IS-T-855

Chromatography of metal ions with a triazine chelating resin

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M.S. Thesis submitted to Iowa State University

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DISCLAIMER

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Chromatography of metal ions with a triazine chelating resin

by

Wang-Nang Wang

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TABLE OF CONTENTS

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ABSTRACT

The synthesis, characterization and some analytical applications of a new triazine resin are described. Separation of group I B, IIB, VIB and VIIB metal ions from group VIII metal ions is achieved by this PDT-4 resin. Calcium(II) and Magnesium(II) are taken up at pH = 6, 0.1 M acetate and are eluted at pH = 6, 0.1 M sodium nitrate. Copper(II) is retained at pH = 6, 0.1 M acetate and pH = 1 hydrochloric acid and is eluted subsequently by 5 M perchloric acid. Molybdenum(VI) is sorbed selectively from 0.1 N sulfuric acid or hydrochloric acid and is eluted in a tight band by 0.1 N sodium hydroxide. Numerous rapid column chromatographic separations are reported using this new resin, including analysis of NBS standard samples.

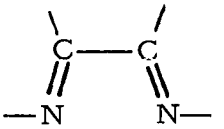
INTRODUCTION

It is often necessary to separate the chemical components in a system before a quantitative analysis can be carried out. The purpose of the separation is to isolate the desired component from any interference of the matrix and/or to concentrate a component by removing it from the bulk of the sample. The techniques of extraction and chromatography are two important methods of separation used in analytical chemistry. The mechanisms of these methods differ but both are based on a partitioning of the chemical component between two media. In the extraction method, these media are usually two immiscible liquids. In chromatography, the media may be combinations of solids, liquids, or gases. Over the past decade the progress of the basic theory and techniques on liquid chromatography has made possible the analysis of very complex mixtures. Commercial instrumentation using high-pressure pulseless pumps, solvent programming, macroporous beads and highly sensitive universal detectors has made high performance liquid chromatography the technique of choice for many analyses.

Much of the work accomplished in this area has been in the separation and determination of organic compounds. The use of high-performance liquid chromatographic techniques employing automatic detection for the analysis of inorganic ions has only recently come into common practice. In recent years much of the interest in

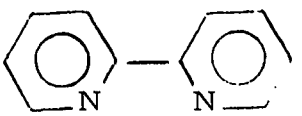
inorganic chromatographic analysis has been with chelating resins chemically bonded to a polymer matrix. Resins of this type exhibit greater selectivity and faster kinetics than simple ion exchangers. Since the functional group is chemically bonded to the polymer matrix, the problems associated with phase bleeding are also eliminated.

The chelating functional group that was attached to the polymer matrix is 3-(2-pyridyl)-5, 6-diphenyl-1, 2, 4-triazine (PDT). It is a compound related to 1, 10-phenanthroline and 2,2′-bipyridine which has a ferroin group (α, α'-diimine group.)

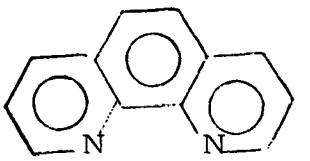


ferroin group

Interest in organic compounds containing the ferroin group dates back to the late nineteenth century. The first representative, 2, 2′-bipyridine was described by Fritz Blau (1). An exhaustive study of this first outstanding example of ferroin-reacting compound was published by him (2) as well as the synthesis of the second example, 1, 10-phenanthroline (3).



2, 2′- bipyridine



1, 10-phenanthroline

In a remarkably thorough study of these compounds Blau prepared the intensely colored iron(II) complexes of both 2, 2´-bipyridine and 1, 10-phenanthroline, the iron(III) complexes of both compounds were also prepared. Through a series of potentiometric studies he demonstrated the reversible nature of the oxidation of the iron(II) complexes of the two compounds, and the reactivity of the compounds towards a number of other metals. All the complexes formed were correctly recognized as coordination compounds. He also discovered that only the 2, 2´-isomer of bipyridine would form colored iron(II) complexes. Blau monitored the progress of the synthesis of 2, 2´-bibyridine by forming its colored iron(II) complex, and in doing so demonstrated the first analytical use of the complex (2).

Although Blau's work clearly indicated that these compounds had potential as analytical reagents, only limited use was made of them until 1931. Hammett, Walden and Chapman renewed interest in them by describing the use of the iron(II) complexes of 1, 10-phenanthroline and 2, 2´-bipyridine as high potential, reversible oxidation-reduction indicators (4).

To a large extent credit for the development of the analytical potential of compounds related to 1, 10-phenanthroline belongs to Professors Francis H. Case of Temple University, G. Frederick Smith of the University of Illinois, and their co-workers. Beginning in the 1940's Professor Case began systematically synthesizing

compounds related to 1, 10-phenanthroline and, until his retirement, Professor Smith and his co-workers studied the chelation properties and analytical utilities of the compounds. In recent years the characterization of the compounds synthesized by Professor Case has been performed by Professor Alfred A. Schilt and his co-workers at Northern Illinois University.

Although these joint ventures have produced an array of outstanding analytical reagents with numerous and diverse applications, perhaps the most prominent result has been the elucidation of correlations between structural features of the organic compounds and physical and analytical useful properties of their metal complexes. Knowledge of these correlations has made it possible to synthesize analytical reagents with predictable analytical properties rather than relying on the serendipitous discovery of compounds with desired analytical properties.

The structural feature of compounds related to 1, 10-phenanthroline that is responsible for their ability to form metal complexes is the α, α'-diimine group. This grouping is often referred to by its trivial name, the ferroin group. In 1953, as the result of the study of a large number of aromatic and aliphatic compounds containing the ferroin group, Krumhotz concluded that aliphatic compounds were also capable of forming metal complexes, although generally less stable than those formed by aromatic compounds (5).

Even though a great number of compounds containing the ferroin group have been synthesized and characterized as analytical reagents, many other organic compounds containing the ferroin group have yet to be prepared and characterized to the extent that one can predict the analytical properties of their derivatives.

The analytical applications of ferroin type compounds are many and diverse, including such uses as oxidation-reduction indicators, precipitants, separation reagents, and masking and scavenging reagents. Perhaps the most widespread use of ferroin type compounds is as colorimetric reagents for metals. Their versatility as iron reagents is especially significant. Specific reagents and analytical procedures have been developed affording sensitive and selective iron analyses under a wide variety of experimental conditions. Procedures or reagents for determining iron directly in strongly acidic media however have been lacking. In acidic media the competition between protons and metal ions for the basic sights on the complexing agent usually greatly favors the protons and thus prevents iron complexation.

Recent work done by Chriswell (6), Stookey (7), and Gibbs (8) has shown that among all the newly synthesized ferroin compounds 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) is one of the most stable and sensitive ferroin compounds for iron(II), copper(II), and cobalt(II). PDT coated on Amberlite XAD-2 by Schilt (9) has been shown to be specific for concentration and group separation

of metal ions such as iron(II), cobalt(II), nickel(II), and copper(I), zinc(II), lead(II), chromium(III), cadmium(II) and manganese(II).

The purpose of this research, therefore, is to synthesize and investigate a chelating resin containing the chemically bonded PDT functional group. To check the applicability of the method to real samples several NBS standards are analyzed.

EXPERIMENTAL

Apparatus

Liquid chromatograph

The system for liquid chromatography with automatic detection has been described previously (10). A small modification has been made for the separate pressure control of eluent and color-forming reagent. Sample loop of 214 µl and a 75 mm by 2 mm i. d. column are used for the separations. A schematic diagram of the unit is shown in Figure 1. The resin used in the column was taken from 250 - 235 mesh fraction from grinding and sieving. It was slurried with methanol, allowed to settle, and the suspended fines were decanted. This fractionation process was repeated several times after the synthetic step.

Detector

A Tracor 970 Variable Wavelength Detector was used for the continuous spectrophotometric monitoring of the column effluent. All chromatograms were recorded on a Houston Instrument Omniscribe Recorder.

Column

The analytical column was constructed of two Altex 200 - 28 glass connectors fused together. The column had an i. d. of 2 mm and an overall length of 75 mm. A helium pressure of 26 p. s. i. was required to attain a flow of 2 ml/min.

Figure 1. Schematic diagram of the liquid chromatograph

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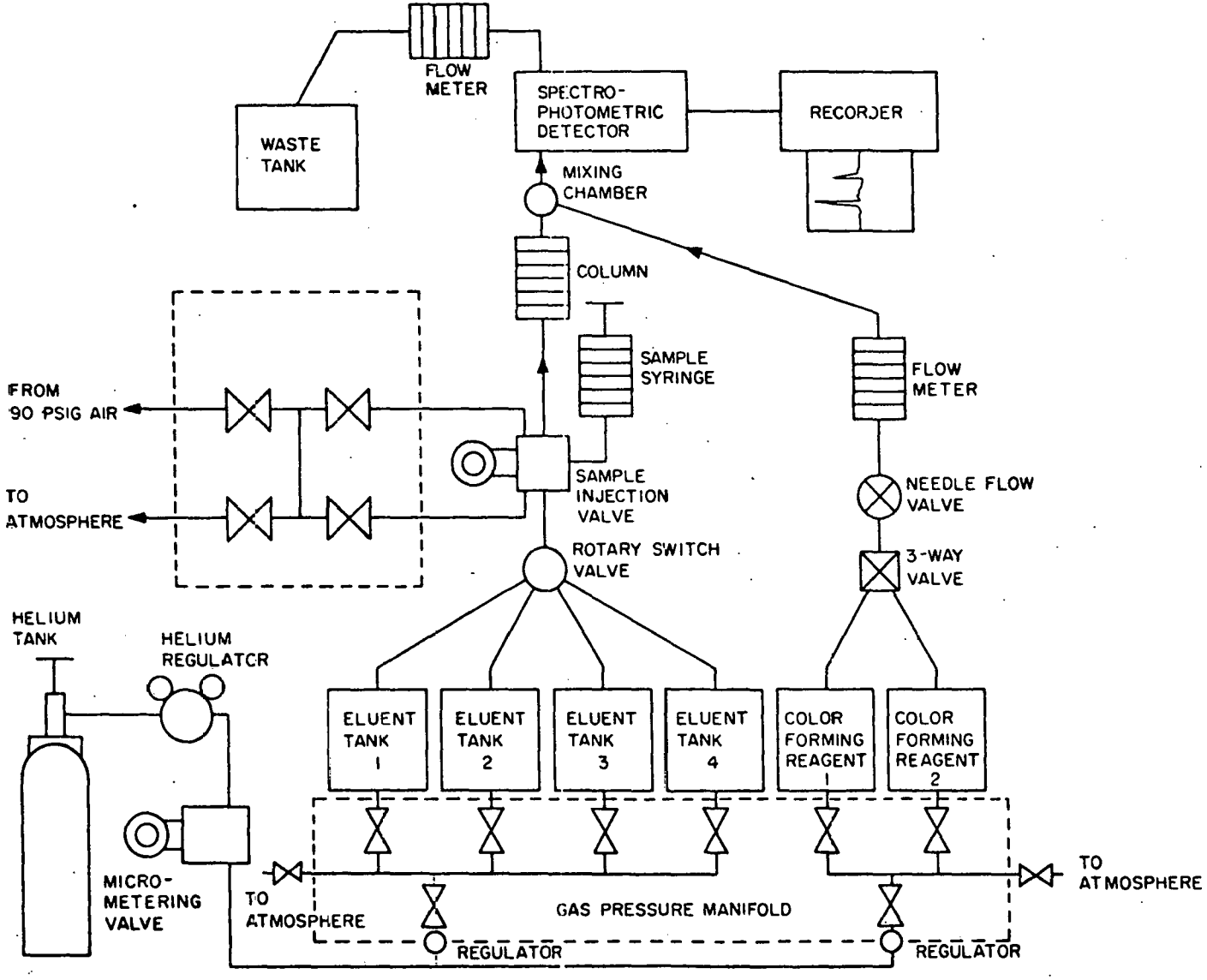
FLOW METER
WASTE TANK
SPECTRO-PHOTOMETRIC DETECTOR
RECORDER
MIXING CHAMBER
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FLOW METER
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TO ATMOSPHERE
SAMPLE INJECTION VALVE
NEEDLE FLOW VALVE
ROTARY SWITCH VALVE
3-WAY VALVE
HELIUM TANK
HELIUM REGULATOR
ELUENT TANK 1
ELUENT TANK 2
ELUENT TANK 3
ELUENT TANK 4
COLOR FORMING REAGENT 1
COLOR FORMING REAGENT 2
MICRO-METERING VALVE
TO ATMOSPHERE
GAS PRESSURE MANIFOLD
TO ATMOSPHERE
REGULATOR
REGULATOR

