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THE STUDY OF HYDROXYOXIMES AND
HYDROXAMIC ACIDS SUPPORTED ON
MACROPOROUS RESINS AND THEIR USE IN
THE RAPID SEPARATION OF METALS

by

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LIST OF ABBREVIATIONS

EDTA	ethylenediaminetetra-acetic acid
i.r.	infra-red
n.m.r.	nuclear magnetic resonance
TLC	thin-layer chromatography
u.v.	ultra-violet

SUMMARY

The macroporous Amberlite XAD resins were coated with LIX-64N and examined for the rate of uptake of copper. XAD-7 was by far the best support and gave a satisfactory rate of uptake up to loadings of 60% (w/w). The specific surface area of XAD-7 was measured by the adsorption of methylene blue from aqueous solution. The area of the wetted resin was five times less than that of the dry resin.

LIX-65N was purified and the anti isomer characterised using spectroscopic techniques. The rate of uptake of copper was not improved by use of purified LIX-65N or by addition of LIX-63. XAD-7 coated with LIX-65N was used in columns. Elution curves for copper showed negligible tailing, and rapid separations of copper from iron (III), nickel, cobalt and magnesium by selective absorption were achieved. Copper was concentrated from very dilute solution at a flow rate of 50 ml min^{-1} , and a 99% recovery was obtained. The method was applied to the rapid determination of copper in brass and bronze.

A series of long-chain hydroxamic acids were synthesised and tested for suitability as stationary phase on XAD-7. Oleohydroxamic acid and naphthenohydroxamic acid were the most promising. The rate of uptake of copper was reduced by the use of nonylphenol or amyl alcohol as a diluent. The capacities for copper of the hydroxamic acids were less

when supported on XAD-7 than when used as liquid ion-exchangers. The distribution coefficients of cobalt, nickel, zinc, lead, vanadium, uranium, iron (III) and copper were measured as a function of pH. XAD-7 coated with oleohydroxamic acid was used in columns for the rapid separation of iron (III) from copper and of copper from nickel, cobalt, lead and zinc. Copper was concentrated from very dilute solution at a flow rate of 45 ml min^{-1} and a 100,8% recovery was obtained. Copper was successfully separated from nickel by selective elution. The elution curves obtained show negligible tailing. The resin loaded with oleohydroxamic acid lost capacity due to chemical instability. Naphthenohydroxamic acid supported on XAD-7 was not suitable for use in columns, because it was physically unstable.

1. GENERAL INTRODUCTION

1.1 HISTORICAL BACKGROUND TO EXTRACTION CHROMATOGRAPHY

Extraction chromatography is a particular form of liquid-liquid column chromatography used for analytical separations. In this technique a column is packed with a solid support which is impregnated with an organic stationary phase. An aqueous sample is added to the column and various solutes are distributed between organic and aqueous phases. The column is then eluted with an aqueous solution so that the inorganic solutes move down the column at different rates and are separated. Extraction chromatography couples the favourable selectivity features of the organic compounds used in liquid-liquid extraction, with the multistage character of a chromatographic process.¹

The idea of impregnating solid substrates with liquid reagents to confer on the solid the properties of the reagent is not new. The technique was developed by Tswett at the turn of the century.² He used carbons and diatomaceous earths as substrates. Since these lacked physical strength, such impregnates were displaced by the advent of ion-exchange resins. It is only fairly recently that interest in impregnation of solid substrates has re-awakened. Braun and Ghersini edited a book in 1975¹ which contains an excellent review of the subject and covers the wide variety of supports and stationary phases which have been used. An earlier review by Cerrai and

Ghersini appeared in 1970.³

The first application of chelating reagents in extraction chromatography was reported in 1952 from the Chemical Research Laboratory, Teddington.⁴ In 1953, Carrit described an extraction column with dithizone for the separation and concentration of traces of metals from natural waters⁵. A concise account of the use of chelating agents as stationary phases has been given by Sebesta⁴.

The impregnation of resins was first attempted using microreticular resins. Relatively little work has been done with macroporous resins as supports. Several authors have used them, but the great practical advantages of resins of high surface area ($100 - 300 \text{ m}^2 \text{ g}^{-1}$) for both chromatographic separations and process applications were first pointed out by Warshawsky² who used Amberlite XAD resins.

1.2 ADVANTAGES AND DISADVANTAGES OF EXTRACTION CHROMATOGRAPHY

The hydrometallurgical development of solvent extraction processes has made great strides in recent years, but the process becomes uneconomic in the handling of large volumes of solutions with low metal content⁶. Solvent extraction processes are known to suffer the disadvantage that both the reagent and the diluent are lost over a period of time - owing to solubility or entrainment of the organics in the aqueous phase. Such losses can make a major contribution to the operational costs of the process and may cause an

environmental problem by polluting the effluent⁷. Solvent extraction, of course, requires mixing of the phases to provide sufficient interfacial area for a satisfactory rate of extraction, followed by the gravity settling of the mixed phases. There is, therefore, an innate attractiveness in creating a solid phase in small bead form, which has properties identical to that of the liquid organic phase in solvent extraction, but without the mixing and settling requirements and loss of solvent through entrainment⁸. However, conventional ion-exchange resins have only limited selectivity⁹, so it is necessary to incorporate selective chelating groups into the resin. The chelating ion-exchange resins date from 1952 when Gregor et al published a paper⁹ on "the first of a new class of ion-exchange resin in which the chelate groups are substituted in a highly cross-linked and therefore insoluble hydrocarbon matrix". The use of chelating resins is limited by difficulties in their preparation and high cost². It is therefore not surprising that the idea of absorbing an organic chelating reagent onto a solid polymeric support has attracted growing attention in recent years. However, despite their attractiveness, chelating resins and extraction chromatography have not yet been applied to hydrometallurgy, but have only been used for analytical separations. The difficulties that had to be overcome in the initial stages of extraction chromatography, were those of providing suitable supports onto which the reagents would bind sufficiently without massive leakage, and also of providing sufficient hydrophilic character to the reagent so that the

rates of uptake of ions would be acceptable. These two difficulties have to a large extent been overcome by the use of macroporous resins and new impregnation techniques⁸. Physical loss of the organic phase, nevertheless, remains a problem and requires further investigation. Fritz has suggested¹⁰ that presaturation of the eluent with the organic solvent will help to prevent 'bleeding'.

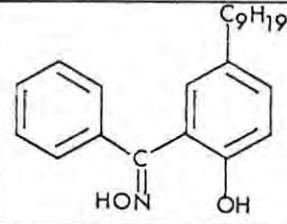
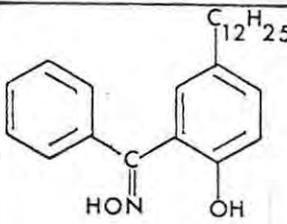
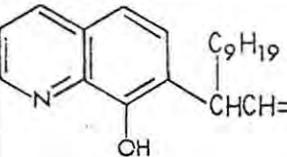
Since the rate of uptake of ions depends on the 'wettability' of the resin, it is important for the resin to have a certain amount of hydrophilic character. The method of impregnation described in this work involves the removal of the organic solvent under reduced pressure. If a non-polar, polystyrene type of resin is used, the resin will not 'wet' after this method of impregnation, and cannot be used to take up ions. The methods used to confer hydrophilicity on the impregnated resin have been described by Flett⁸. These include surface sulphonation of the support, addition of a detergent to the aqueous solution in contact with the impregnated resin, and the use of a diluent.

1.3 EXTRACTANTS FOR COPPER

Much of the work in the field of extraction chromatography has been concerned with the uptake of copper. Commercial reagents that have been used are the copper-specific hydroxyoxime compounds produced by General Mills Inc. and Shell Chemicals, and the alkylated 8-hydroxyquinoline produced by Ashland Chemicals⁸. Ashbrook has written a comprehensive

review¹¹ of the composition and mechanism of extraction of the commercial LIX reagents (substituted 2-hydroxybenzophenone oximes) produced by General Mills Inc. and the Kelex reagents (substituted 8-hydroxyquinoline) produced by the Ashland Chemical Co. LIX-64N and LIX-65N were used for the work described in subsequent sections. LIX-64N is a mixture of LIX-65N and LIX-63 (~ 1 volume %). The structures of these extractants and other copper-selective extractants are shown in Table 1.1.

TABLE 1.1: Structures of some of the chelating extractants

Commercial Name	Chemical Name	Structure
LIX-63	5,8-diethyl-7-hydroxy-6-dodecanone	$\text{CH}_3(\text{CH}_2)_3\overset{\text{C}_2\text{H}_5}{\underset{\text{HONOH}}{\text{C}}}\overset{\text{C}_2\text{H}_5}{\text{C}}\text{CH}(\text{CH}_2)_3\text{CH}_3$
LIX-65N	2-hydroxy-5-nonylbenzophenone oxime	
LIX-64	2-hydroxy-5-dodecylbenzophenone oxime + LIX-63	 + LIX-63
KELEX 100	7-dodecenyloxyquinoline	
	cis-9-octadecenoylhydroxylamine (oleohydroxamic acid)	$\text{CH}_3(\text{CH}_2)_{17}\text{CH}=\text{CH}(\text{CH}_2)_7\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{OH}$

Although hydroxamic acids are not as yet used commercially, they were chosen for use as chelating agents for the extraction of copper. Clingman and Parrish¹² used oleo-hydroxamic acid supported on a polystyrene-divinylbenzene copolymer to selectively absorb iron (III), aluminium (III) and copper (II) at pH 4. Although very little use has been made of hydroxamic acids in extraction chromatography, they are selective for many metals, especially copper (II), iron (III), vanadium (V) and uranium (VI).

1.4 THE AIMS OF THIS RESEARCH

As has already been mentioned, Warshawsky was the first to point out the advantages of using supports with high surface area². He investigated the adsorption capacities of a series of supports and found that the porous resins of high surface area had the highest capacity. The macroporous supports he investigated were the Amberlite XAD series (Rohm and Haas Co., Philadelphia). Of this series, the resin with the greatest adsorption capacity was XAD-7, a poly (acrylic ester) resin. The great advantage of using this resin as a support for an organic reagent is that it permits rapid penetration by aqueous solutions. Rates of exchange are fast and rapid separations are possible. Parrish investigated the Amberlite XAD resins as supports for the liquid ion-exchanger, 'Kelex 100',¹³. He found that the XAD-7 resin had the fastest rates of exchange and recommended it as a support for other stationary phases.

