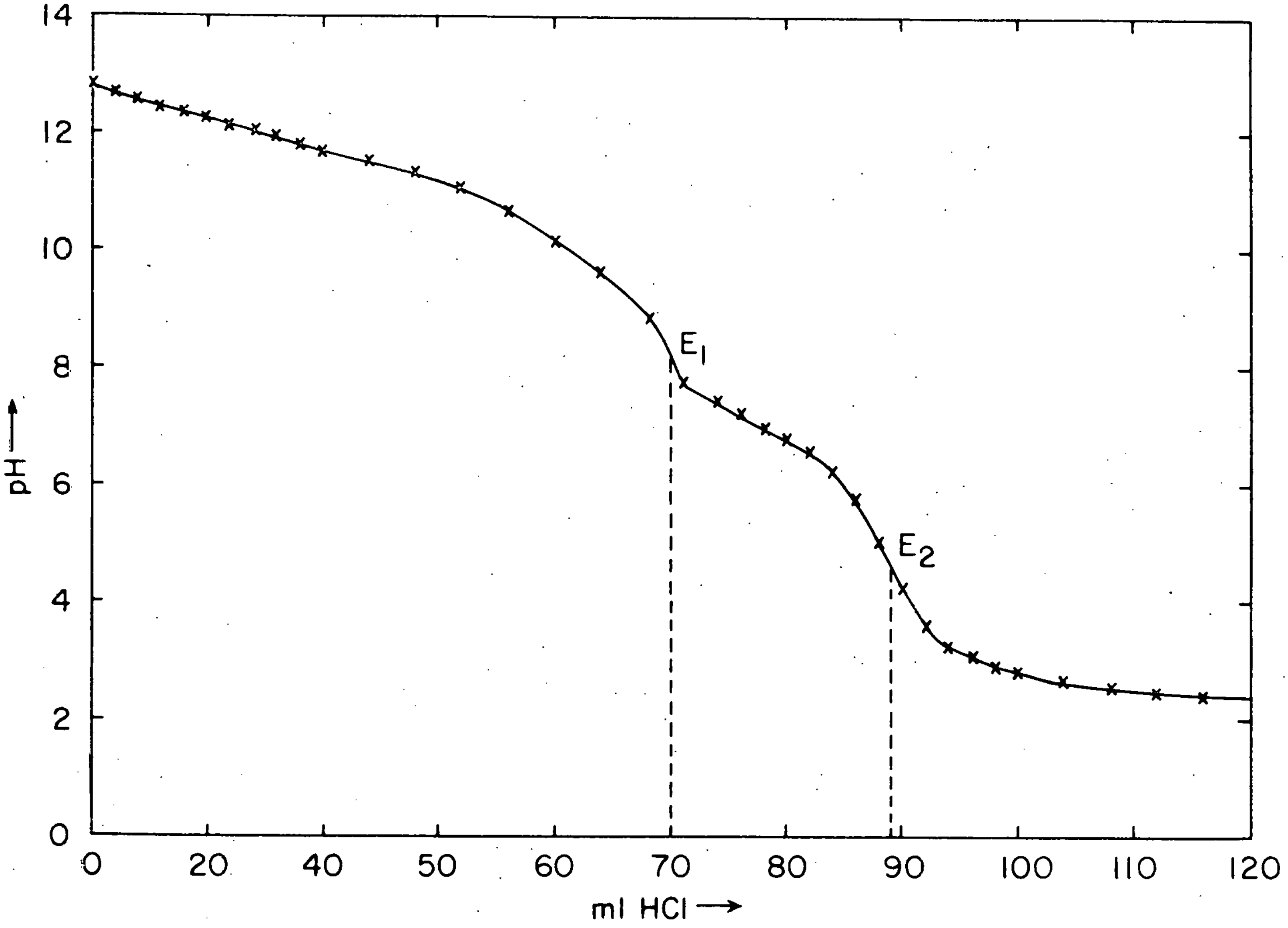


Figure 4. Titration curve of HEDTA - 4 + excess NaOH
E_1 = first endpoint, E_2 = second endpoint

the acetylation step. Carbon tetrachloride has also been tried as the solvent but found to be no better than petroleum ether. In the esterification step, pyridine used as the solvent is more basic than petroleum ether. Pyridine is a better solvent for HEDTA but is not too basic to interfere with the esterification mechanism. The temperature of 40° for the acetylation has been found to be the optimum with carbon disulfide as solvent. With petroleum ether as solvent and a temperature of 65° for the acetylation, the product had a tendency to decompose. Similarly, a temperature of 70° was found to be the optimum for the esterification step.