Miscellaneous equipment

All pH measurements were made with an Orion Model 701 Digital pH Meter.

The resin was ground with a Model 4-E Quaker City Mill and sieved with a Tyler Portable Sieve.

All atomic absorption analyses were performed using a Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

The CHN content of the resin was obtained using a Perkin-Elmer 240 Elemental Analyzer. All infrared spectra were taken using a Beckmann Infrared Spectrophotometer Model -425D.

Reagents

Copper standard solution was prepared by dissolving 6.354 g of copper metal in a minimum amount of nitric acid and diluting to 1.000 l with distilled, deionized water. Molybdenum standard solution was prepared by dissolving 14.394 g of molybdenum trioxide in a minimum amount of ammonium hydroxide and diluting to 1.000 l with distilled, deionized water.

Stock solutions of 0.001 M metal ion were prepared from reagent grade chloride or nitrate salts. All stock metal solutions, with the exception of lead and mercury, were in a 0.1 M tartaric acid - sodium tartrate buffer with pH 5.0. Lead was prepared in a 0.1 M acetic acid-sodium acetate buffer with pH 5.0. The lead solution was prepared in acetate buffer because insoluble salt was

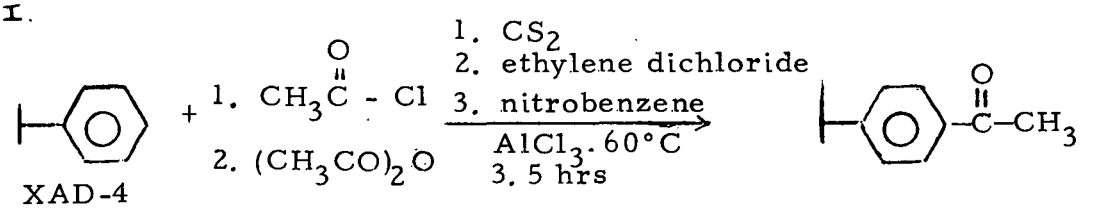
formed when it was prepared in the tartrate buffer.

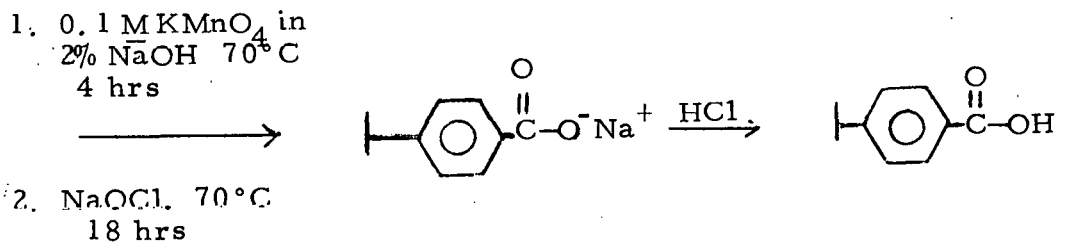
The preparations of the various color-forming reagents are described in detail further in this work. All of the dyes were used as received with no further purifications. Acids, bases, and all other chemicals used to prepare various solutions were reagent grade or better and were used as received.

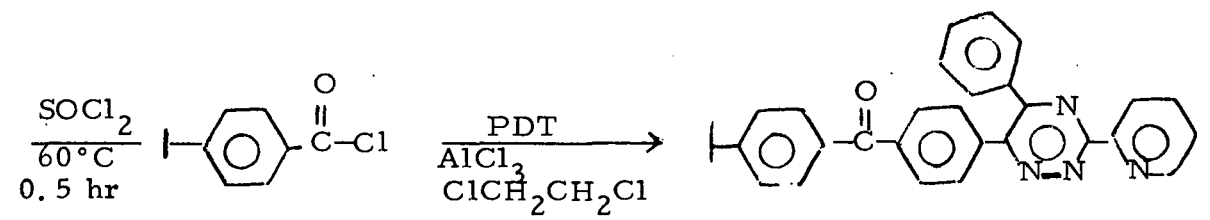
Synthesis

There are mainly two synthetic schemes which were tried to attach the PDT functional group to the XAD-4 polymer matrix.

I.







Direct Acylation
PDT-4

Acetylation

XAD-4, a macroporous styrene-divinylbenzene copolymer, was obtained from the Rohm and Haas Co. The beads were Sohxlet extracted overnight with methanol, dried, ground, and sieved. The 250 - 325 mesh fraction was collected and further washed with concentrated hydrochloric acid, water, methanol, and acetone. Then the beads were dried in an oven at 110°C to ensure complete removal of water and methanol. The reaction vessel consisted of 250-ml three-neck flask equipped with an overhead stirrer, reflux condenser, addition funnel, and nitrogen inlet. Acetyl chloride 3.0 g (or acetic anhydride) was added to 6.7 g of anhydrous aluminum chloride suspended in 25 ml of carbon disulfide. To this mixture XAD-4 2.6 g suspended in 20 ml carbon disulfide was added with stirring. After complete addition the mixture was refluxed for 1.5 hours with stirring. The reaction mixture was hydrolyzed by pouring it with stirring into a methanol-ice-hydrochloric acid mixture (2:1:1). The resin was washed with water, 1 M hydrochloric acid, water, methanol, acetone, and dried. When the ethylenedichloride or nitro-benzene were used as the solvent, the clear solution of acetyl chloride-aluminum chloride complex had to be cooled in ice water to prevent the vigorous reaction between XAD-4 and the complex.

Oxidation of acetylated resin

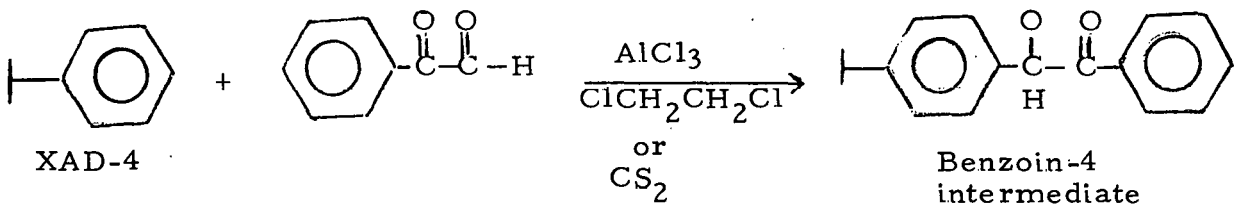
The acetylation product was oxidized with 0.1 M potassium

permanganate in 2% sodium hydroxide at 70°C for a few hours to form the sodium salt of carboxylic acid. This was washed with concentrated ammonium hydroxide, 4 N hydrochloric acid, water, methanol, acetone and dried. Another reagent used for the oxidation of acetylation resin is 5.25% sodium hypochlorite aqueous solution. The methanol was used to moisten the XAD-4 resin. The mixture of resin and hypochlorite was refluxed for 18 hours. After the first 12 hours the old hypochlorite solution was decanted, a fresh sodium hypochlorite was added. After sixteen hours fresh sodium hypochlorite was added again. The sodium salt of carboxylic resin was washed with 4 N hydrochloric acid, water, methanol, acetone and dried.

Friedel - Crafts acylation

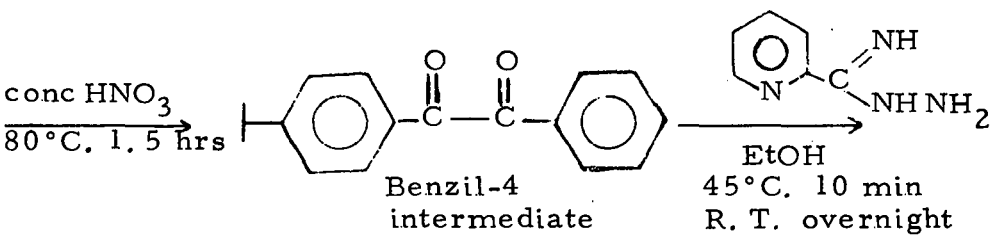
The carboxylic resin was refluxed with thionyl chloride at 60°C for 1/2 hour to form the benzoyl chloride XAD-4 intermediate. The excess thionyl chloride was removed by vacuum distillation. 8 g of PDT was dissolved in 25 ml of ethylene dichloride. This solution was added dropwise into the mixture of aluminum chloride (3 g) and benzoyl chloride XAD-4 (2 g) suspended in 20 ml of ethylene dichloride. After complete addition the mixture was refluxed for 1 hour with stirring. The reaction mixture was hydrolyzed by pouring it into a methanol-ice-hydrochloric acid (2:1:1) mixture. The resin was then washed with water, methanol, acetone and dried.

II.