The aims of this research were to investigate suitable systems for the rapid separation of metals. The XAD resins were studied to see whether XAD-7 was the most suitable of the series when used as a support for other organic reagents. The resin with the best rates of exchange was then impregnated with copper-selective chelating reagents like those mentioned in 1.3, and tested in columns for the rapid separation of metals. Since very little work has been done using hydroxamic acids as stationary phase, the synthesis and characterisation of the hydroxamic acids were emphasized. Several hydroxamic acids were synthesised and tested to see which were the most suitable for use in columns.

For convenience, the work done in this research has been discussed in three separate sections, dealing respectively with macroporous resins as supports, hydroxyoximes as stationary phase and hydroxamic acids as stationary phase.

2. MACROPOROUS RESINS AS SUPPORTS

2.1 INTRODUCTION

2.1.1 Supports used in Extraction Chromatography

Katykhin has given an excellent account of the types of supports that have been used in extraction chromatography¹⁴. Unfortunately, it appears as if availability has been the prime reason for the choice of a particular support. This inconsistency has made it difficult to categorize all the supports, and Katykhin has had to resort to long lists giving their different characteristics. In his review¹⁴ he listed some requirements for supports in extraction chromatography. Amongst these he has listed chemical and mechanical stability, large surface area and good wettability.

Many of the supports used for reagents selective for copper have been microreticular, and as a result, certain difficulties have been encountered. Clingman and Parrish¹² found that the rate of elution using a polystyrene-divinylbenzene copolymer impregnated with oleohydroxamic acid was very slow. Cerrai and Ghersini¹⁵ studied the separation of copper by extraction chromatography on cellulose powder treated with the commercial reagent, LIX-64. They separated copper from five other metals, but the elution curves for copper showed considerable tailing, even at a flow rate of 1 ml min^{-1} . Microporous supports for

hydroxamic acids include granular Teflon¹⁶ which has a surface area $2 - 4 \text{ m}^2 \text{ g}^{-1}$, Celite 545 (hydrophobized kieselguhr)¹⁷ and microthene¹⁸.

The advantages of resins with large surface areas over the microporous supports seem to be obvious, i.e. improved kinetics, higher capacity and greater efficiency. Warshawsky² put this down to the fact that the reagent was able to spread itself over the surface of the macroporous resin as a thin, homogeneous layer. The early impregnated materials with low surface areas would absorb films consisting of many layers. Such films would restrict the diffusion of hydrated metal complexes into the pores of the resin and would make elution by an aqueous solution almost impossible.

Fritz et al¹⁹ separated copper successfully from eighteen other metals using XAD-2 impregnated with aliphatic α -hydroxyoximes. They were able to use fast flow rates, but some tailing of copper was shown at a flow rate of 20 ml min^{-1} . Their results were an improvement on those obtained by Cerrai and Ghersini on cellulose treated with LIX-64¹⁵. Although it is not clear whether the improved results were caused by the use of a macroporous resin support or by the use of specially prepared hydroxyoximes, it seems reasonable to conclude that the support played an important part in this improvement.

Hughes and Purdey recommended the use of an expanded polyurethane foam, Oleogon, impregnated with LIX-64N for the extraction of copper⁷. They used a very high loading of

the stationary phase (3,2 g LIX-64N per gram of polymer) and managed to achieve flow rates of up to 20 ml min⁻¹. Although it is difficult to make a comparison of their results with those obtained on the XAD-2 impregnated resin, it does seem as if the foam is not suitable for analytical work. The capacity of the packing for copper was 0,026 g copper per gram impregnated Oleogon at pH 3,5. This may be interpreted as 26 mg copper taken up by 3,2 g LIX-64N. Vernon and Eccles²⁰ found that XAD-2 resin loaded with 33% LIX-65N had a copper capacity at pH 2 of 7,7 mg g⁻¹ resin, or 75 mg on 3,2 g LIX-65N. It thus appears as if a large proportion of the LIX-64N on Oleogon was not available to form a chelate complex with copper.

Of the XAD series of resins, XAD-2 has been the most popular for use in extraction chromatography. Fritz and Kennedy²¹ extracted uranium from aqueous perchlorate media into dioctyl sulphoxide supported on XAD-2. Warshawsky²² absorbed palladium, platinum and nickel onto XAD-2 loaded with α -diphenylglyoxime. XAD-2 was also chosen by Willis and Sangster²³ who used the resin to absorb the 1,10-phenanthroline complex with iron from aqueous solution. Cheng and Guh²⁴ used XAD-2 as a support for the following ligands - sodium tetraphenyl boron, 1,10-phenanthroline, 8,8'(ethylene-diimino)-diquinoline, 8-hydroxyquinoline and 5-chlorobenzotriazole. They attempted several metal separations using the various impregnated resins. Although these authors did not give reasons for choosing XAD-2 as a support, Warshawsky² mentioned that it was the most readily available

of the XAD resins. Warshawsky² showed that XAD-2 had the lowest adsorption capacity of the range, and Parrish¹³ showed that it had the lowest water regain and the worst kinetics of the XAD series. Both these authors^{2,13} found XAD-7 to be the most suitable adsorbent of the range.

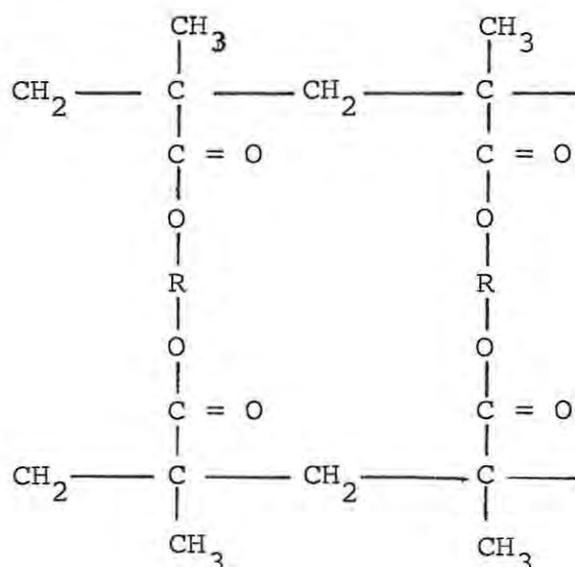
The aim of the experimental work described in this section was to ascertain whether XAD-7 would be the most suitable resin of the series if impregnated with LIX-64N. The capacities and rates of uptake of copper of the impregnated resins were compared and the most suitable support chosen for further work.

2.1.2 Properties of the Amberlite XAD Resins

XAD-7 is a poly (acrylic ester) resin and has the structure shown in Figure 2.1.²⁵ Numerical values for the properties of the XAD resins are given in Table 2.1, but are briefly summarized here. XAD-7 is of intermediate polarity, having an inherent dipole moment of 1,8. Of the XAD series, XAD-7 has the highest porosity, but intermediate surface area and pore diameter. XAD-2 and XAD-4 are both non-polar styrene-divinylbenzene polymers. XAD-8 is a poly (acrylic ester) resin of intermediate polarity and XAD-11 is a polar, poly (amide) resin. These properties may be arranged as follows:

Porosity : XAD-7 > XAD-4 > XAD-8 > XAD-2 > XAD-11
 Surface area : XAD-4 > XAD-7 > XAD-2 > XAD-8 > XAD-11
 Pore diameter : XAD-11 > XAD-8 > XAD-7 ~ XAD-2 > XAD-4
 Polarity : XAD-11 > XAD-7 ~ XAD-8 > XAD-2 ~ XAD-4

Figure 2.1: The structure of XAD-7.



2.1.3 Measurement of Surface Area

The properties of the XAD resins have been published by the manufacturers²⁵. All the measurements were done on the dry material. Since the pore size and specific surface area would be different when the resin is in contact with a solution, it would be helpful to have some idea of the surface area in the solvated state. If the surface area of the solvated resin is known, it will be possible to load the resin with sufficient reagent to complete a monolayer. Warshawsky² did some rough calculations on the impregnated

XAD-2 and concluded that a loading of 30% of the reagent would spread itself over the resin in a monolayer. This would give a surface area of $180 \text{ m}^2 \text{ g}^{-1}$ for the wetted resin as against $300 \text{ m}^2 \text{ g}^{-1}$ for the dry resin. Lundgren and Schilt²⁶ measured the adsorption isotherm of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine on XAD-2. They calculated the monolayer concentration to be $270 \pm 30 \mu\text{mol}$ of reagent per gram of resin. Since the size of the molecule was not known, the surface area could not be calculated. Rough calculations give $1,8 \times 10^{20}$ molecules of reagent per gram of resin. If the assumption is made that the size of the molecule is approximately that of methylene blue, namely $1,00 \text{ nm}^2$, the surface area may be calculated as $180 \text{ m}^2 \text{ g}^{-1}$. This result agrees with that obtained by Warshawsky².

Although it is experimentally simple to measure adsorption from solution, there are a number of factors which complicate the calculations. It is therefore necessary to treat the method with caution. These difficulties have been enumerated by Gregg and Sing²⁷. Firstly, there might be adsorption of the solvent as well as the solute. Since the individual isotherm of the solute is needed for the calculation of the monolayer capacity, it is clear that unless the adsorption of the solvent is negligible, the measured isotherm will differ widely from the required isotherm. Another problem is that of identifying the point on the adsorption isotherm that corresponds to the monolayer. Then, it is necessary to know the size and orientation of the adsorbed molecules. Kipling and Wilson²⁸ studied the adsorption of methylene blue in the determination of surface

areas and calculated the area of the methylene blue molecule to be between 1,02 - 1,08 nm². They concluded that methylene blue could be used semi-quantitatively, but that more needed to be known about its adsorption before it could be used to give reliable quantitative results.

However, since it would be useful to know what loading of reagent would correspond to a monolayer so that maximum efficiency could be achieved, it was considered important to attempt to measure the isotherm. If the reagent is spread over the support in a monolayer, the impregnated support will closely resemble a chelating resin which has the functional groups spread evenly over the surface. The manufacturer has stated²⁵ that XAD-7 will absorb phenol from water. It can thus be assumed that adsorption of water will be negligible when a solution of methylene blue in water is equilibrated with the resin. The measured isotherm can thus be assumed to be the isotherm of the adsorption of the dye. Keeping the other difficulties in mind, the results must be regarded as qualitative.