A solid phase reaction had also been attempted but to no avail. When this was attempted the vacuum tube exploded, perhaps due to the vaporization of the concentrated sulfuric acid present as a catalyst.

Spectroscopic characterization

The infrared spectrum of the resin (Figure 5) also shows the presence of peaks from both the XAD-4 and the HEDTA (Table I). This helps to confirm that the synthesis has been a success.

Percentage yield

According to the capacity found for the resin, the yield of the synthesis based on the original amount of XAD-4 used is 17.8% in terms of the degree of substitution.

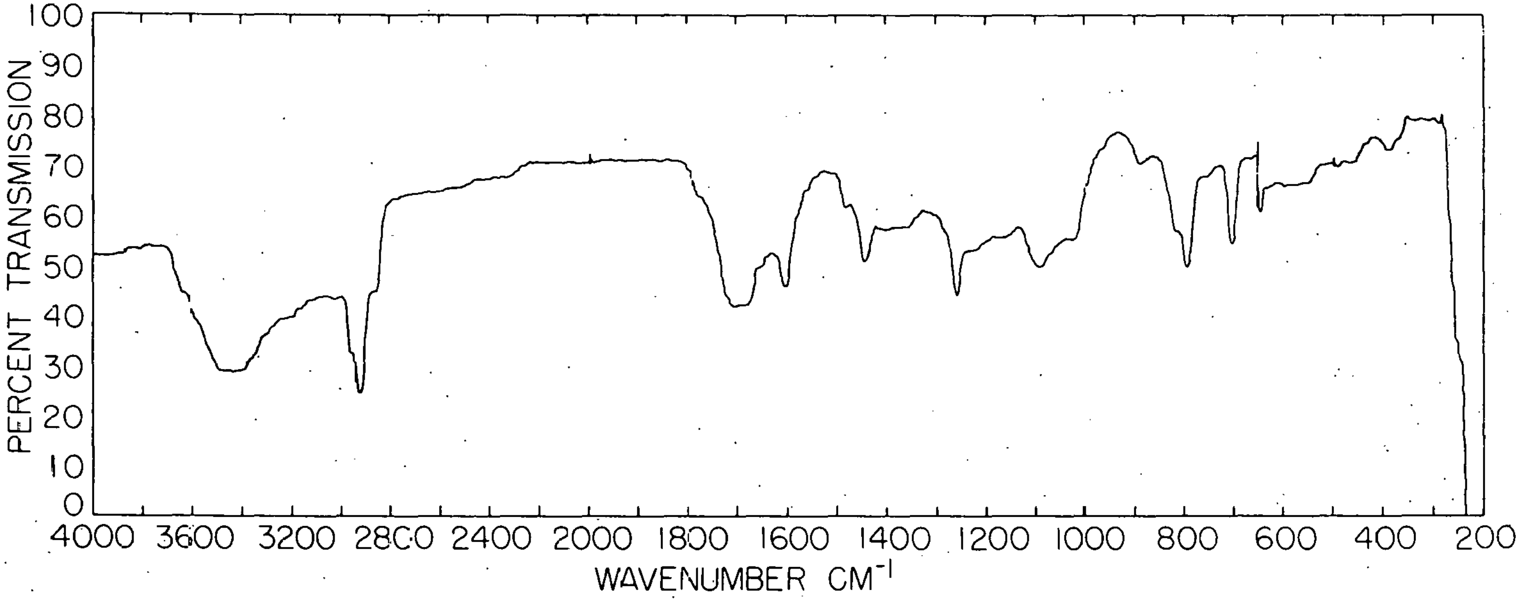


Figure 5. Infrared spectrum of HEDTA-4 taken in solid form at 600 cm^{-1}/min

Table I. The IR spectrum of HEDTA-4 taken in the solid form in a KI pellet at 600 cm^{-1}/min.