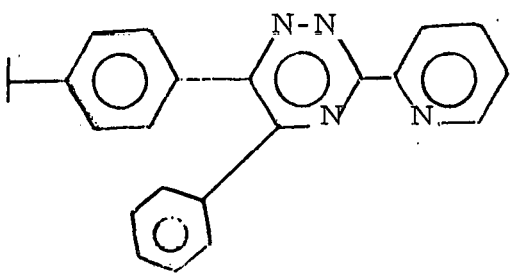


XAD-4

Benzoin-4 intermediate



Benzil-4 intermediate



PDT-4

Anhydrous phenyl gloxal was prepared by the method of Riley and Gray (11) with an added modification by Arnold and Fuson (12). A 200 ml of dioxane, 37 g (1/3 mole) of selenium oxide, and 20 ml of water were placed in a 250 ml three necked round-bottomed flask fitted with a liquid sealed stirrer and a reflux condenser. The mixture was heated to 50-55°C and stirred until the solid went into solution. 40 g (1/3 mole) of acetophenone was added in one lot, and the resulting mixture was refluxed with continued stirring for four hours. The hot solution was decanted from the precipitated selenium and distilled under atmospheric pressure until nearly all the dioxane passed over. At this point 30 ml of xylene was added, and the solution was distilled at atmospheric pressure until the distillate was no longer turbid. The solution was transferred to a Claisen flask, and the distillation completed under diminished pressure. The anhydrous phenyl gloxal (30 g) was collected at 95-97°C/25 mm. The yield was 69-72%. Hydrazidine was prepared by the method of Case (13) with an added modification in the extraction solvent. A mixture of 0.05 mole of 2-cyanopyridine, 9 ml of cthanol, and 15 ml of 95% hydrazine was stirred at room temperature for 2 hours. It was then diluted with an equal volume of water, extracted with methylene chloride, and dried over anhydrous sodium sulfate. After removal of methylene chloride, the residue was crystallized from benzene 7.8 g of hydrazidine was collected which indicated the yield was about 66%.

The reaction vessel consisted of 250 ml three-neck flask equipped with an overhead stirrer, reflux condenser, additional funnel, and nitrogen inlet. Clean XAD-4 (3.3 g) was slowly added to 13.3 g of anhydrous aluminum chloride suspended in 50 ml of ethylene dichloride. To this mixture, 10.8 g of anhydrous phenylgloxal in 20 ml of ethylene dichloride was added dropwise with stirring. After complete addition (0.5 hour) the mixture was refluxed for 4 hours. The temperature was decreased to 60°C and the mixture reacted over night with stirring. The reaction mixture was hydrolyzed by pouring it with stirring over an ice-hydrochloric acid, water, methanol, acetone, and dried (Benzoin-4). The Benzoin-4 was oxidized to Benzil-4 by 15 ml of concentrated nitric acid in 80°C for 1.5 hours with occasional shaking. The product was then washed with water and dried.

2 g of Benzil-4 was reacted with 2.7 g of hydrazidine in 25 ml ethanol at 45°C for 10 minutes to form the PDT-4 resin. The reaction mixture was cooled to room temperature and allowed to stand overnight. Upon completion of the reaction, the solvent was decanted, and the resin was washed several times with ethanol, then 1 M hydrochloric acid, then methanol, then acetone, and dried.

Color-forming Reagent

PAR (4-(2-pyridylazo)-resorcinol) was used for the detection of manganese(II), iron(II), iron(III), cadmium(II), cobalt(II), copper(I), copper(II), nickel(II), zinc(II), and uranium(VI). These ions were all monitored at 495 nm.

The PAR solution was prepared by dissolving 121.1 g of THAM (tris(hydroxylmethyl)amine methane in approximately 750 ml of distilled water. PAR (0.125 g) was then added and the pH was adjusted to 9.0 with concentrated hydrochloric acid. The final solution was diluted to 1.0 l with distilled water.

Arsenazo I was used for the detection of calcium(II), magnesium(II), thorium(IV), uranium(VI), manganese(II), and zinc(II). These were all monitored at 590 nm. The Arsenazo I solution was prepared by the same procedure as that already described earlier for PAR.

Thiolactic acid was used for the detection of molybdenum(VI) and tungsten(VI). These two ions were monitored at 365 nm. The reagent was prepared by adding 57.5 ml of glacial acetic to 900 ml water and adjusting the pH to 4.0 with 20% sodium hydroxide. Then 1.90 g of thiolactic acid is added and the solution diluted to 1.0 l.

4 M hydrochloric acid was used for the detection of iron(III) and copper(II). These were monitored at 235 nm.

Characterization

A small sample of the PDT-4 resin was dried at 105°C for 2 hours and analyzed for nitrogen content. Column capacity was determined for copper(I), Copper(II), Iron(II), Iron(III), and molybdenum(VI). The gravity flow column was packed with 0.3465 g PDT-4. The resin was conditioned by passing 25 ml of pH = 6, 0.1 M acetate through the column at 2 ml/min. After conditioning 0.1 M copper(I), copper(II), iron(II), and iron(III) in the acetate solution were passed through the

resin until saturation was reached. The column was then washed with 50 ml of pH = 6, 0.1 M acetate solution. Copper(I) and copper(II) were eluted with 25 ml of 5 M perchloric acid. Iron(II) and iron(III) were eluted with 0.1 M hydrochloric acid. For molybdenum(VI) the column was conditioned with 0.1 M hydrochloric acid, and molybdenum(VI) was eluted with 25 ml of 0.1 N sodium hydroxide.

Recovery of small amounts of metal ions at a different pH was also tried on the gravity flow column.

Separation Procedures

Calcium(II) or magnesium(II) and zinc(II)

1. Prior to introduction of the sample onto the column, allow pH = 6, 0.1 M acetate to flow through the column at a flow rate of 2 ml/min for five minutes.

2. Inject the sample onto the column.

3. Allow pH = 6, 0.1 N sodium nitrate buffer to flow through the column at a flow rate of 2 ml/min for 5 min to elute calcium(II) and magnesium(II) from the column.

4. Change the eluent to pH = 2 perchloric acid at a flow rate of 2 ml/min for five minutes to elute zinc(II) from the column.

Group separations (cadmium(II), manganese(II), zinc(II), and throium(IV) from cobalt(II), iron(III), nickel(II) and uranium(VI))

1. Prior to introduction of the sample onto the column, allow pH = 2.5 hydrochloric acid or pH = 2 perchloric acid to flow through the column at a flow rate of 2 ml/min for 5 min.

2. Inject the sample onto the column.

3. Allow pH = 2.5 hydrochloric acid or pH = 2 perchloric acid to flow through the column at a flow rate of 2 ml/min for 5 min to elute cadmiun(II), zinc(II), manganese(II) and thorium(IV).

4. Change the eluent to 0.1 M hydrochloric acid at a flow rate of 2 ml/min for 5 min to elute cobalt(II), iron(III), nickel(II) and uranium(VI).

Cobalt(II), iron(III), nickel(II) from copper(II)

1. Prior to introduction of the sample onto the column, allow 0.1 M hydrochloric acid to flow through the column at a flow rate of 2 ml/min for 5 min.

2. Inject the sample onto the column.

3. Allow 0.1 M hydrochloric acid to flow through the column at a rate of 2 ml/min for 5 min to elute cobalt(II), iron(III), nickel(II).

4. Change the eluent to 5 M perchloric acid at a flow rate of 2 ml/min for 10 min to elute copper(II).

Molybdenum(VI)

The following procedure was used to separate molybdenum from noninterfering metal ions.

1. Prior to introduction of the sample onto the column, allow 0.1 M hydrochloric acid to flow through the column at a flow rate of 2 ml/min for 5 min.

2. Inject the sample onto the column.

3. Allow 0.1 M hydrochloric acid to flow through the column at a flow rate of 2 ml/min for 5 min to separate the non-interfering ions from molybdenum.

4. Change the eluent to 0.1 N sodium hydroxide at a flow rate of 1.6 ml/min for five min to elute molybdenum from the column.

Analysis of NBS Standards

Molybdenum

0.1337 g of NBS sample number 134 A, a molybdenum-chromium-tungsten-vanadium steel, was dissolved by gently heating in 4 ml of concentrated hydrofluoric acid and 4 ml of concentrated nitric acid in a platinum dish. After cooling, the solution was transferred to a 250-ml volumetric flask that contained 50 ml of a saturated sodium borate solution and 50 ml of a 0.5 M sodium tartrate solution. The resulting solution was diluted to the mark with distilled water. The final pH of the solution was between two and three.

0.401 g of NBS sample number 160, a chromium-nickel-molybdenum steel, was dissolved by gently heating in 50 ml of 1:6 sulfuric acid and 2 ml of concentrated hydrochloric acid. The solution was cooled, transferred to a 250-ml volumetric flask, and diluted to the mark with distilled water.

These two solutions were then analyzed for molybdenum content by the procedure described in the previous section.

RESULTS AND DISCUSSION

Resin Synthesis and Characterization

XAD-1, 2, and 4 were compared to see which was the best substrate for the chelating resin. The information in Table 1 showed that XAD-4 has the largest porosity, largest surface area, smallest pore diameter and lowest percentage of degradation. Based on these results XAD-4 was chosen as the substrate for the synthesis of the chelating resin. Directly attaching the functional group to the polymer matrix was considered to be the best way to achieve a highly pure chelating resin. But the direct acylation synthetic steps give a very low yield; the nitrogen content of the final product is only 0.47%. The low yield might result from the acetylation step, oxidation step, or the final acylation step. Different methods were tried to improve the final yield (Tables 2, 3). However, even with a high yield intermediate, the last Friedel-Crafts acylation step still gave a poor yield due to large steric hindrance of 3-(2-pyridyl)-5,6-diphenyl-1, 2,4-triazine. Therefore, the resin used for the analytical investigation was prepared by the second synthetic scheme.

Several other synthetic routes on the second synthetic scheme were tried. In an attempt to introduce a triazine functional group into the resin in high yield, the Friedel-Crafts reaction was first tried using α-bromophenyl acetyl chloride. However, the reaction was extremely fast and caused the degradation of the polymer matrix. The procedure

Table 1. Comparison of general properties of three different XAD resins

		XAD-1	XAD-2	XAD-4
Helium porosity (Vol.%)		37	42	51
Surface area: (m^2/gram)		100	300	780
Average pore diameter (Å)		205	90	50
Elemental analysis	C	90.79%	91.05%	90.96%
	H	7.94%	8.22%	7.93%
	Total	98.73%	99.27%	98.89%
After acetylation with Acetyl chloride	C	84.75%	83.94%	84.11%
	H	7.32%	7.51%	7.26%
	O	7.93%	8.55%	8.63%
After acetylation percentage of degradation		high	medium	low
TGS Scan weight loss between 120°C-200°C		larger than 2%	——	less than 1%
carboxylic functional group after oxidation with NaOCl		2.355 meq/g	1.502 meq/g	1.896 meq/g

Table 2. Comparison of different acylation methods[a]

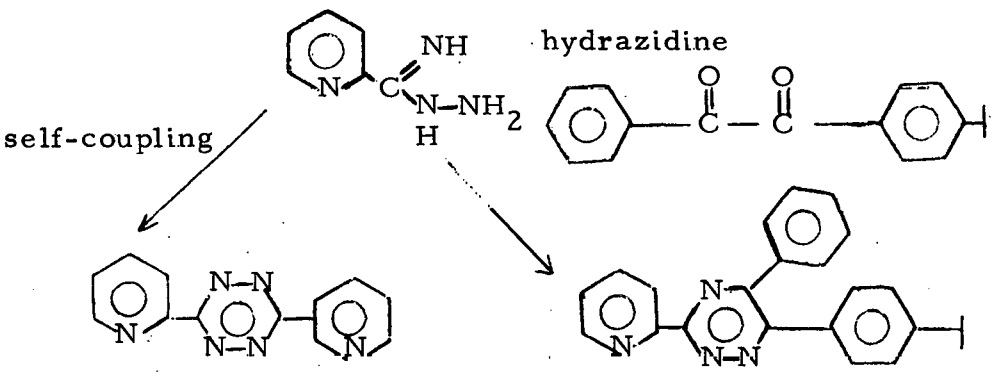
	C	H	O	Yield %
1. CS_2 + $AlCl_3$ + Acetyl chloride	84.90	7.36	7.74	55.84
2. EDC + $AlCl_3$ + Acetyl chloride	84.12	7.26	8.62	62.29
3. Nitrobenzene + $AlCl_3$ + Acetylchloride	83.83	7.22	8.95	64.50

[a]All studies were done on 250-325 mesh XAD-4 resin.