2.2 EXPERIMENTAL

2.2.1 Preparation of the Supports

The Amberlite adsorbents XAD-2, XAD-4, XAD-7, XAD-8 and XAD-11 (Rohm and Haas Co., Philadelphia, Pa.) were washed with ethanol to displace air from the pores and to remove

residual monomers and solvents. They were then washed with water until the washings were free of chloride ions. The washed resins were dried at 110°C overnight before impregnation with a liquid ion-exchanger.

2.2.2 Impregnation of the Supports

A known mass of the dry adsorbent in a round-bottomed flask was covered with a solution of the required amount of untreated LIX-64N (General Mills Inc.) in heptane. The heptane was removed at room temperature on a rotary evaporator, and the temperature raised to 100°C. The coated resin was wetted before use by covering it with 1M sodium hydroxide solution, and removing air from the pores by water-pump suction. It was then washed on a sintered glass filter with 1M hydrochloric acid, water, pH 5 acetate buffer and water in turn, and was stored wet.

2.2.3 Measurement of Water Regain

Water regains of the coated resins were measured by blotting the wet resin between sheets of filter paper, weighing the blotted resin, and weighing the resin after drying overnight at 110°C. The water regain was then calculated from the following formula:

$$\frac{\text{Mass wet resin (g)} - \text{Mass dry resin (g)}}{\text{mass dry resin (g)}}$$

2.2.4 Determination of Rates of Uptake of Metal Ion

Equilibrium capacities were measured by immersing 1,00 g of the wet resin in 50 ml 0,2M copper sulphate solution and 15 ml acetate buffer. The pH of the buffer was adjusted, by mixing 1M sodium acetate with 1M hydrochloric acid, to give a final pH of 5,0 when added to the copper sulphate solution. After 24 hours on a mechanical shaker at 20°C, the resin was filtered off and washed thoroughly with water. Absorbed copper was eluted with 50 ml 2M hydrochloric acid, and was titrated with EDTA after adjustment to pH 5 with 4 M sodium hydroxide and with acetate buffer. Xylenol orange indicator was used in the presence of 1,10-phenanthroline.

As a practical measure of the exchange rates, the uptake of copper in 2 min by resins of particle diameter 0,25 - 0,85 mm, expressed as a percentage of the equilibrium capacity (the $P_{2\text{min}}$ value), was determined. 2 min contact with the copper sulphate solution was allowed, while they were shaken vigorously by hand.

2.2.5 Determination of Adsorption Isotherms

The isotherms for the adsorption of methylene blue from unbuffered aqueous solutions at 20°C were measured with XAD-7 as adsorbent. 1 g of accurately weighed resin was equilibrated with 50 ml of the appropriate methylene blue solution in a stoppered 150 ml flask. The methylene blue (medicinal, E. Merck) was used as supplied. After 24 hours

on a mechanical shaker at 20°C, the resin was filtered off and the absorbance of the filtrate measured at $\lambda = 665$ nm, using a Bausch and Lomb Spectronic 21 spectrophotometer. The amount of dye adsorbed on the resin was calculated, and a plot made of number of moles adsorbed per gram of dry resin, against the equilibrium concentration. The data were then examined for conformity to the Freundlich model.

2.3 RESULTS AND DISCUSSION

2.3.1 Properties of the Supports

The porosity, specific pore volume, specific surface area, and average pore diameter of each of the Amberlite adsorbents used in this work have been determined by the manufacturer²⁵. These supports cover a wide range of physical properties, and range in polarity from the non-polar XAD-2 and XAD-4 (styrene-divinylbenzene copolymers), through XAD-7 and XAD-8 (acrylic ester polymers) to the polar XAD-11 (substituted acrylamide polymer). Some of these properties are summarized in Table 2.1. The more polar solvents expand when the air in the pores is displaced by alcohol or water, and therefore the water regain is a more realistic property to measure than the pore volume of the dry support. Water regains of the coated supports are included in Table 2.2. Table 2.2 shows that XAD-7, whether bare or coated, has the highest water regain of the resins used.

Table 2.1: Summary of some physical properties of Amberlite adsorbents²⁵.

Amberlite Adsorbent	Helium Porosity (cm ³ /gram)	Surface Area (m ² g ⁻¹)	Average Pore Diameter (nm)
XAD-2	0,693	300	9,0
XAD-4	0,998	784	5,0
XAD-7	1,080	450	9,0
XAD-8	0,822	140	23,5
XAD-11	0,616	69	35,2

2.3.2 Rates of Uptake of Copper

The experimental details of the measurement of the rates of uptake of copper are given in 2.2.4. Since slow rates of diffusion of ions into and out of the solid phase can cause tailing, poor efficiency, and difficult elution in extraction chromatography, the P_{2min} value was measured for each resin. Experience has shown that, under the conditions chosen for this measurement, a resin should have a P_{2min} value of at least 50% for satisfactory performance when used in columns for rapid separations. It should be noted that the P_{2min} values are determined on particles of 0,25 - 0,85 mm, whereas column separations are done on particles of 0,075 - 0,15 mm. The rate of extraction is, of course, much faster on particles of smaller size. The values in Table 2.2 show that XAD-7 is the best support. The rapid uptake of copper correlates with the high water

regains of the bare and coated resin. A similar result was obtained by Parrish for resins coated with the extractant "Kelex 100"¹³.

Table 2.2: Comparison of macroporous resins loaded with LIX-64N.

Water Regain ^a	Resin	Loading (%)	P _{2min} (%)	Water Regain ^b	Capacity (meq g ⁻¹) ^c
0,70	XAD-2	10	44	0,44	0,16
0,70	XAD-2	60	20	0,51	0,68
1,10	XAD-4	10	44	0,27	0,01
1,10	XAD-4	60	34	0,63	0,68
2,16	XAD-7	10	82	1,96	0,31
2,16	XAD-7	60	72	1,43	0,62
1,36	XAD-8	10	53	0,72	0,16
1,36	XAD-8	60	53	0,79	0,62
1,44	XAD-11	10	57	0,84	0,19
1,44	XAD-11	60	42	0,70	0,61

- a. Water regain of bare support¹³.
- b. Water regain of coated support.
- c. The capacity refers to the dry loaded resin, and the P_{2min} value is the percentage of the equilibrium capacity attained in 2 min.

2.3.3 Effect of Loading on the Rate of Uptake of Copper

As can be seen from Table 2.2, the rate of uptake of copper, in general, decreases as the loading is increased from 10 to 60%, but the rate for XAD-7 with 60% loading is still very good. The rate probably decreases due to the fact that the monolayer capacity of the resin is exceeded, and multilayers of the reagent are formed. The metal ions have then to diffuse through the thicker coating of reagent. Braun and Farag²⁹, who used polyurethane foam impregnated with zinc dithizonate to take up traces of silver from aqueous solutions, obtained a similar result. They found that the rate of recovery of silver from the foam material which contained the lowest concentration of dithizone, was the highest i.e. the rate of exchange increased with decreased loading.

The very low capacity shown by XAD-4 with 10% loading is probably the result of inadequate wetting of the resin. This explanation is suggested by the low water regain for the coated resin, and the effect is understandable in view of the hydrophobic nature, small pore diameter (5 nm), and high specific surface area ($784 \text{ m}^2 \text{ g}^{-1}$) of the support. A loading of 10% of the more polar LIX-64N is probably insufficient to form even a monolayer on the internal surface of this resin, and alcohol cannot be used to displace air from the coated resin, because it would also remove the LIX-64N. There is no significant difference between the capacities of the different resins at 60% loading, presumably because better wetting is achieved.

2.3.4 Adsorption Isotherms

Lundgren and Schilt²⁶ measured the adsorption of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) from methanol on XAD-2, and the adsorption of the PDT complex of iron (II) from aqueous solution on XAD-2. The adsorption approached saturation typical of a monolayer process and the adsorption isotherms at 25°C conformed to the Langmuir equation.

It was thought that a similar treatment of XAD-7 would allow the surface area of the solvated resin to be calculated. Since the area of the hydroxamic acid molecule is not known, it was decided to measure the adsorption of methylene blue on XAD-7. The experimental details are given in 2.2.5. From previous measurements using methylene blue²⁸, the adsorbed molecule is assumed to occupy an area between 1,02 and 1,08 nm². Gregg and Sing²⁷ mentioned that the thickness of the adsorbed layer on the walls of the pores in porous solids is limited by the width of the pores and that the formation of multilayers is thereby inhibited. However, it was found that the adsorption isotherm conformed to the Type IV isotherm described by Gregg and Sing²⁷ for multilayer adsorption. The plot of amount adsorbed per gram of dry resin against equilibrium concentration has a point of inflection corresponding to an adsorption of 13×10^{-5} moles methylene blue per gram dry resin. This point can be roughly taken as representing the completion of a monolayer and can be used to determine the order of magnitude of the specific surface area in solution. The result must be regarded as approximate. The adsorption isotherm conformed

readily to the Freundlich model as shown by the linearity of a plot of $\log n_s$ against $\log n_2$, where n_s = number of moles solute adsorbed per gram of dry resin and n_2 = number of moles solute in solution at equilibrium. Unfortunately, the Freundlich model does not allow for the calculation of the monolayer concentration and hence the inflection point must be used for this purpose. If the area of the methylene blue molecule is taken to be $1,02 \text{ nm}^2$, the area of the monolayer is 80 m^2 per gram of dry resin. The specific surface area of the wetted resin is thus five times less than the dry specific surface area (450 m^2 per gram²⁵). The plots corresponding to the adsorption isotherm and the Freundlich treatment are shown in Figures 2.2 and 2.3 respectively.

Figure 2.2.: Adsorption Isotherm of Methylene Blue on XAD-7.
(n_s = number of moles solute adsorbed per gram dry resin,
 n_2 = number of moles solute in solution at equilibrium).