Wavelength of peak (cm^{-1})	Peak in common with the IR spectrum of
3400-3500	HEDTA
2920	XAD-4
1700	HEDTA
1600	XAD-4
1450	XAD-4
1095	HEDTA
795	HEDTA
700	XAD-4
395	HEDTA

The effect of pH

The effect of pH on the retention of ions on the resin is shown in Table II. Chromium(III) could sometimes be partially retained even at pH 2. Thorium(IV), for some reason, cannot be eluted with pH 2 nitric acid but is eluted with pH 2 perchloric acid. Further investigation would be desirable. Calcium and magnesium are only slightly retained at pH 5.

Below pH 3, the resin is more selective for chromium(III), copper(II), lead(II), mercury(II), uranium(VI), zirconium(IV), and zinc(II). Since these are some trace metals found in ground water, this resin is potentially useful for determining trace metals in water.

Complexing character

In a high salt concentration of 2 M sodium chloride at pH 5.7, a few selected metal ion solutions, uranium(VI), thorium(IV), zirconium (IV), and lead(II), were retained and subsequently could be eluted with pH 2 eluent. Since sodium would undergo ion-exchange rather than complexation with the resin, this shows that the mechanism of attraction is likely one of complexation. Figure 6 shows the elution of uranium(VI) in the absence of 2 M sodium chloride and Figure 7 shows its retention in the presence of 2 M sodium chloride and subsequent elution with pH 2 nitric acid.

Table II. Effect of pH on the retention of metal ions on HEDTA-4.

Ion (10^{-4} M)	Lowest pH at which the ions are retained	Ions eluted with:
Th(IV)	pH 2 (HNO_3)	pH 2 ($HClO_4$)
Cr(III)	pH 3 (HNO_3)	pH 2 (HNO_3)
Cu(II)	"	"
Pb(II)	"	"
Hg(II)	"	"
U(VI)	"	"
Zr(IV)	"	"
Zn(II)	"	"
Fe(III)	pH 4 (HCl, KHP)	pH 3 (HNO_3)
Mo(VI)	"	"
Co(II)	"	"
Ni(II)	"	"
Cd(II)	"	"
Mn(II)	pH 5 (acetate)	pH 4 (HNO_3)
Ca(II)	"	0.1 M HCl
Mg(II)	"	"