Table 3. Comparison of different oxidation methods

Oxidation method	pH value	Type of resin	Capacity of carboxylic functional group
High temperature 100°C reflux 12 hrs. Aqueous solution of NaOCl	11	XAD-4	1.89 meq/g
$KMnO_4$ (0.1 M) + NaOH(2%) 70°C 4 hrs - twice	12.5	XAD-4	1.95 meq/g
Medium temp. 70°C reflux 12 hrs. Aqueous solution of NaOCl	11	XAD-4	1.46 meq/g
Medium temp. 70°C $KMnO_4$ (0.1 M)+NaOH(2%) Then AaOCl aqueous solution. 12 hrs.	12.5 11	XAD-4	2.94 meq/g
Medium temp. 70°C NaOCl 12 hrs. Then $KMnD_4$ (0.1 M)+NaOH(2%)	11 12.5	XAD-4	2.26 meq/g
NaOCl, 70°C 12 hrs., 4hrs., 2hrs.	11	XAD-4	3.10 meq/g

described in the experimental section gives the maximum yield with least degradation of the polymer matrix. At the last step of this synthesis careful control of water and temperature levels is necessary to avoid self-coupling by the hydrazidine intermediate, which produces 1,4-dipyridyl-dihydrotetrazine. This impurity complexes ferrous iron, resulting in a blue color.



1,4-di-pyridyl-dihydrotetrazine PDT-4

The infrared spectra at each step in the synthesis are shown in Figure 2a-d. Figure 2a is the spectrum of the starting material, XAD-4. Figure 2b and 2c are the spectra of the benzoin-4 and benzil-4 intermediates. Figure 2d is the spectrum of the final produce, 3-(2-pyridyl)-5,6-diphenyl-1-2,4,-triazine XAD-4(PDT-4). N=N and C=N stretch bands are evident at 1600 and 1505 cm^{-1}. The success of the synthesis can also be easily detected by passing 1×10^{-4} M

Figure 2a. Infrared spectrum of XAD-4 resin

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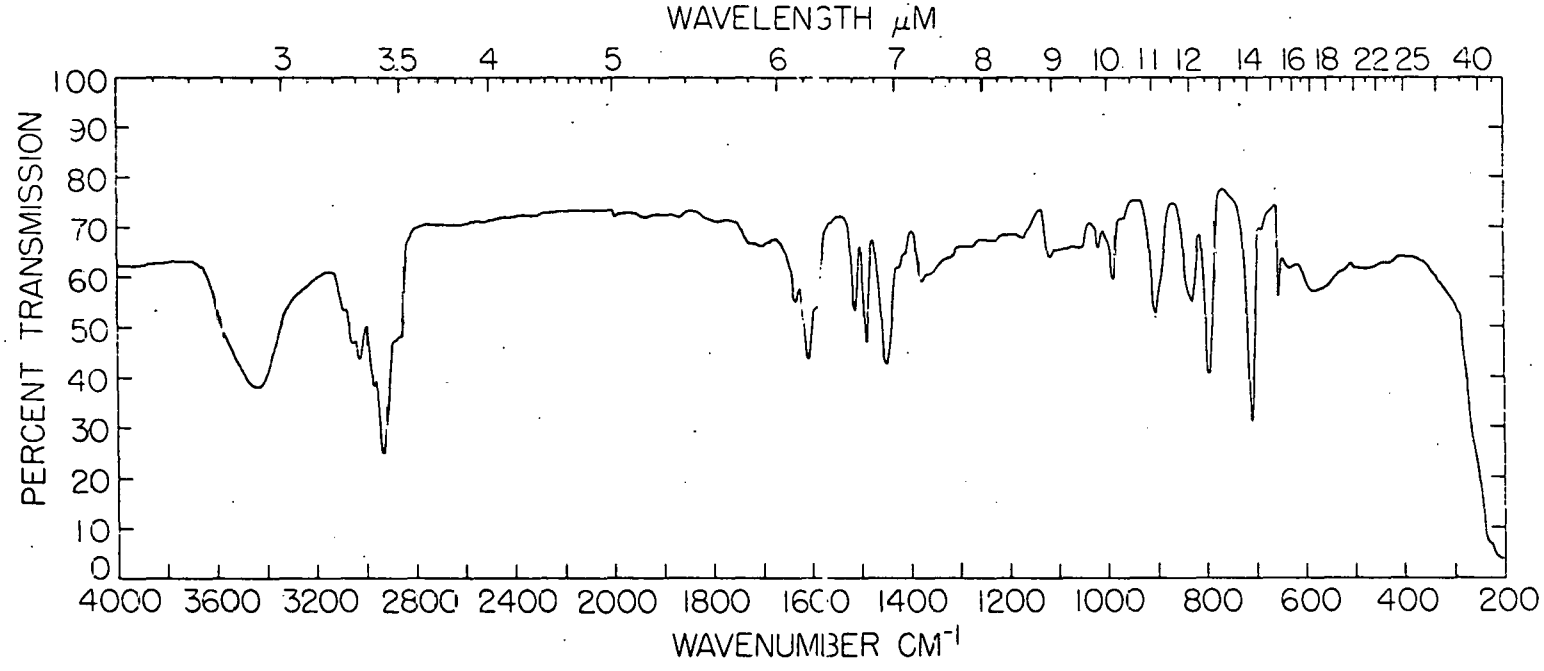
WAVELENGTH μM
3
3.5
4
5
6
7
8
9
10
11
12
14
16
18
22
25
40
PERCENT TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER CM⁻¹

Figure 2b. Infrared spectrum of the Benzoin-4 resin

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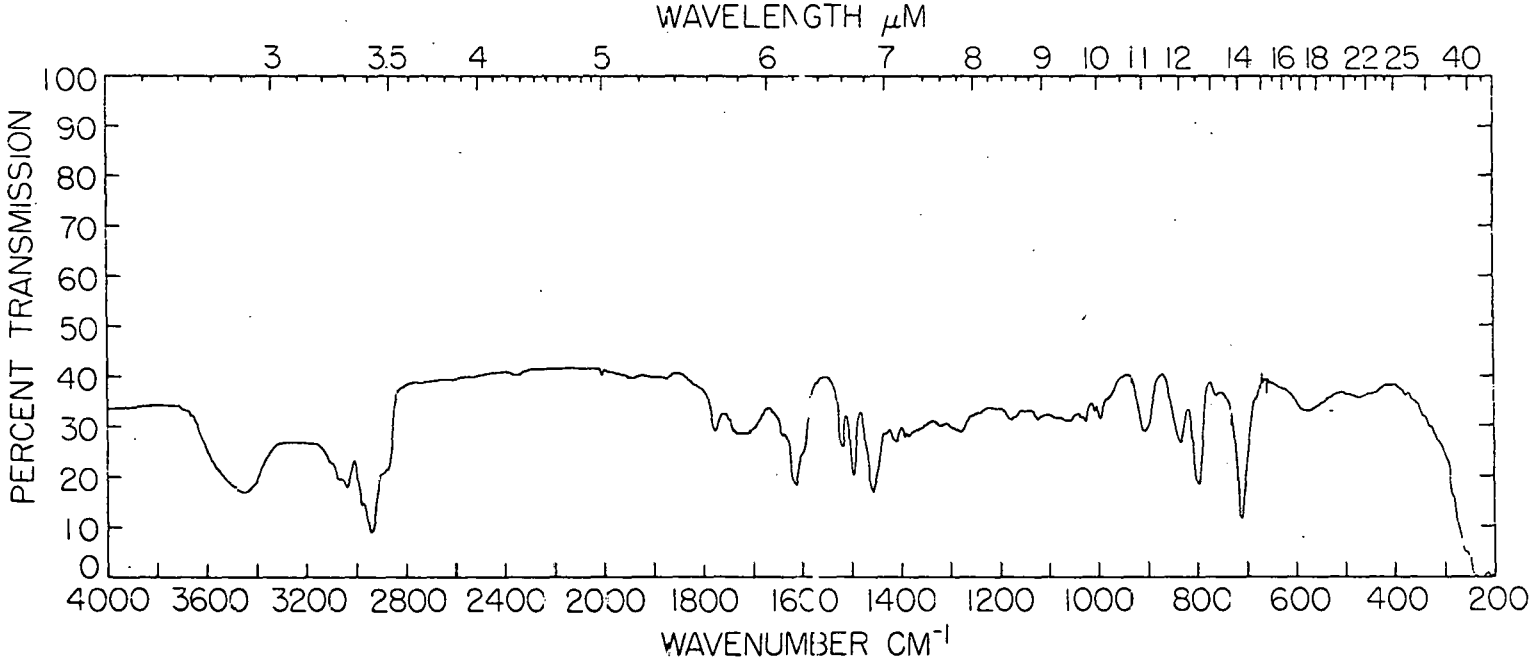
WAVELENGTH μM
3 3.5 4 5 6 7 8 9 10 11 12 14 16 18 22 25 40
PERCENT TRANSMISSION
100 90 80 70 60 50 40 30 20 10 0
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400 200
WAVENUMBER CM⁻¹