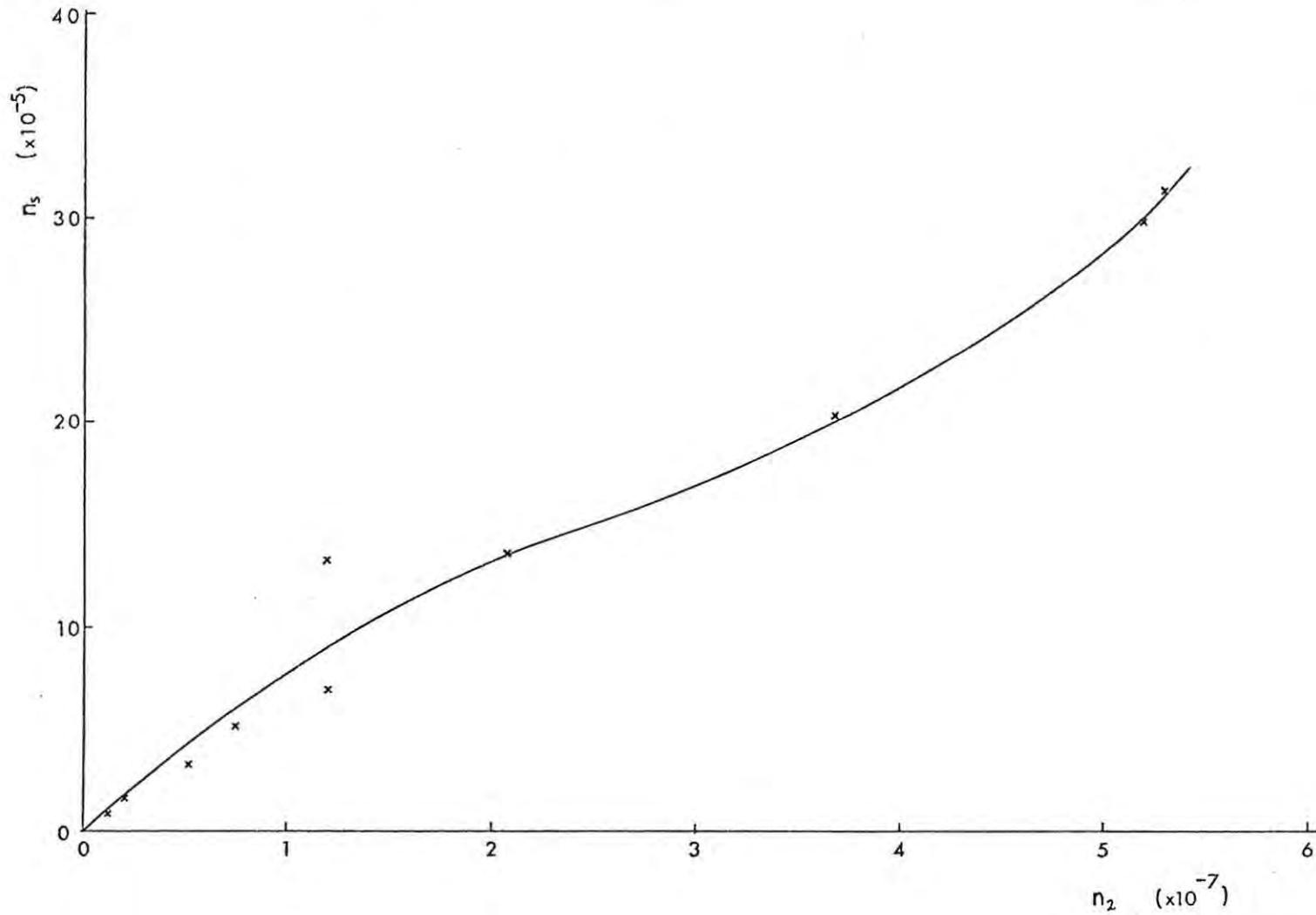
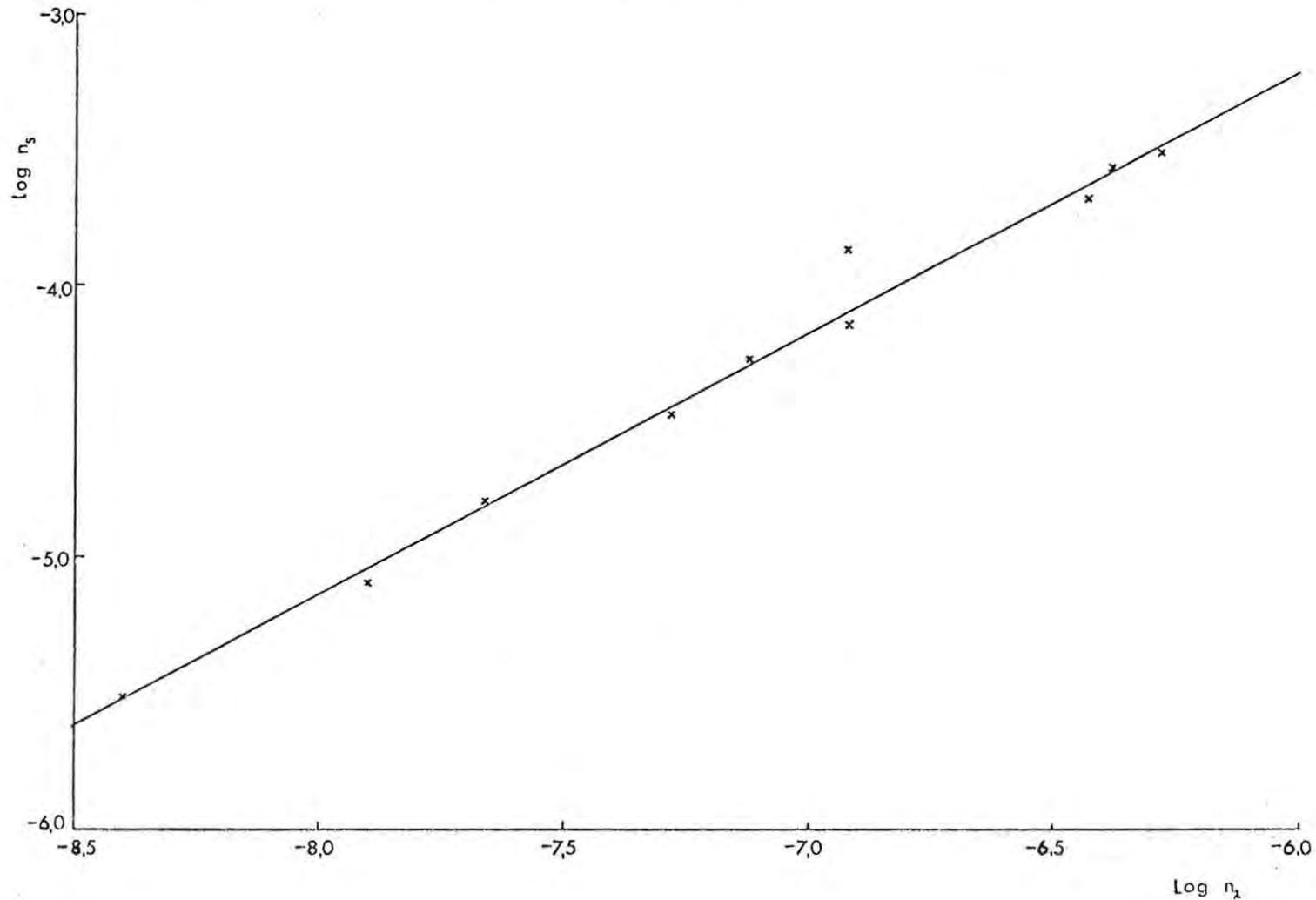


Figure 2.3: Data fitted to Freundlich model.
($\log n_s = 1/\beta \log n_2 + \text{constant}$, where n_s = number of moles solute adsorbed per gram dry resin, n_2 = number^s of moles solute in solution at equilibrium, and β = constant.)



3. HYDROXYOXIMES AS STATIONARY PHASE

3.1 INTRODUCTION

3.1.1 Structure and Composition of the α -hydroxyoximes

Mention was made in 1.3 of the commercially available extractants for copper. Their structure, composition and purification has been discussed fully by Ashbrook^{11,30,31} and by Atwood and Miller³². All the aromatic LIX reagents contain about 40% of an inert diluent¹¹. Ashbrook has suggested³¹ that this is probably Napoleum 470, an aliphatic diluent produced by Kerr-McGee, Inc. The diluent is necessary to improve the handling characteristics, since the α -hydroxyoximes are very viscous liquids. Apart from the diluent, approximately 1 volume % of LIX-63 is added to LIX-64 and LIX-64N. The 2-hydroxybenzophenone oximes exist in two isomeric forms, the syn and anti isomers which are shown in Figure 3.1. Ashbrook³¹ separated the isomers and determined the approximate concentration of each in the commercial mixture. For LIX-65N he found the ratio of anti to syn to be 5,4. The anti to syn ratio is the result of an equilibrium between the two forms. Both isomers can therefore be expected to be present in the commercially available extractants. However, only the anti isomer is active in that it is able to form a chelate complex with metal ions, whereas the syn isomer cannot. The structure of the chelate complex is shown in Figure 3.2. In LIX-64N only about 45% of the

3.1.2 α -Hydroxyoximes in Extraction Chromatography

The α -hydroxyoximes are highly selective for copper, their chelating action being dependent on the 2-hydroxyoxime grouping³³. Cerrai and Ghersini¹⁵ used LIX-64 as the stationary phase in extraction chromatography on paper and cellulose powder columns. They reported the R_F -spectra of several metals at various pH. These results were utilized for the column separation of copper from iron (III), iron (II), cobalt, nickel, manganese and chromium. As pointed out in 2.1.1, the elution curves showed considerable tailing, which they explained as being due to the excessive length of the column. Fritz et al. found that two samples of LIX-64 had different copper (II) capacities and somewhat different physical properties¹⁹. As a result they synthesized their own α -hydroxyoximes and tested them for the separation of metals by extraction chromatography. The two oximes were 10-hydroxyeicosan-9-oxime and 5,8-diethyl-7-hydroxydodecan-6-oxime. They reported R_F -spectra of 32 metal ions on Whatman 1 paper impregnated with 10% toluene solution of the oxime. In the column separations, copper was successfully separated from 18 other metal ions at pH 5. The separations were rapid, a flow rate of 20 ml min⁻¹ being used. Separation of Mo(VI) from each of 10 different metal ions was studied, using the same extraction column³⁴. Vernon and Eccles²⁰ investigated the use of LIX-65N supported on XAD-2. In a paper given at a conference, they described their evaluation of the resin in terms of metal capacities, equilibration rates and possible metal separations. Their results have not been published

in an accepted journal, but are nevertheless included here for the sake of completeness. They found the resin impregnated with LIX-65N to be selective for copper, vanadium, and iron at pH 2. The copper capacity of the resin increased with pH over the range pH 1 to 2. A separation of copper from iron (III) was feasible provided a fast flow rate could be achieved since the rate of uptake of copper was much faster than the rate of uptake of iron (III). At the same conference, Warshawsky and Patchornik³⁵ described their attempts to improve the efficiency of extraction of copper by resins impregnated with LIX-64N and similar α -hydroxyoximes. Warshawsky² had previously found that LIX-64N showed a decrease in its complexing ability when impregnated on XAD-2. He attributed this to either the poor wettability of the resin or to the decreased mobility of the ligand which made it difficult to form a square planar complex. As a result, Warshawsky and Patchornik³⁵ prepared a series of phenone oximes with either hydrophobic or hydrophilic groups attached. These were coated on the hydrophobic XAD-2 type resins and on a hydrophilic polystyrene-polyoxyethylene graft copolymer. They concluded that hydrophilic reagents, added modifiers or hydrophilic polymers helped in overcoming the hydration problems and improved the kinetics of extraction and elution.