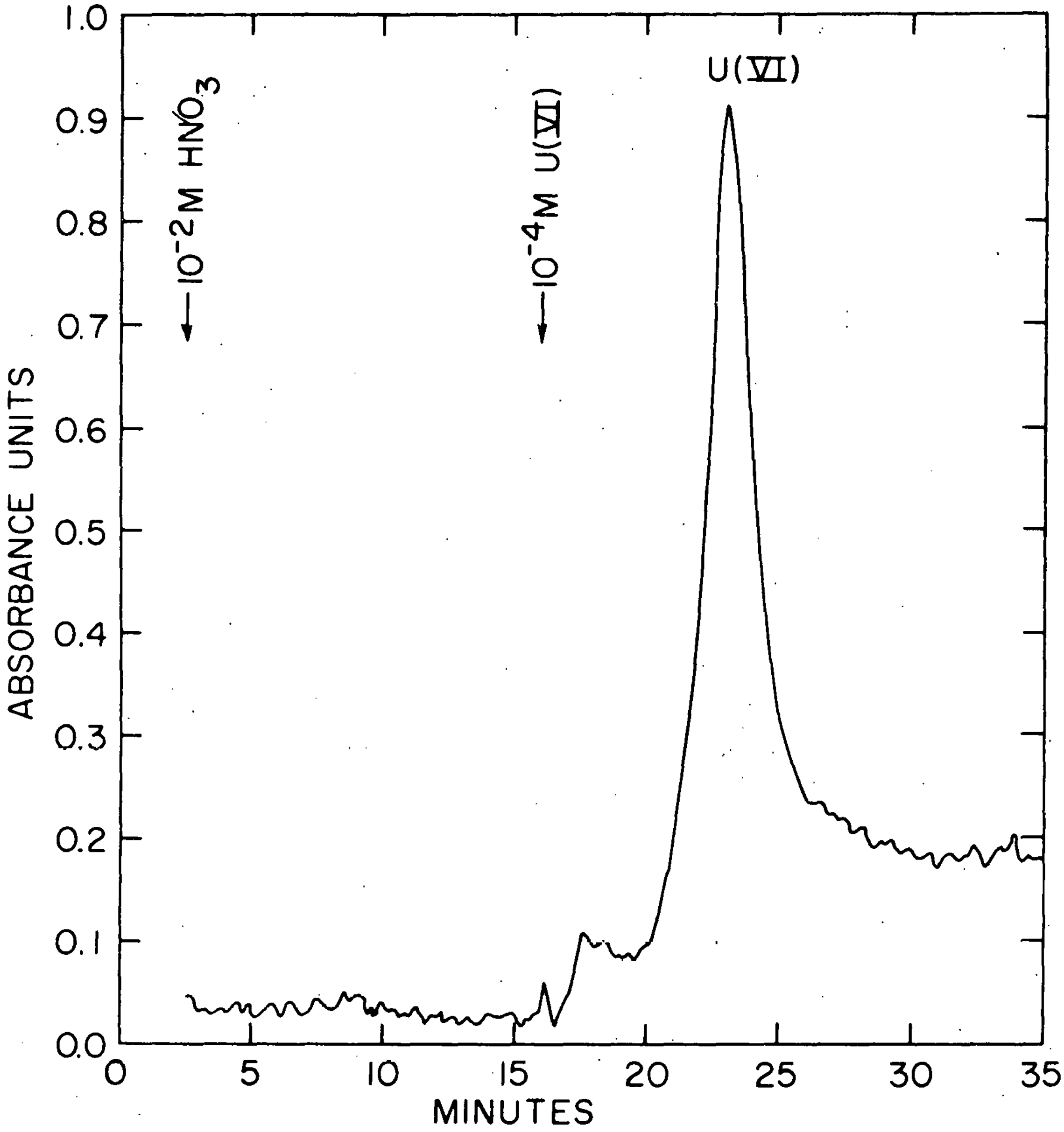


Figure 6. Elution of U(VI) in pH 2

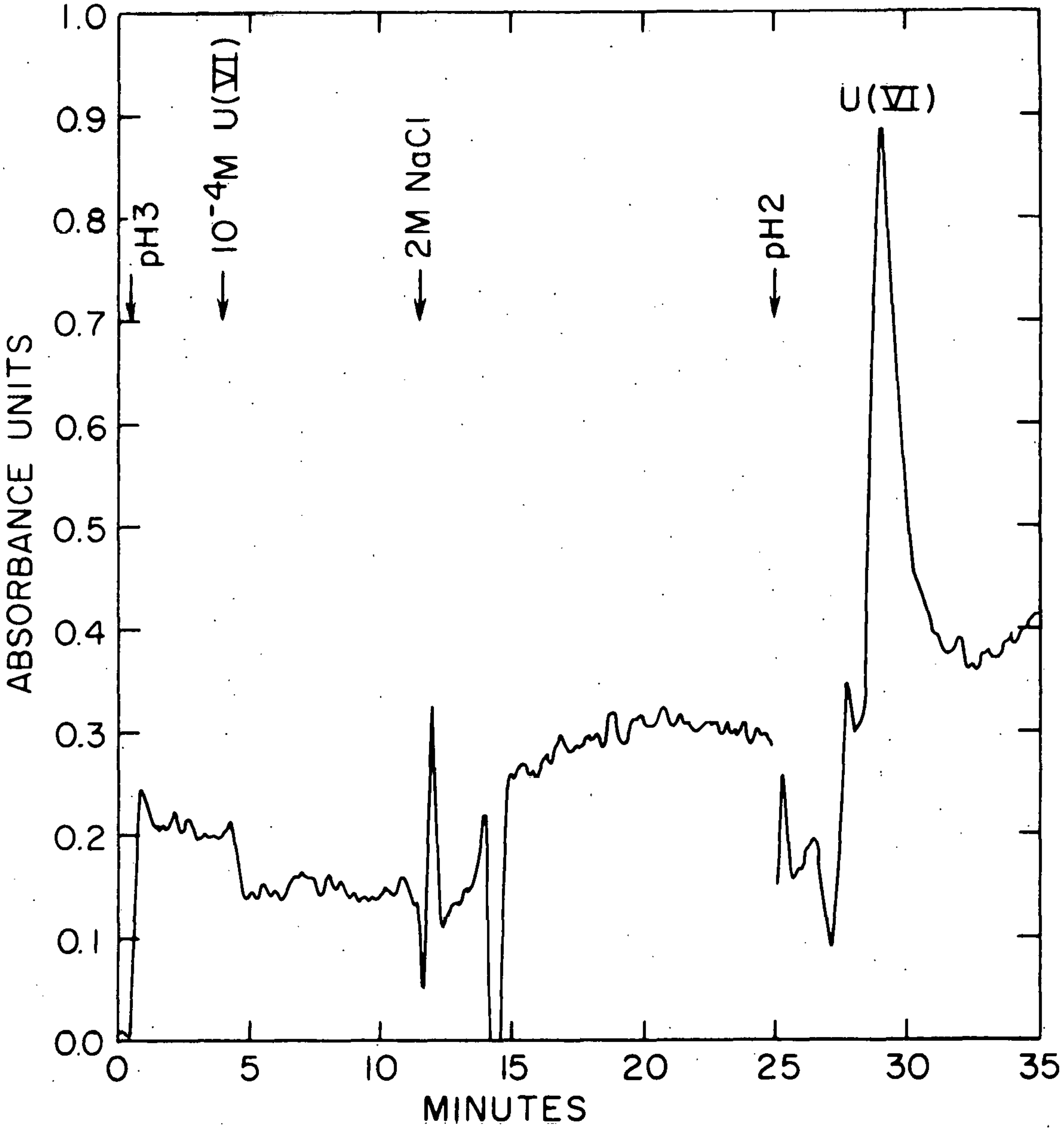


Figure 7. Retention of U(VI) in presence of 2 M NaCl

The retention of a small amount of zinc in the presence of a large excess of calcium or magnesium at pH 8 and pH 5, as indicated by the atomic absorption result, is shown in Table III. The subsequent elution of the zinc and calcium with 0.1 M hydrochloric acid is shown in Figure 8. The selectivity of the resin for the retention of zinc in large excess of calcium and magnesium further supports the assumption that the resin is chelating instead of ion-exchange. This also implies that the resin can be useful for the elimination of trace metal ions in drinking water which contains a much higher concentration of calcium and magnesium. The application of chelating ion-exchange resins as purifiers have proved to be more effective than other methods such as extraction, electrodialysis, evaporation and precipitation methods (19).

Table III. Percentage retention of a mixture of Zn(II) in excess of Ca or Mg in the molar ratio of 50,000 : 1 at pH 8 and pH 5

Wt. of resin used	pH	Excess ion (0.987 M)	% retention of Excess ion (0.987 M)	% retention of Zn(II) (2×10^{-5} M)
0.2 g	8	Ca	2.1	100.0
		Mg	37.7	100.0
0.2 g	5	Ca	25.3	100.0
		Mg	34.8	100.0
0.1 g	8	Ca	0.0	99.9
		Mg	20.7	100.0
0.1 g	5	Ca	0.0	98.8
		Mg	26.5	100.0