Figure 2c. Infrared spectrum of the Bezil-4 intermediate resin

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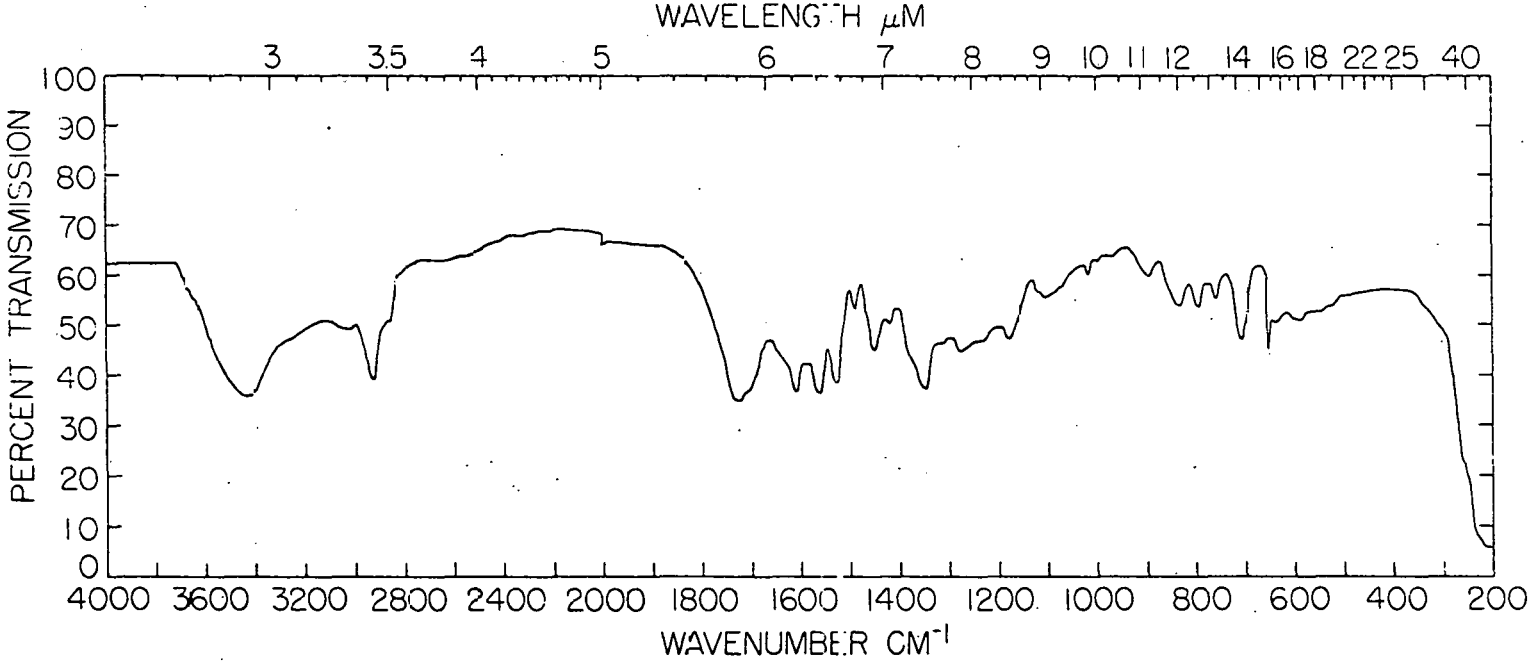
WAVELENGTH μM
3
3.5
4
5
6
7
8
9
10
11
12
14
16
18
22
25
40
PERCENT TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER CM⁻¹

Figure 2d. Infrared spectrum of the PDT-4 resin

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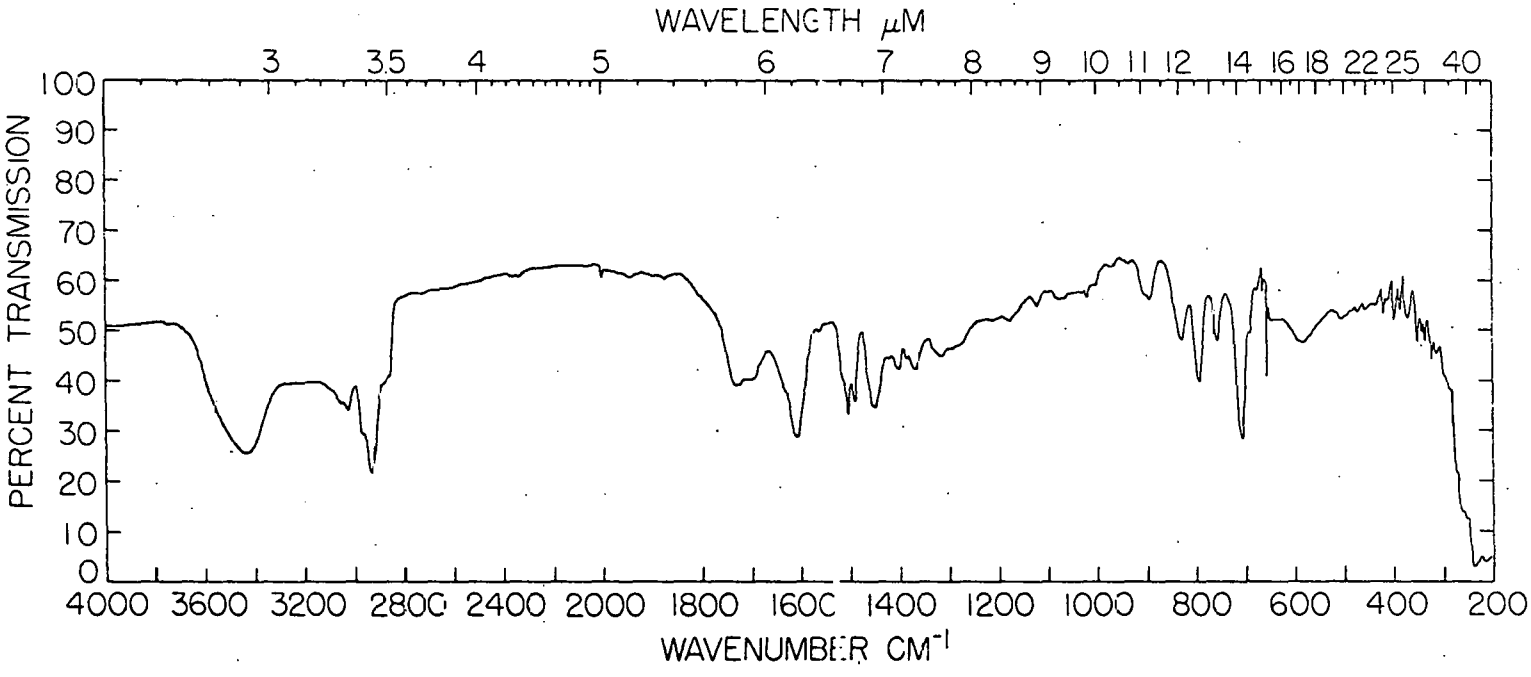
WAVELENGTH μM
3
3.5
4
5
6
7
8
9
10
11
12
14
16
18
22
25
40
PERCENT TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER CM⁻¹

ferrous iron through the column of PDT-4. The resin will immediately show a thin purple Fe(II)-(PDT-4) complex layer on the top of the column.

Elemental analysis gave an average nitrogen content of 7.48%. Assuming that all of the nitrogen is from the triazine, the resin should contain 1.33 meq of the desired functional group per gram of resin.

Column capacities of some metal ions are shown in Table 4. The lower metal ion capacities may result from the orientation of the bulky functional group which ordinarily restricts geometries of chelation, preventing formation of fully coordinated species and discouraging strong retention of metal ions.

Chromatographic Separations

The retention behavior of the following metal ions was surveyed using a column of PDT-4 resin with simple gravity flow. The metal ions studied are Ca(II), Mg(II), Cd(II), Mn(II), Zn(II), Pb(II), Co(II), Fe(III), Ni(II), Cu(II), MoO_2(II), UO_2(II), VO(II), Th(IV).

All ions studied were retained at pH = 6, 0.1 M acetate buffer. Ca(II) and Mg(II) were eluted at pH = 6, 0.1 N sodium nitrate. Most other ions were eluted by pH = 2, perchloric acid, but Co(II), Fe(III), Ni(II), Cu(II), UO(II), VO(II), MoO_2(II) were still retained. Hydrochloric acid was used to elute Co(II), Fe(III), VO(II), UO_2(II) and NI(II). Sodium hydroxide 0.1 N was used to elute MoO_2(II). In 0.1 N sodium hydroxide Cu(II) was still retained by the column but can be eluted with 5 M perchloric acid.

Table 4. Capacity of the PDT-4 resin*

ion	column capacity* (meq/g)
Fe(II)	0.146
Fe(III)	0.123
Cu(II)	0.188
Cu(II)	0.170
Mo(VI)	0.090

*The capacity of PDT-4 resin analyzed by nitrogen content is 1.33 meq/g.

Most of the above metal ions were retained by the benzoin-4 and benzil-4 intermediates at pH = 6, 0.1 M acetate, but eluted completely at higher pH (pH > 3). Even with very low capacity, the direct acylation triazine resin showed the similar properties with PDT-4. The recoveries of some metal ions are shown in Table 5.

Calcium(II) and Magnesium(II) Sorption

The uptake of alkaline earth ions in pH = 6, 0.1 M acetate was surprising. These ions were not expected to complex with the triazine group, but would be taken up by carboxyl , benzoin and benzil functional groups which were introduced by the phenyl gloxal acylation and the oxidation with concentrated nitric acid. The separation of Mg(II) from Zn(II) is shown in Figure 3. The interference study shown on Table 6 showed that Mg(II) and Ca(II) can be determined in the presence of Cd(II), Mn(II), Zn(II), Co(II), Fe(III), Ni(II), Cr(III), Th(IV), UO_2(II), W(VI), VO(II), and MoO_2(II).

Group Separation

Based on the work by Lundgren and Schilt (9) on a PDT coated XAD-2, it was expected that the present resin PDT-4 would strongly retain Cu(II), Fe(III), Ni(II), UO_2(II), and Co(II) from pH 2.0 perchloric acid or pH 2.5 hydrochloric acid. Th(IV), Cd(II), Zn(II), and Mn(II) would not be retained. Figures 4 and 5 show the group separation of these ions.

Table 5. Recovery of metal ions in PDT-4 resin using gravity flow

ion	sorption	elution/recovery		elution/recovery	
Ca^{+2}	pH=6, 0.1 M acetate	pH=6, 0.1 N $NaNO_3$	/100.0%		
Mg^{+2}	"	"	/100.%		
Cd^{+2}	"	pH=2, $HClO_4$	/99.04%	0.1 M HCl	/100.%
Zn^{+2}	"	"	/99.73%	"	/100.%
Mn^{+2}	"	"	/100.3%	"	/100%
Pb^{+2}	"	"	/96.7%	"	/100%
Th^{+4}	"	"	/98.7%	"	/100%
VO^{+2}	"	"	/0%	"	/100%
UO_2^{+2}	"	"	/3.6%	"	/100%
CO^{+2}	"	"	/3.2%	"	/100%
Fe^{+2}	"	"	/64%	"	/97.4%
Fe^{+3}	"	"	/2.1%	"	/96.9%
Ni^{+2}	"	"	/0%	"	/99.1%
Cu^{+2}	0.1 M HCl	5 M $HClO_4$	/97.2%		
Mo^{+6}	0.1 M HCl	0.1 N NaOH	/100.0%		

Figure 3. Separation of Zinc(II) from Magnesium(II)

Column: 75 mm x 2mm
Detection. Arsenazo-1 color forming reagent, 1.2 ml/min; 590 nm; 1.28 absorbance unit full scale
Sample: 214 µl