Hughes and Purdey⁷ investigated the extraction of copper using expanded polyurethane foam, Oleogen, impregnated with LIX-64N. Their column had high selectivity for copper and flow rates up to 20 ml min^{-1} were achieved. They

compared their results with those obtained using gel-type resins. They found that the loading of copper was about the same for both types, but that a much larger volume of regenerant was needed for the impregnated foam. No separations were attempted so it is not possible to say whether the polymer is of any use for the rapid separation of metals. It appears that it might find application in the concentration of copper from mine effluents, rather than in the analytical separation of metals.

The aim of the work described in this chapter was to investigate the effect of the purification of LIX-65N and the addition of LIX-63 to the rate of extraction. XAD-7 impregnated with LIX-65N was used in columns for the rapid separation of copper from other metals. The efficiency of the column was investigated by plotting elution curves. The method was applied to the rapid determination of copper in brass and bronze alloys.

3.1.3 Diluent Effects in Solvent Extraction

Akaza has discussed the correlation between extraction chromatography and liquid-liquid extraction³⁶. He came to the conclusion that knowledge of the extraction constants obtained by liquid-liquid extraction and of the stability constants of the complexes make it possible to predict separations of various metals using extraction chromatography. It is thus helpful to know as much about the solvent extraction system as possible. Whewell and his co-workers^{37,38,39,40}

have studied the mechanism of extraction by the LIX reagents in some detail. Some of the more interesting conclusions that they have come to are the following. The aqueous solubility of the oxime increases markedly above a certain threshold pH value⁴⁰. The presence of nonylphenol in the extractants is deleterious to the kinetic performance³⁷. They gave no explanation as to the mechanism of interference by nonylphenol, but Dalton et al⁴¹ proposed that there is interaction between the phenolic -OH group of the oxime and an aromatic diluent, in this case, nonylphenol. This would represent an additional barrier to be overcome before complex formation can take place. This effect could possibly be the same when the reagent is coated on the support. In fact, Parrish⁴² found that the presence of nonylphenol and also toluene retarded the rate of uptake of copper by resins impregnated with LIX-64N.

Whewell and co-workers³⁹ found that LIX-63 improves the kinetics of extraction since it protonates most readily and thus lowers the interfacial tension. Because the problem of interfacial tension falls away when the reagent is spread out in a thin layer over the support, one would not expect LIX-63 to have any effect on the kinetics in extraction chromatography. Flett did, in fact, point out in his review⁸ that the presence of LIX-63 has no effect on the kinetics of extraction when the reagent is adsorbed onto a support.

3.2 EXPERIMENTAL

3.2.1 Apparatus

For the spectroscopic analyses a Perkin Elmer R12 n.m.r. spectrometer, a Perkin Elmer 180 Grating IR spectrophotometer, and a Unicam SP 800 ultra-violet spectrometer were used. The mass spectra were obtained using an AEI MS 30 spectrometer. Atomic absorption measurements were made using a Varian-Techtron model 1000 spectrophotometer. In column experiments, a Watson-Marlow MHRE Flow Inducer was used to maintain the required flow rate, and a Pye Model 290 pH meter was used to test the pH of solutions.

3.2.2 Reagents

Standard 0.01 M aqueous solutions of metal salts (A.R. grade quality) were used. The metal salts used were $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Hopkin and Williams), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (E. Merck), $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (E. Merck), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Hopkin and Williams) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (BDH). LIX-65N and LIX-64N (General Mills Inc.) were used as supplied and also in purified form. The pure anti isomer of 2-hydroxy-5-nonylbenzophenoneoxime was obtained from LIX-64N by column chromatography on silica gel, but the method was slow, and the yield poor. Better results were obtained by precipitation of the copper chelate from alcoholic solution, a method previously used to separate the isomers of 2-hydroxy-5-t-octylbenzophenoneoxime³³. An

ethanolic solution of copper (II) acetate was heated under reflux with an excess of LIX-64N for 3 hours. After standing overnight the precipitate was collected, washed with cold ethanol, and recrystallised from ethanol. The copper complex was decomposed by shaking a solution in carbon tetrachloride with 2 M hydrochloric acid. After washing and drying, the organic solvent was removed under reduced pressure, leaving the anti isomer as a yellow viscous liquid. This material produced a single spot on thin-layer chromatography; its mass spectrum showed a molecular ion at m/e 339, and its i.r., u.v. and 1H n.m.r. spectra were in agreement with those published³⁰ for the pure anti isomer of LIX-65N. The results obtained for the spectra were as follows: u.v. (λ_{max} (EtOH) 315; 261; 226 (sh); 211 nm; $\log \epsilon_{max}$ 3,47; 3,94; 4,39; 4,53), i.r. (ν (CCl_4) 3580; 3395; 2950; 1620; 1292; 965 cm^{-1}), n.m.r. (τ (CCl_4) -1,0 (1 H, bonded OH; very broad); 1,6 (1H, NOH; very broad); 2,6 - 3,3 (multiplet); 9,0 (multiplet)).

3.2.3 Thin-Layer Chromatography

TLC plates were prepared by coating microscope slides with silica gel G in chloroform. The spots of liquid ion-exchanger were developed in a 24 to 1 mixture of toluene to ethyl acetate, and rendered visible by placing the developed plates in a jar containing iodine crystals. To obtain better separation of the spots, Eastman Chromatogram sheets (type K301 R) were used. They were developed in

the same solvent, but the spots were rendered visible by spraying with 0,2M ammoniacal cupric sulphate solution.

3.2.4 Impregnation of the Resin

A known mass of dry XAD-7 was coated with the required amount of liquid extractant as described above in 2.2.2.

Since delays were experienced in obtaining fresh supplies of Amberlite XAD-7, a resin with very similar properties was used. The resin was made by Parrish⁴² as follows: 0,1 g Azo-di-isobutyronitrile was dissolved in 25 ml ethylene-glycoldimethacrylate and 50 ml amyl acetate, and the mixture was suspended in a solution of 2,5 g gelatin and 25 g sodium chloride in 250 ml water. The flask (500 ml), fitted with a stirrer and reflux condensor, was heated to 60°C in a waterbath. The stirring rate was adjusted to give droplets of suitable size, and after 30 min the temperature was raised to 80 - 85°C and held there for 6 hours. The resin beads were washed on a sieve with water, and then transferred to a sintered glass funnel. They were washed with acetone and then alcohol, and were air dried before final sieving to 0,25 - 0,85 mm diameter. The water regain of this resin was 2,2, and when loaded with up to 60% (w/w) of a liquid ion-exchanger, its reaction rate and capacity were very close to those of similarly loaded XAD-7 resin.

3.2.5 Rapid Separations

The procedure described by Parrish⁴³ for column separations was followed. The column was prepared by pouring a slurry of coated resin (particle size 75 - 150 μm) into a glass column retained with a cotton wool plug. The column was tapped to allow the resin to pack evenly. A plug of cotton wool was placed at the top of the resin bed to keep it in place. To condition the column to the correct pH, 25 ml buffer solution was pumped through, followed by 25 ml water. In order to achieve separation of copper from other metal ions, the column was conditioned to the pH required for the separation of the two metals being used. A mixture of appropriate amounts of the metal ion solutions and 5 ml buffer solution were pumped through the column at a flow rate of 10 ml min^{-1} . To ensure complete elution of the unabsorbed ions, 25 ml buffer solution were pumped through. The column was then reversed, and the adsorbed copper eluted with 25 ml 2M hydrochloric acid followed by 25 ml water. The separated metals were determined by titration with EDTA, or by atomic absorption for the smaller amounts. Elution curves were obtained by the use of a commercial chromatographic column with low dead volume (type LC-9MA; Laboratory Data Control, Florida). 2 ml fractions were collected and analysed by atomic absorption spectrometry.

For the concentration of 10 μmol of copper from 1 litre of solution, a column (9 mm x 30 mm) was used at a flow rate of 50 ml min^{-1} . The copper was recovered by elution with 25 ml hydrochloric acid at 10 ml min^{-1} .

3.2.6 Determination of Metals

The separated metals were determined using standard EDTA titrations described by Vogel⁴⁴. Xylenol Orange was used as the indicator at pH 5 - 6 for the copper, cobalt and nickel determinations. A drop of 1,10-phenanthroline was added to improve the endpoint. The solutions containing cobalt and nickel had to be warmed in order to get a sharp endpoint. Magnesium was determined at pH 10 using Eriochrome Black T as indicator. Iron was best determined by means of a back-titration. Excess EDTA was titrated with copper sulphate solution at pH 5 with Xylenol Orange.

Smaller amounts of the metals were determined using atomic absorption spectrophotometry. The wavelengths at which the measurements were carried out were 327,4 nm (copper); 248,3 nm (iron); 285,2 nm (magnesium) and 231,09 nm (nickel).

3.2.7 Analysis of Alloys

0,2 g of the alloy was covered with a solution of 0,6 g tartaric acid in 3 ml water. 3 ml concentrated nitric acid was then added. When dissolution was complete, the solution was diluted to 1 litre, and a 25 ml aliquot was used for the separation of copper. Copper was eluted in the reverse direction with 25 ml 2M hydrochloric acid, followed by 25 ml water. After adjustment of the pH to 5, the copper was determined by titration with 0,01M EDTA.