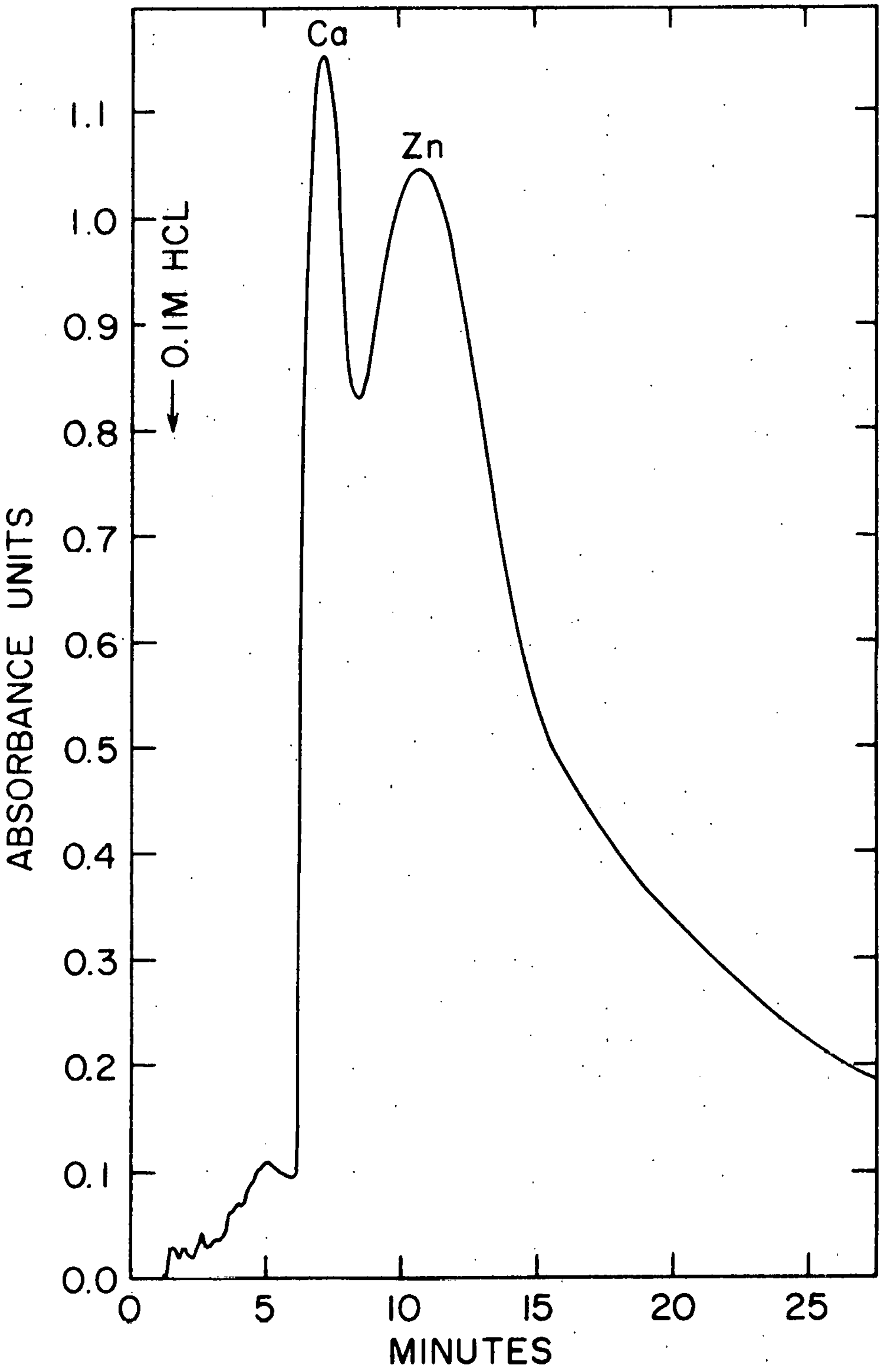


Figure 8. Separation of 2×10^{-5} $\underline{M}$ Zn(II) from 0.987 $\underline{M}$ Ca(II)

SUMMARY

A chelating ion-exchange resin with N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) used as the ligand chemically bonded to XAD-4 by an ester linkage, HEDTA-4, was synthesized. It is stable under normal experimental conditions with the liquid chromatograph. The structure of the resin was confirmed by an infrared spectrum, and by potentiometric titrations. The capacity of the resin was also obtained by potentiometric titration and by a nitrogen analysis. The resin was used to pack a column of 5 mm internal diameter and 5 cm long. The effect of pH on the retention of different metal ions on the resin was studied. It was found that the resin was most selective for chromium(III), copper(II), lead(II), mercury(II), uranium(VI), zirconium(IV) and zinc(II) at a pH of less than 3. Furthermore, the resin proves to be functioning with a chelating mechanism rather than ion-exchange, and it can concentrate trace metal ions in the presence of a large excess of calcium and magnesium. This makes the resin potentially useful for purifying and analyzing drinking water.

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ACKNOWLEDGMENT

Appreciation is extended to Dr. James S. Fritz for his guidance in this work and to John Richard for his performance of the nitrogen analysis.