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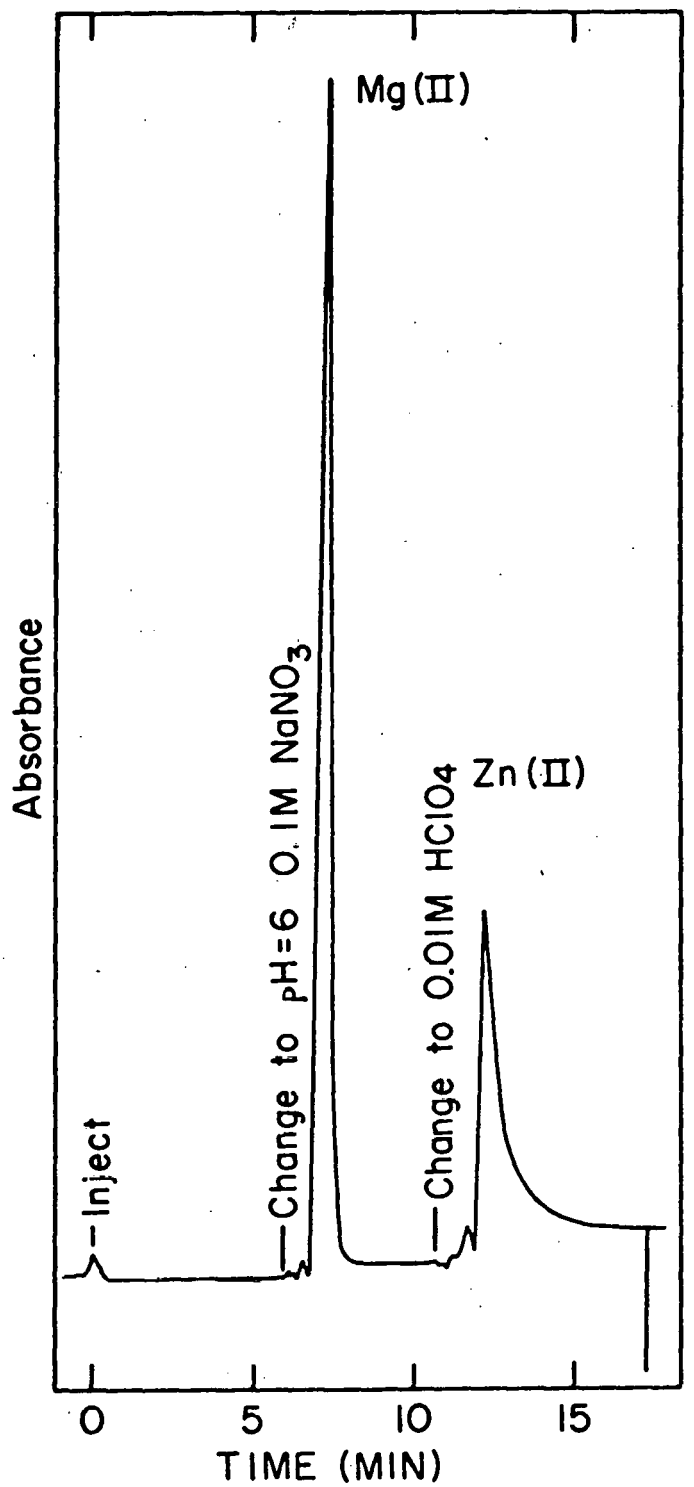
Mg(II)
Absorbance
Change to pH=6 0.1M NaNO3
Zn(II)
Change to 0.01M HClO4
Inject
0
5
10
15
TIME (MIN)

Table 6. Interference study of foreign ions on the determination of calcium(II), magnesium(II) and molybdenum(VI). (each 0.0005 M)

ion	conc. (M)	Ca, Mg det'n	Mo det'n
Acetate	0.10	—	100.0
Cadmium(II)	0.001	101.9	97.2
Calcium(II)	0.001	—	98.4
Chloride	0.01	100.0	100.0
Chromium(III)	0.001	100.0	97.2
Citrate	0.001	—	96.5
Cobalt(II)	0.001	100.0	96.5
Copper(II)	0.001	100.0	97.9
Fluoride	0.01	—	100.0
Iron(II)	0.001	100.0	98.96[a]
Iron(III	0.001	100.0	100.0[a]
Magnesium(II)	0.001	—	102.5
Manganese(II)	0.001	102.5	97.0
Molybdenum(VI)	0.001	100.0	—
Nickel(II)	0.001	100.0	98.22
Nitrate	0.1	—	100.0
Oxalate	0.1	—	97.9
Perchlorate	0.1	100.0	100.0
Phosphate	0.1	—	101.5
Sulfate	0.1	—	96.67

Table 6 (Cont'd)

ion	conc. (M)	ca, Mg det'n	Mo det'n
Tartrate	0.1	—	98.22
Thorium(IV)	0.001	100.0	102.2
Tungsten(VI)	0.0005	100.0	102.09
Uranium(VI)	0.0005	100.0	98.95
Vanadium(IV)	0.0005	100.0	100.0
Zinc(II)	0.001	102.4	100.0

[a] If iron(II) and iron(III) are in pH = 8.5 basic standard solution of molybdenum, then the high results happen (110% recovery).

Figure 4. Separation of Co(II), Ni(II) and Fe(III) from Mn(II), Zn(II) and Cd(II)

Column: 75 mm x 2 mm
Detection: PAR color-forming reagent, 1.2 ml/min; 495 nm; 1.28 absorbance units full scale
Sample: 214 µl

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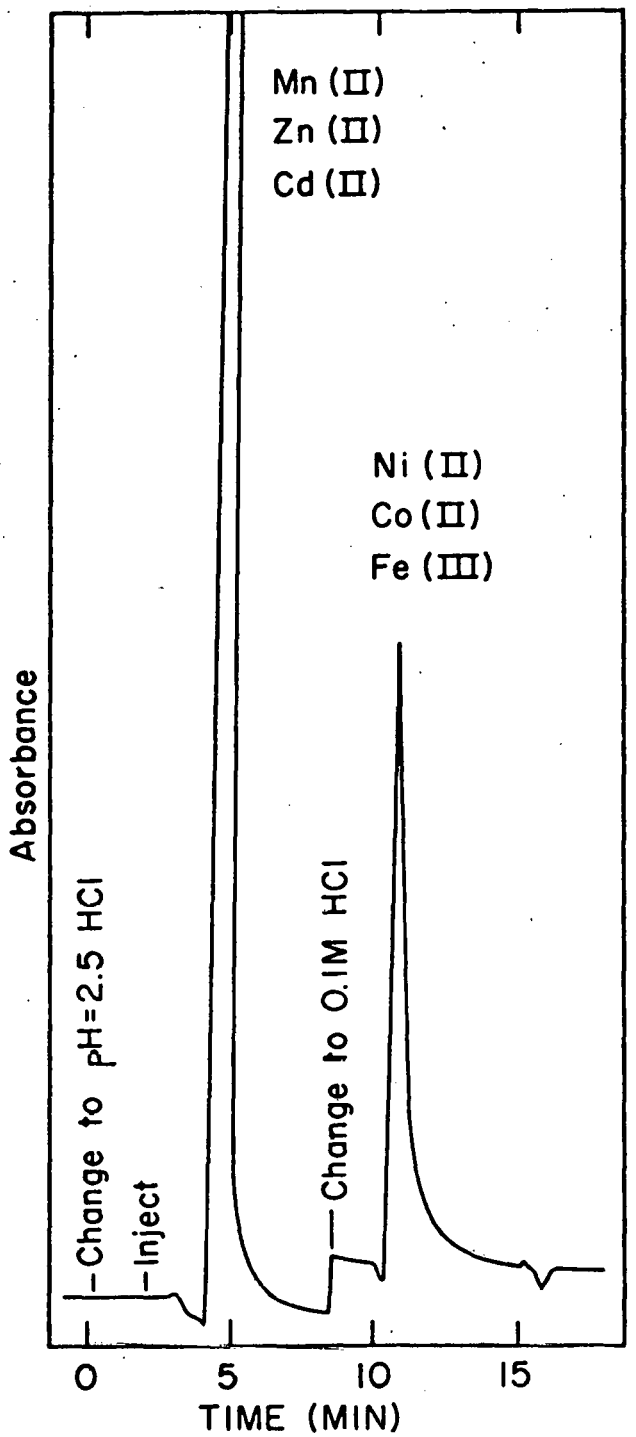
Mn (II)
Zn (II)
Cd (II)
Ni (II)
Co (II)
Fe (III)
Absorbance
Change to pH=2.5 HCl
Inject
Change to 0.1M HCl
0
5
10
15
TIME (MIN)

Figure 5. Separation of Uranium(VI) from Thorium(IV)

Column: 75 mm x 2 mm
Detection: Arsenazo-I color-forming reagent, 1.2 ml/min
590 nm; 1.28 absorbance full scale
Sample: 214 µl

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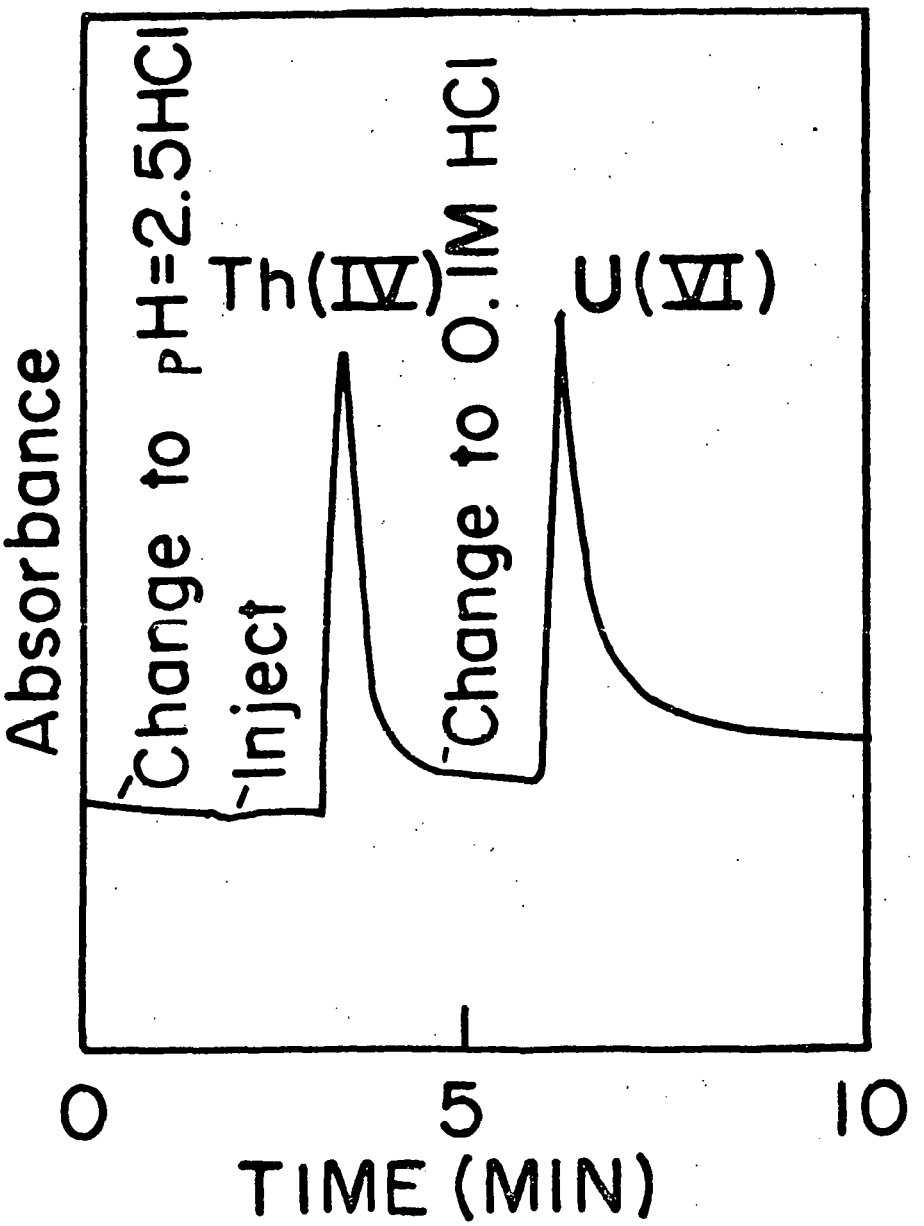
Absorbance
Change to pH=2.5HCl
Inject
Th(IV)
Change to 0.1M HCl
U(VI)
0
5
10
TIME (MIN)