3.3 RESULTS AND DISCUSSION

3.3.1 Purification of LIX-64N

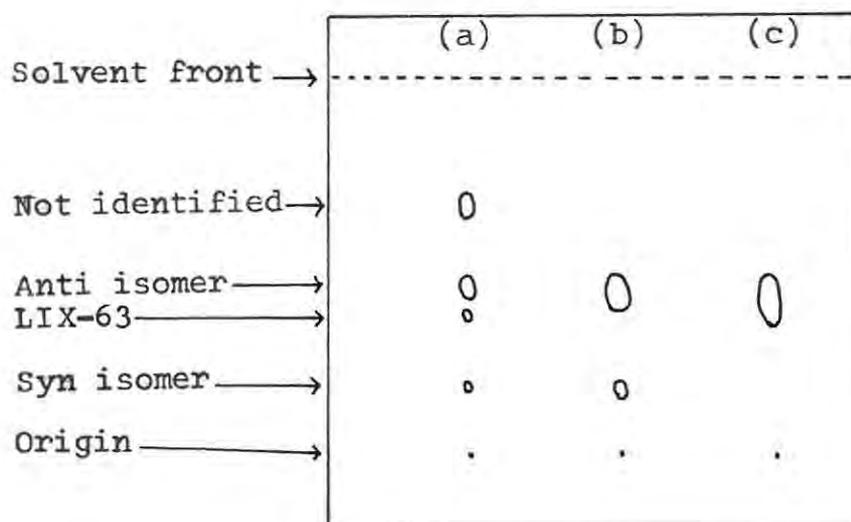
The structures and composition of the LIX extractants have been discussed above. LIX-63 is an aliphatic α -hydroxy-oxime, LIX-65N is 2-hydroxy-5-nonylbenzophenoneoxime with 40% (v/v) of an inert diluent, and LIX-64N is a mixture of LIX-65N with about 1% (v/v) of LIX-63. Different methods of purification of LIX-64N and LIX-65N have been described in the literature^{32,38}. Atwood and Miller³² isolated the components of LIX-64N by formation of the sodium salt of the oxime and separation from the unreacted organic components by centrifugation.

Preston and Whewell³⁸ found that preparative chromatography using a silica gel column gave partially purified samples of the extractant. They therefore used a two-stage method of obtaining the active component of the extractant. In the first stage they formed the sodium salt of the oxime in order to remove the inert diluent and in the second stage they formed the copper complex by reaction of an ethanolic solution of the sodium salt with ammoniacal cupric sulphate. In this laboratory, the method described by Atwood and Miller was followed, but both the syn and the anti isomers of the oxime were obtained. Column chromatography using a silica gel column was tedious and gave a very small yield of the pure anti isomer (6%). A more successful method of purification was by precipitation of the copper

chelate complex in an alcoholic copper acetate solution. The method of purification is described in 3.2.2. The yield (16%) was not very high due to the slight solubility of copper acetate in ethanol, but the product was pure and the method simple. In the formation of the copper chelate complex, an excess of LIX-64N was used, thus facilitating the formation of a 2:1 oxime-copper complex. Fritz et al¹⁹ found that extraction of copper (II) with 5,8-diethyl-7-hydroxydodecan-6-oxime in toluene produced two complexes. At low oxime concentrations a 1:1 complex was formed and at high oxime concentrations a 2:1 complex was formed. Since the solubility of copper acetate in ethanol was limited, it was thought that maximum yield would be obtained by using an excess of the liquid ion-exchanger. The pure anti isomer of LIX-64N was characterised by thin-layer chromatography, and various spectroscopic techniques. The results were in agreement with those published by Ashbrook³⁰. Thin-layer chromatography is a useful technique for identifying the components of the purified product³¹, since the commercial LIX-64N separates into four spots which correspond to the anti isomer (R_F 0,47), LIX-63 (R_F 0,38), the syn isomer (R_F 0,19) and an unidentified spot (R_F 0,69) which may be due to the inert diluent. In Figure 3.1 is shown a TLC plate obtained with the untreated commercial extractant, the partly purified LIX-64N and the pure anti isomer of LIX-64N. The pure anti isomer of 2-hydroxy-5-nonylbenzophenoneoxime will be referred to as "pure LIX-65N" in the text, whether obtained from LIX-64N or LIX-65N. When the percentage loading (w/w) of the

pure reagent on the resin is mentioned, x% loading with pure LIX-65N will be referred to as "x% pure LIX-65N".

Figure 3.3: TLC of (a) untreated LIX-64N, (b) partly purified LIX-64N using the method of sodium salt precipitation and (c) the pure anti isomer of LIX-64N obtained by precipitation of the copper chelate complex.



3.3.2 Effect of the Addition of LIX-63.

It is claimed that LIX-63 accelerates the rate of extraction of copper by LIX-65N in solvent extraction^{11,15}. When the extractants were supported on XAD-7, the results shown in Table 3.1 were obtained. It can be clearly seen that the presence of LIX-63 made no significant difference to the rate. Thus the catalytic effect of LIX-63 is peculiar to solvent extraction and does not apply to extraction chromatography. Table 3.1 also compares the properties

of a resin loaded with the pure anti isomer of LIX-65N with those of a resin loaded with the commercial LIX-65N (containing 39% of the active isomer¹¹). At 60% loading the extraction rate was slightly lower and the capacity slightly higher when the purified material was used. For analytical use, the commercial LIX-65N can be recommended.

Table 3.1: XAD-7 resin loaded with different combinations of LIX extractants.

Stationary Liquid Phase	P_{2min} (%)	Capacity (meq g ⁻¹)
55% LIX-65N + 5% LIX-63	73	0,75
60% LIX-64N	72	0,62
60% LIX-65N	73	0,78
55% pure LIX-65N + 5% LIX-63	69	1,20
60% pure LIX-65N	66	0,90

Warshawsky and Patchornik³⁵ found that LIX-64N showed a decrease in its complexing ability for copper when coated on XAD-2 in comparison to LIX-64N solution in toluene. However, the results in Table 3.2 show that there is no significant decrease in the capacity for copper of LIX-64N when impregnated on XAD-7 as compared with LIX-64N used for liquid-liquid extraction. The capacities in Table 3.2 are expressed in milliequivalents of copper per gram of liquid ion-exchanger and increase when pure LIX-65N is used. The

capacity for the resin impregnated with 55% pure LIX-65N and 5% LIX-63 is higher than for the resin impregnated with 60% pure LIX-65N. This result is to be expected because the molecular mass of LIX-63 (268 g mole^{-1}) is less than that of pure LIX-65N (339 g mole^{-1}).

Table 3.2: The copper capacity of the liquid ion-exchanger expressed in meq Cu^{2+} per gram of extractant.

Liquid ion-exchanger	Capacity (meq g^{-1})
LIX-64N in liquid-liquid extrn.	1,08
60% untreated LIX-64N on XAD-7	1,03
60% pure LIX-65N on XAD-7	1,50
55% pure LIX-65N + 5% LIX-63 on XAD-7	2,00

3.3.3 Elution Curves

The elution of 0,6 mg of copper from XAD-7 loaded with 50% LIX-65N is shown in Figure 3.4. The copper was absorbed at pH 5, and eluted with 2M hydrochloric acid at a flow rate of 1 ml min^{-1} . The plate height was 2,0 mm, and tailing was negligible. This curve should be compared with those in Figures 3 and 4 of reference 15, which showed considerable tailing and represented plate heights of 9,7 mm and 5,2 mm respectively. The separations reported

below were done rapidly by selective absorption, copper being held while other metals passed through the column. However, separations by selective elution are possible with this resin. Figure 3.5 shows the selective elution of nickel and copper after both metals were adsorbed on the resin at pH 5. All the nickel was eluted by acid of pH 2, before any copper appeared in the effluent.

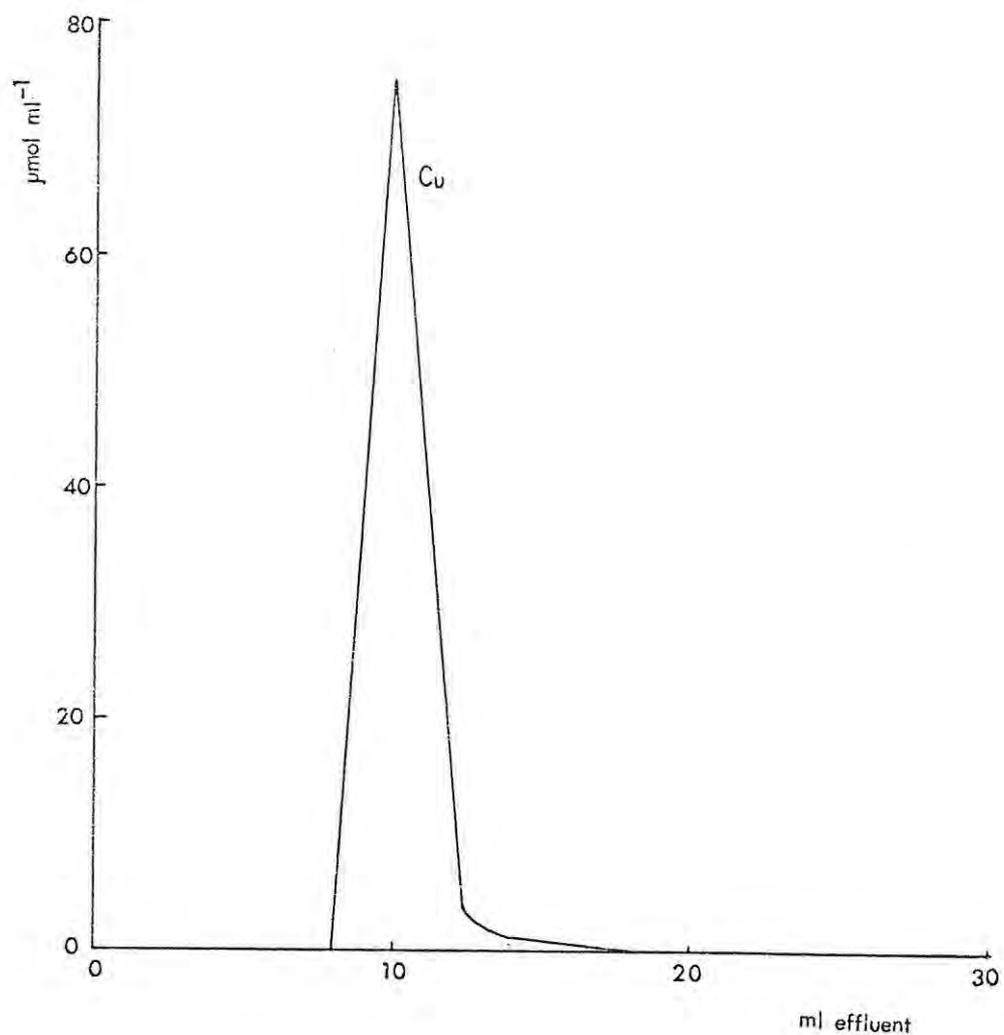
For the separations shown in Figures 3.4 and 3.5 a commercial column with low dead volume was used. Figure 3.6 shows the selective elution of copper and iron using a simple homemade column packed with the same resin. The bad tailing observed for the elution of copper was obviously due to the dead volume of the column, since it was eliminated by using the commercial column.