Copper(II) Sorption

It is surprising that copper(II) was sorbed onto a resin column from an aqueous solution of 0.1 M hydrochloric acid. Based on the discussion by Schilt (14), it was expected that Cu(II) would form a complex with the triazine functional group of PDT-4 at pH 1-6. Interestingly, hydrogen ions appear to behave much like metal ions by forming complex species with the ferroin group of 2, 2´-bipyridine and 1, 10-phenanthroline at a lower pH. The pK_a value reported for $H(bipy)^+$ is 4.35 (potentiometric, μ = 0.025, 25°C)(15), pK_a reported for $H_2(bipy)^{++}$ and $H_2(phen)^{++}$ are -0.2 and -1.6, respectively (16, 17). The unpublished work done by K. Schuett and A. A. Schilt showed that 3-(2-pyridyl)-5, 6-diphenyl-1, 2, 4-triazine (PDT monomer) exists predominantly in its protonated form in 1 to 4 M strong acid. The formation constant of monoprotonated PDT monomer is equal to 9.0×10^{-2} at 25°C.

The PDT-4 resin was therefore expected to be the forms of $H(PDT\text{-}4)^+$ and $H_2(PDT\text{-}4)^{++}$ and to show both chelation and anion-exchange properties under low pH conditions.

In 4-5 M hydrochloric acid, Cu(II) was expected to form an anion chloride complex and hence be retained by the PDT-4. Using the anion-exchange distribution coefficients of the elements as a function of HCl concentration (18), Pd(II), Au(III) and Pt(IV) were predicted to show similar properties to Cu(II). This was confirmed by the liquid chromatography experiments. The Cu(II) could be stripped with 5 M perchloric

acid. The separation of Cu(II) from Co(II), Fe(III), and Ni(II) was shown in Figure 6. However, this separation does not lend itself well to quantitative automatic detection because of the large tailing peak.

Molybdenum(VI) Sorption

Previous studies by Mitchell (19), Allen (20) and Walton (21) have shown that ferroin functional groups will form complexes with molybdenum(III), (IV) and (V). The predominant species of molybdenum ion in the solution of different pH values are MoO_2^{+2}, MoO_4^{-2}.

$$4H^+ + MoO_4^{=} \rightleftharpoons MoO_2^{++} + 2H_2O$$

Therefore the uptake of molybdenum(VI) by the PDT-4 resin can occur either by chelation or by anion exchange. Because of these characteristics of PDT-4, the eluent used throughout this work to load the column with molybdenum was 0.1 M hydrochloric acid. The 0.1 N sulfuric acid will give lower recovery of molybdenum.

The molybdenum can be stripped off the column in a tight band by switching to 0.1 N sodium hydroxide. An interference study showed that in slightly basic solutions iron will give a positive interference. This is because of some hydroxide anion complex formation (Table 6). With 0.1 N hydrochloric acid as eluent molybdenum(VI) was successfully separated from 25 metal ions and anions (Table 6). No foreign ions investigated interfered between pH 1 and 3. Since copper(II) is not eluted with 0.1 N sodium hydroxide, molybdenum can also be separated from copper. The calibration curve of peak height vs

Figure 6. Separation of copper(II) from Cobalt(II), Nickel(II) and Iron(III)

Column: 75 mm x 2 mm
Detection: 6 M HCl, 1.4 ml/min 235 nm; 1.28 units full scale
Sample: 214 µl

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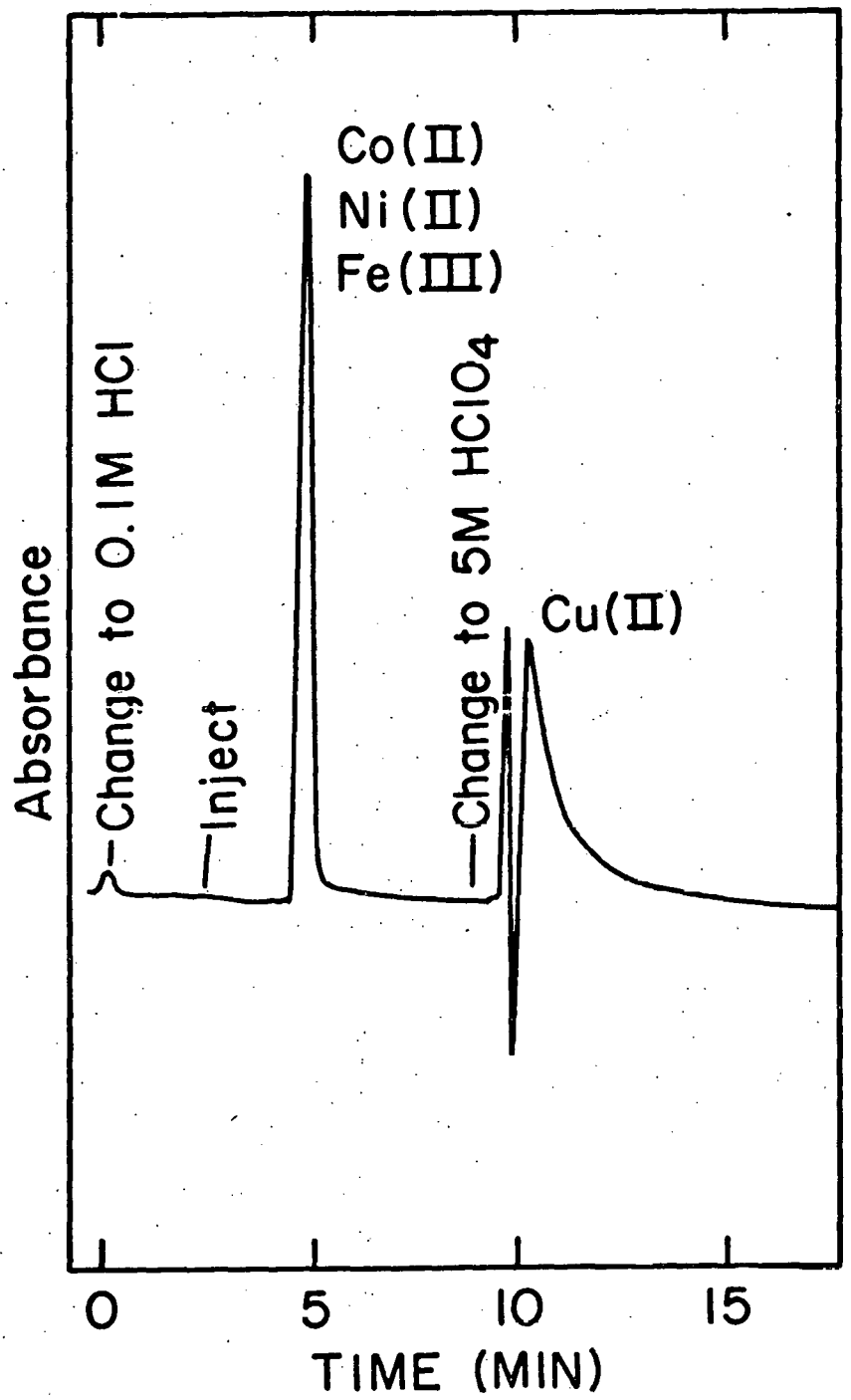
Absorbance
Change to 0.1M HCl
Inject
Co(II)
Ni(II)
Fe(III)
Change to 5M HClO4
Cu(II)
0
5
10
15
TIME (MIN)

amount of molybdenum is linear using thiolactic acid as a dye. (Figure 7, 8). Separation of molybdenum from non-interfering ions is shown in Figure 9. All the molybdenum solutions used for the calibration and interference studies had to be freshly prepared.

Analysis of NBS Standards

Results of three independent analyses for each of two NBS standard samples are given in Table 7. These results are in good agreement with the certified value.

Figure 7. Calibration peak of Molybdenum(VI) using high speed liquid chromatography.

Column: 75 mm x 2 mm
Detection: Thiolactic acid color-forming reagent, 1.5 ml/min; 365 nm; 1.28 units full scale
Sample: 214 µl