3.3.4 Rapid Separation of Metals

The procedure for column separations was described in 3.2.5. 0,01M solutions of nickel, cobalt or magnesium were mixed with 0,01M copper solution and the pH was adjusted by addition of sodium acetate-hydrochloric acid buffers. A 11 mm x 130 mm column of XAD-7 (75 - 150 μ m particles) coated with 25% of LIX-64N was used for the separations listed in Table 3.3.

The separation of copper from iron (III) was not quantitative without an additional complexing agent to mask the iron. This finding is in agreement with previous work

Figure 3.4: Elution curve of copper from XAD-7 resin.



Elution of copper (0,6 mg) from XAD-7 resin loaded with 50% (w/w) of LIX-65N.

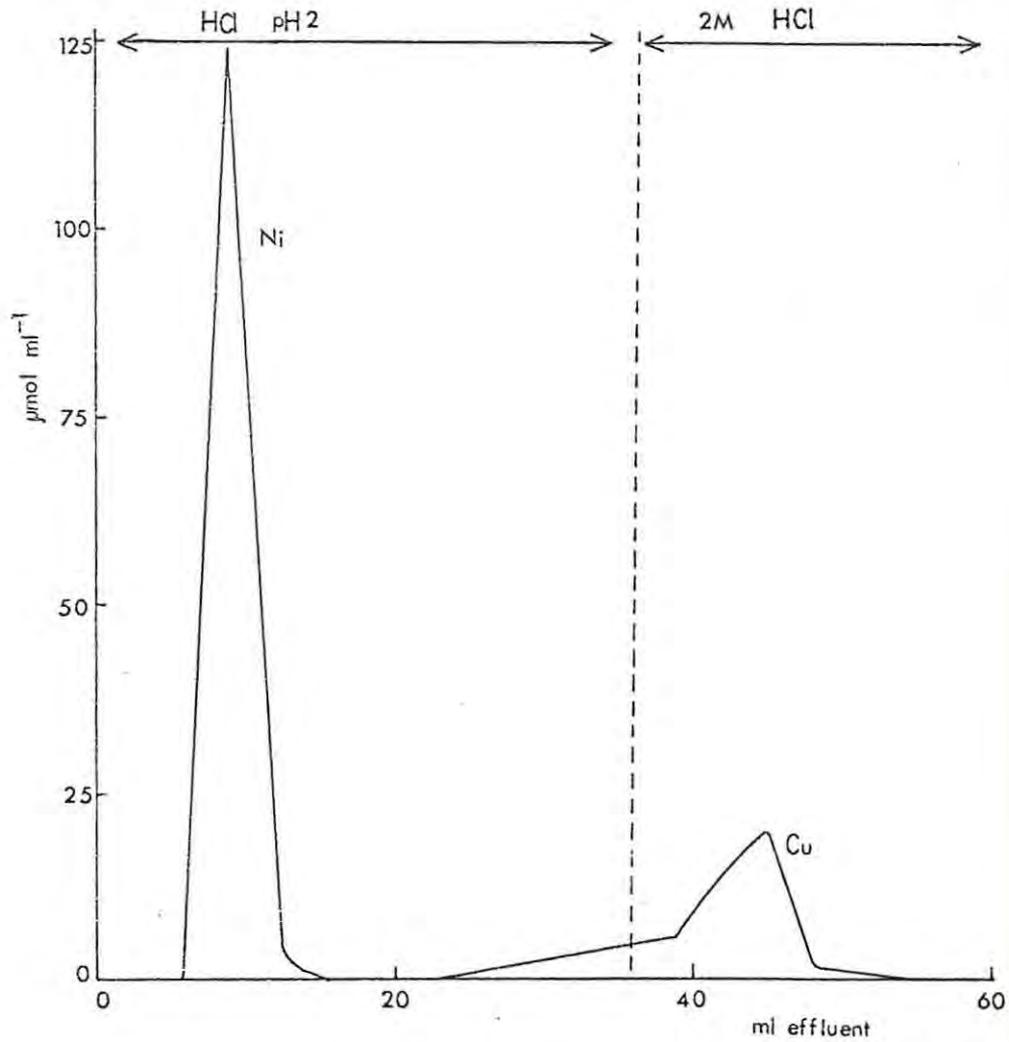
Eluent: 2M HCl

Column dimensions: 9mm x 130mm

Flow rate: 1 ml min⁻¹

Particle size of resin: 75 - 150 μm .

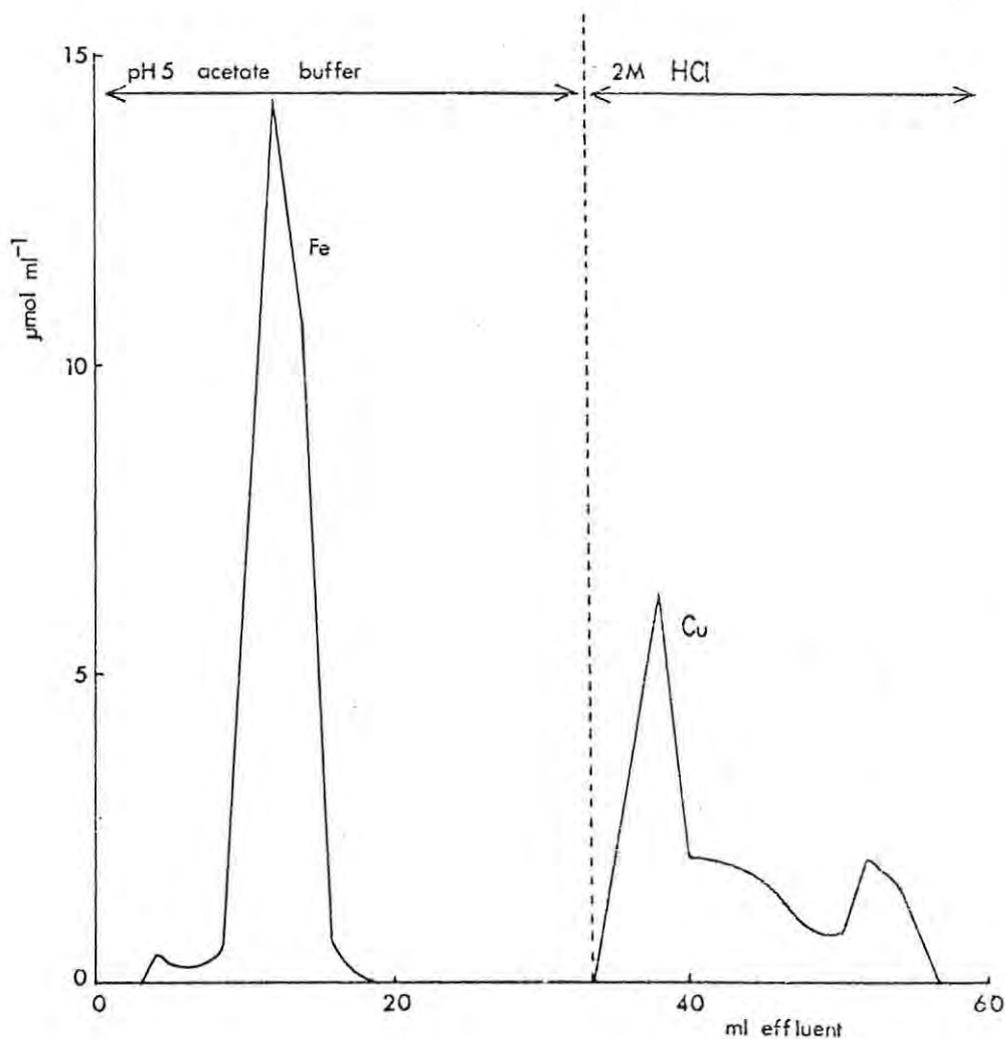
Figure 3.5: Selective elution of nickel and copper.



Selective elution of 0,01 mmol nickel and 0,005 mmol copper with HCl of pH 2, and with 2M HCl.

Other conditions as in Figure 3.4.

Figure 3.6: Selective elution of iron (III) and copper.



Selective elution of 0,02 mmol iron (III) and 0,01 mmol copper with pH 5 acetate buffer and 2M HCl.

Column dimensions: 8-mm x 185 mm.

Flow rate: 1 ml min⁻¹

Particle size of resin: 75 - 150 μm .

0,5 g potassium sodium tartrate was added to complex the iron (III).

on hydroxy oximes. Thus Cerrai and Ghersini (ref. 15) used fluoride ion in the eluent for the iron (III), and Fritz et al.¹⁹ added tartaric acid to the iron solution "to minimize tailing". For the separations reported in Table 3.3, up to 0,5 g of potassium sodium tartrate was added per 0,1 mmole of iron. This prevented any retention of iron by the resin, but it also reduced the effective capacity of the resin for copper. It was therefore necessary to avoid overloading the column with copper. A similar result was obtained by Vernon and Eccles⁴⁵ who found that the capacity of a poly (hydroxamic acid) ion-exchange resin for iron, copper, cobalt and nickel was greatly reduced in the presence of citrate. It was also found that use of a complexing agent made it difficult to determine the iron by EDTA titration. It was thus decided to take smaller amounts of iron (III) and to determine the iron using atomic adsorption. The resin used for the separation of copper from iron was coated with 50% of LIX-65N. The same resin in a 9 mm x 30 mm column was used to concentrate copper from very dilute solution. 1 litre water containing 0,623 mg of copper was adjusted to pH 5 and was pumped through the column at 50 ml min⁻¹. The recovery of copper was 99%.

The separation of copper from iron (III) appeared feasible at pH 1,5 since it was possible to get 99,8% recovery of copper when the column was loaded with 0,01 mmole (10 ml) at that pH. No iron (III) was taken up when the column was separately loaded with 0,005 mmole iron (III) (5 ml).