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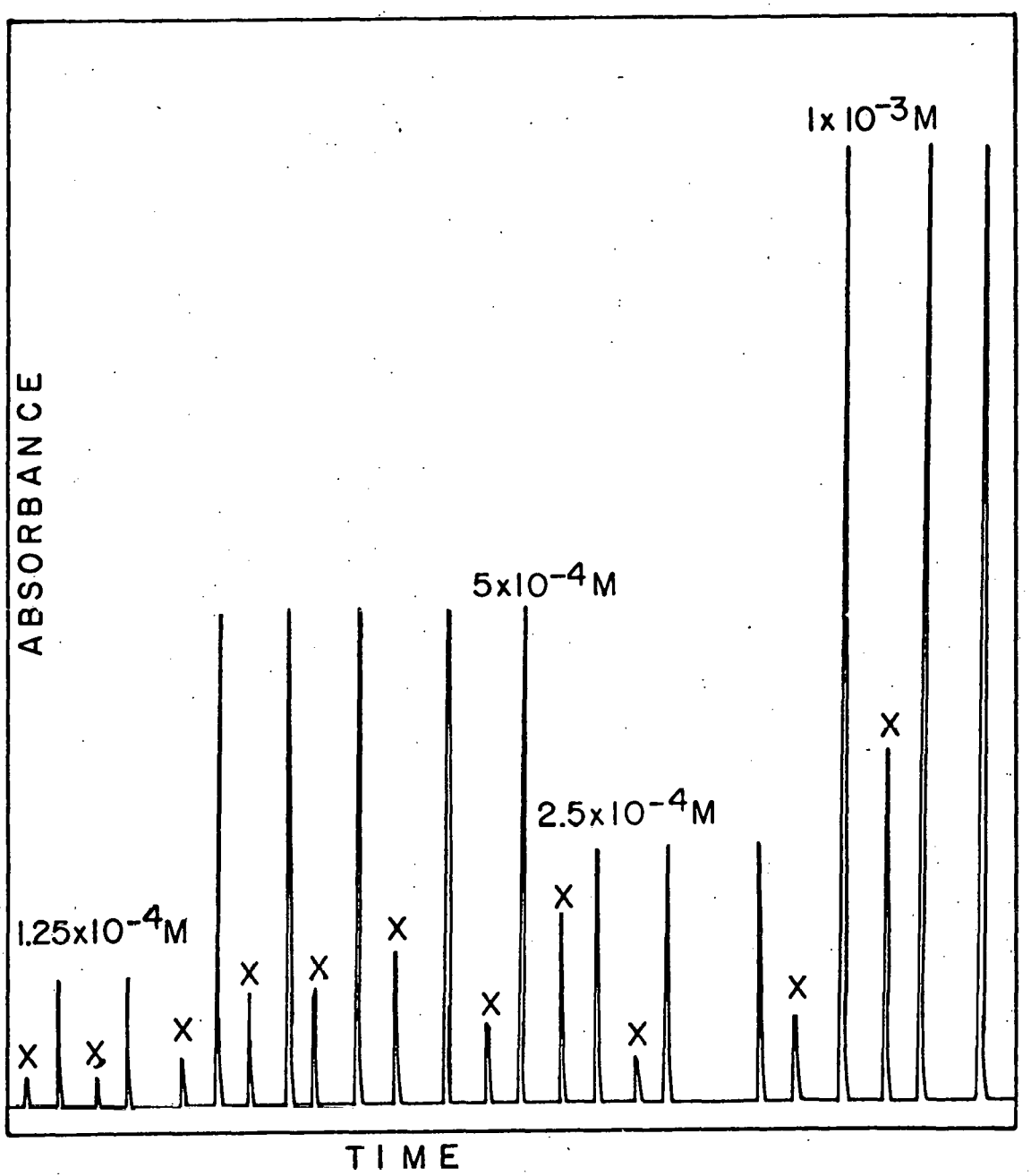
1x10⁻³M
5x10⁻⁴M
2.5x10⁻⁴M
1.25x10⁻⁴M
ABSORBANCE
TIME

Figure 8. Calibration curve of Molybdenum(VI) from 2.56 μg to 20 μg

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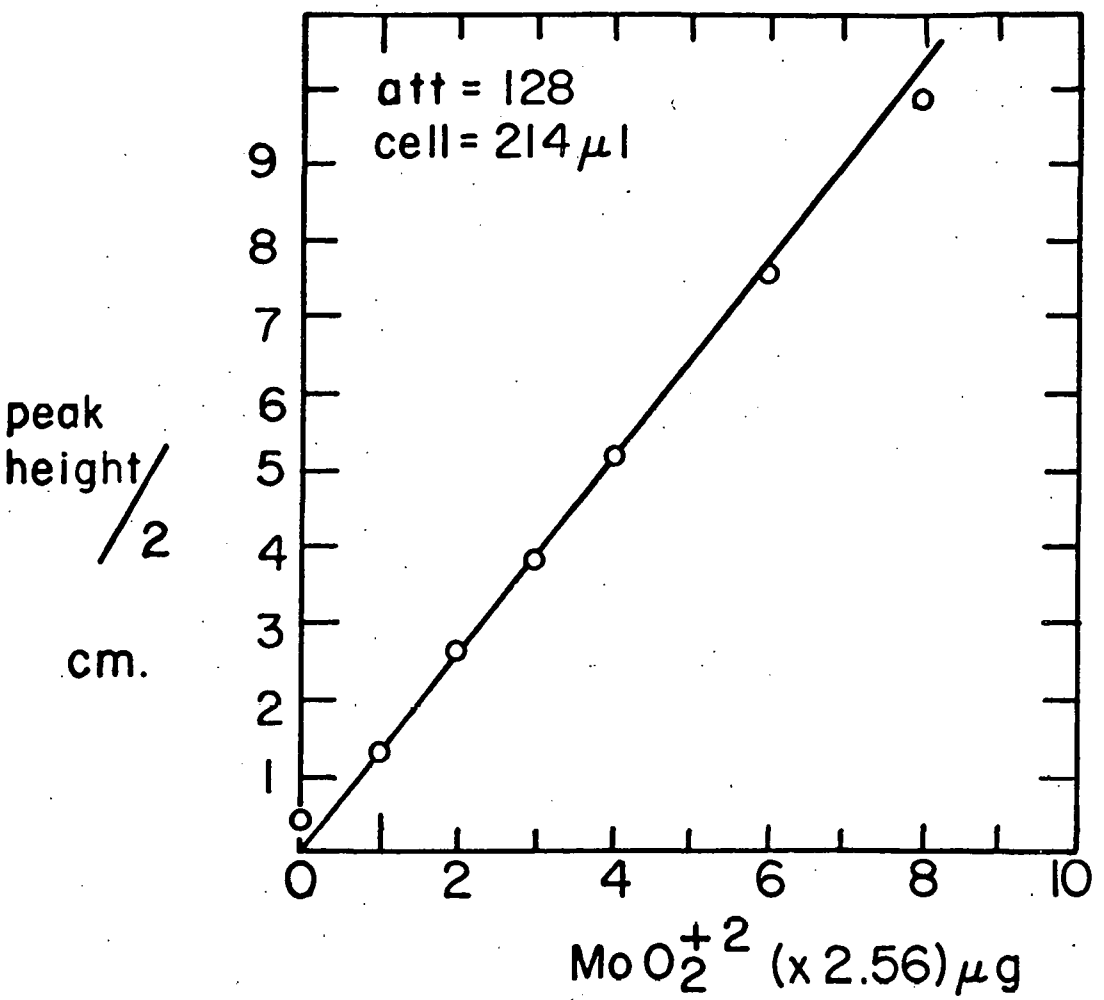
att = 128
cell = 214 μl
peak height / 2
cm.
0
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10
MoO_2^{+2} (x 2.56) μg

Figure 9. Separation of Molybdenum(VI) from Cobalt(II), Chromium(III), Nickel(II), Manganese(II), Tungsten(VI), and Vanadium(IV)

Column: 75 mm x 2 mm
Detection: Thiolactic acid color-forming reagent, 1.5 ml/min; 365 nm; 1.28 units full scale
Sample: 214 µl

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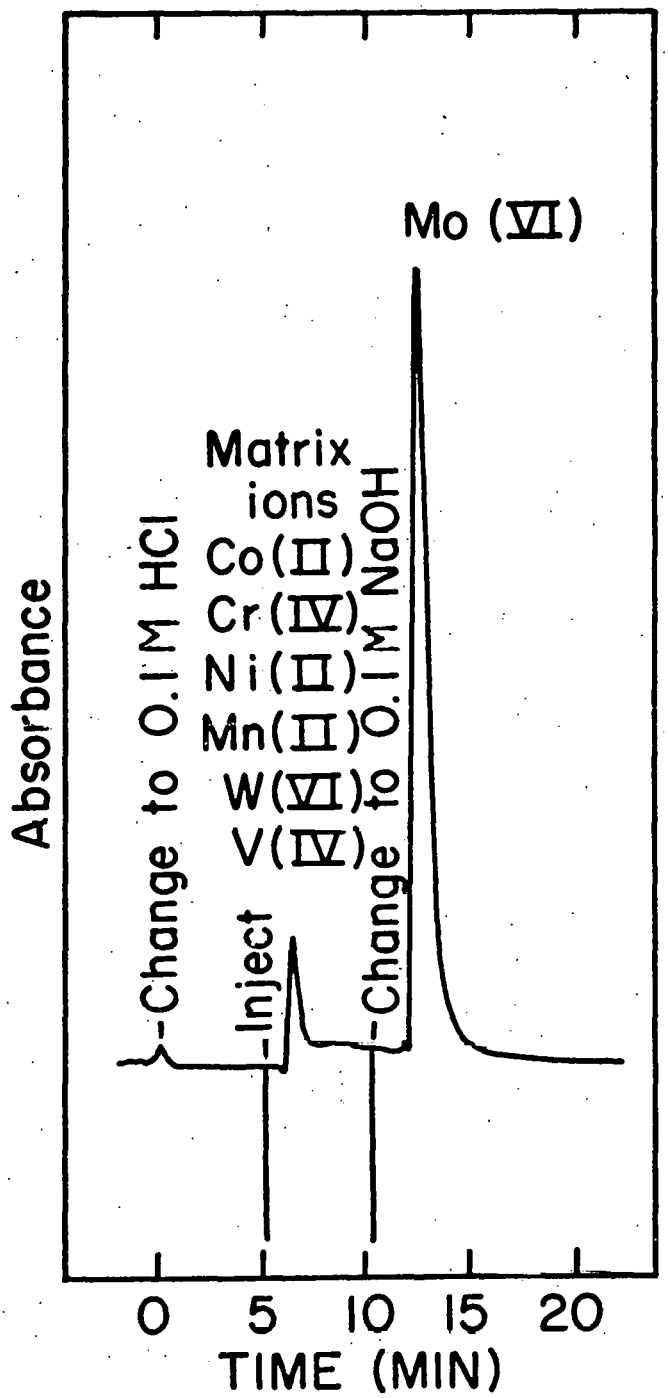
Mo (VI)
Matrix
ions
Co(II)
Cr(IV)
Ni(II)
Mn(II)
W(VI)
V(IV)
Change to 0.1 M HCl
Inject
Change to 0.1 M NaOH
Absorbance
0
5
10
15
20
TIME (MIN)

Table 7. Analysis of NBS standards.

sample number	elements present	%	found%	standard deviation
134A	Mo	8.35	8.33	0.195
	W	2.00		
	V	1.25		
	Cr	3.67		
	P, S, Ni	0.1		
	Mn, Si, Cu, C	1		
160	Cr	19.12		
	Ni	8.91		
	Mo	2.95	2.93	0.154
	Si	1.13		
	Mn	1		
	C, P, S, Cu	0.1		
	V, Co, N	0.1		

CONCLUSIONS

A chelating ion-exchange resin incorporating a 3-(2-pyridyl), 5, 6-diphenyl-1, 2, 4, -triazine (PDT) functional group onto an XAD-4 polymer matrix has been synthesized. This resin has been used for the group separations: Group I B from group VIII metal ions, and group VIII from group II B, VI B, VII B metal ions. Calcium(II), magnesium(II), and molybdenum(VI) were also determined quantitatively by this resin using high speed liquid chromatography.

Due to the bulky molecule of PDT this chemically bonded resin had shown a monolayer, Langmuir type of chromatogram in high speed liquid chromatography. The chelation and concomitant adsorption of metal ions in PDT-4 resin is sufficiently rapid to allow very rapid flow rates of 1-20 ml/min and column lengths of 20-100cm.

Applications of this PDT-4 resin will include the determination of hardness in tap water, purification of reagents, concentration of trace metal ions from dilute solutions, and group separation of metal ions prior to analysis.

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