Table 3.3: Rapid separations of metals from copper.
 (Flow rate, 10 ml min⁻¹. Elution of
 copper with 2M HCl. Tartrate was added
 to solution containing iron (III)).

pH	Metal	Taken (mmole)	Found (mmole)	Recovery (%)
2,8	Ni	0,0991	0,0994	100,3
	Cu	0,0990	0,0989	99,8
2,8	Ni	0,2463	0,2473	100,4
	Cu	0,0990	0,984	99,3
3,5	Co	0,2659	0,2676	100,6
	Cu	0,0990	0,0989	99,9
3,5	Mg	0,2325	0,2325	100,0
	Cu	0,0990	0,0999	100,9
3,5	Mg	0,0970	0,0973	100,3
	Cu	0,0990	0,0988	99,8
5,5	Fe(III)	0,1000	0,1009	100,9
	Cu	0,1000	0,0994	99,4
5,5	Fe(III)	0,1000	0,0998	99,8
	Cu	0,0100	0,0099	99,0
5,5	Fe(III)	0,0250	0,02505	100,2
	Cu	0,0100	0,0099	99,0
5,5	Fe(III)	0,0100	0,0099	99,0
	Cu	0,0100	0,0099	99,0

However, when a mixture of 0,005 mmole copper (5 ml) and 0,005 mmole iron (III) (5 ml) was pumped through the column at pH 1,5, only 9% recovery of copper was achieved. Since the total volume of solution being pumped through the column was not altered, the volume could not have had any effect on the column capacity. A similar effect was noticed for the separation of copper from nickel. At pH 2, 0,01 mmole copper (10 ml) was quantitatively held by the column when taken up on its own, but in the presence of 0,01 mmole of nickel (10 ml) only 88% recovery of copper was achieved. It thus appeared as if the presence of a second metal ion reduced the capacity of the column for copper. In this instance, the total volume of the solution being pumped through the column was increased from 15 ml for the copper on its own to 25 ml for the copper-nickel mixture. However, it is unlikely that the change in volume can have this effect, since in the case of the copper-iron mixture there is no change in volume. A more reasonable explanation would be a kinetic one. It is possible that the second metal is initially extracted by the resin, thus reducing the capacity of the column for copper. When the additional buffer solution is pumped through the column, the unstable complex between the reagent and the second metal would then be broken and the metal ions eluted.

No mention of this problem was found in the literature, although a similar phenomenon was observed by Vernon and Nyo⁴⁶. They used the zinc and aluminium forms of an oxine

resin to take up copper, and found that the total capacity of the column decreased with decreasing concentration of the copper. They concluded that the sorption and desorption processes were each controlled by solution concentration. However, since the metals were taken up in 1M sodium acetate buffer solution, it is possible that sodium ions were taken up by mass action.

3.3.5 Analysis of Alloys

The rapid determination of copper in analysed samples of bronze and brass was carried out by passing a solution of the alloy at pH 3,5, through a column of XAD-7 resin coated with 25% of the liquid ion-exchanger, to remove the copper. A pH of 3,5 was necessary to avoid the adsorption of zinc. The method of dissolution of the alloy and determination of copper is described in 3.2.7.

The results of duplicate determinations are given in Table 3.4. Since tartaric acid was added to prevent the precipitation of tin, it was necessary to ensure that the column used had sufficient capacity to retain all the copper. The bronze alloy was successfully determined using a column of XAD-7 coated with 25% of the commercial LIX-64N. However, in order to have sufficient capacity for the copper, it was necessary to use a column of XAD-7 coated with 25% of pure LIX-65N to determine the copper content of the brass alloy. The need to use a column with greater capacity was probably due to the combined effects

of the tartaric acid and the zinc that were present in the alloy solution.

Table 3.4: Determination of copper in bronze and brass

Sample	Cu Reported (%)	Cu Found (%)
Bronze "C", No. 207 (British Chemical Standards)	86,84	86,65 86,72
Brass No. 5f (Bureau of Analysed Samples Ltd)	70,8	71,1 70,5

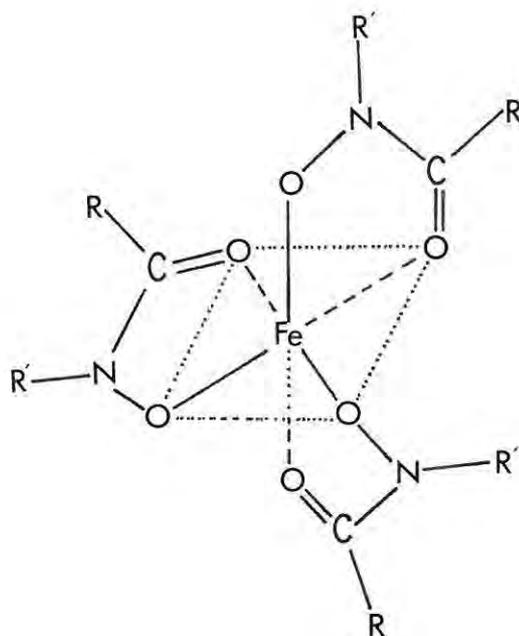
4. HYDROXAMIC ACIDS AS STATIONARY PHASE

4.1 INTRODUCTION

4.1.1 Some Analytical Uses of Hydroxamic Acids

A comprehensive account of the structure and reactivity of hydroxamic acids is given in a review by Yale⁴⁷. The first hydroxamic acid was synthesised in 1869 by Lossen⁴⁸. He treated hydroxylamine with diethyloxalate and obtained a derivative which he called oxalohydroxamic acid. It was early recognized that these compounds yielded isocyanates on heating and formed highly coloured complexes with iron (III). Hydroxamic acids are weak acids ($pK_a \sim 9$) and form stable five-membered ring chelates with metal ions⁴⁸. The binding with iron (III) occurs in a stepwise manner as the pH is raised, the tris chelate complex occurring at higher pH (see Figure 4.1). The deep reddish-brown colour is characteristic of the iron hydroxamate which absorbs in the visible range between 420 to 450 nm. Apart from iron (III), hydroxamic acids easily form stable complexes with a great number of other metal ions such as vanadium (V), zirconium (IV), niobium (IV), molybdenum (V) and copper (II), and generally with actinides and lanthanides.

Figure 4.1: The tris chelate iron hydroxamate.



Shome introduced N-benzoyl-N-phenylhydroxylamine as an analytical reagent in 1950⁴⁹. The analytical use of this reagent was reviewed by Shendrikar⁵⁰ who compared it with the many other N-aryl derivatives that have been described in the literature^{51,52,53}. N-benzoyl-N-phenylhydroxylamine extracts most metals in the periodic table and has been used for both colorimetric and gravimetric determinations. It was introduced by Shome as a reagent for the colorimetric determination of vanadium⁵⁴. Bhura and Tandon examined the possibility of using unsaturated N-arylhydroxamic acids as colorimetric reagents for vanadium⁵⁵. Of the 23 hydroxamic acids studied, 20 showed better sensitivity for vanadium than N-benzoyl-N-phenylhydroxylamine.

Vernon and Gunawardhana⁵⁶ have recently investigated the

synthesis and chelating properties of a number of N-benzoyl-N-phenylhydroxylamine derivatives substituted in the N-phenyl ring. An o-chloro derivative was recommended as a selective precipitant for iron (III).

Meloan et al introduced benzohydroxamic acid for the spectrophotometric determination of uranium in 1960⁵⁷.

Gasparini and Polidori⁵⁸ synthesised a series of trialkylaceto-hydroxamic acids for use in the solvent extraction of metals. One of these, neo-tridecanohydroxamic acid was used by Baroncelli and Grossi⁵⁹ for the solvent extraction of uranium (IV).

Lipowski and Finnegan⁶⁰ have patented a procedure for the synthesis of naphthenohydroxamic acid. In the patent they described the solvent extraction of copper and listed 35 other metals which are extracted by the hydroxamic acid.

It can thus be seen that the hydroxamic acid functional group is very versatile. pH control leads to great selectivity and a variety of separations are possible.

Vernon and Khorassani⁶¹ tested benzo-, stearo-, caprylo- and p-cresoxyacetohydroxamic acids for the solvent extraction of iron (III), copper, cobalt and nickel. They established that caprylohydroxamic acid in 1-hexanol was the most suitable, and used it for the extraction of titanium (IV), vanadium (V), chromium (VI), molybdenum (VI) and uranium (IV) from 6M hydrochloric acid.

4.1.2 Chelating Ion-exchange Resins

The obvious potential of incorporating the hydroxamic acid functional group into an ion-exchange resin was recognized by Petrie et al⁶². They briefly described the synthesis of the resin from a carboxylic acid resin and discussed its characterisation.

Vernon and Eccles have published a series of papers^{45,63,64,65} describing the synthesis and applications of chelating ion-exchangers which contain N-substituted hydroxylamine functional groups. They concentrated on separations involving the metals iron (III), copper, vanadium and uranium. The resins had a strong affinity for vanadium and had to be destroyed before the vanadium could be recovered⁴⁵. The advantages of the hydroxamic acid resin⁴⁵ were the fast equilibration rate and high capacity for metal ions.

4.1.3 Hydroxamic Acids in Extraction Chromatography

Clingman and Parrish¹² were the first to use hydroxamic acids in extraction chromatography. They synthesised oleohydroxamic acid, but found that it was not suitable for use in solvent extraction because it stabilized emulsions. They then tested it in a column supported on polystyrene beads. They were able to separate copper and iron (III) from nickel and cobalt at pH 4. Copper was eluted with 2M nitric acid and iron (III) with 5M hydrochloric acid. However, the support had a low specific

surface area, and they experienced the problem of slow elution rates.

Fritz and Sherma⁶⁶ were the first to evaluate the use of N-benzoyl-N-phenylhydroxylamine in extraction chromatography. They studied the chromatographic behaviour of some 35 metal ions using paper impregnated with N-benzoyl-N-phenylhydroxylamine and 2-octanol. Using eluents varying in acidity from 3 to 6M acid, they accomplished a number of selective separations.

Šebesta and co-workers published a series of papers on extraction chromatography using chelating agents. N-benzoyl-N-phenylhydroxylamine was one of the reagents studied. Šebesta and Lázničková¹⁷ investigated the extraction chromatographic behaviour of copper, indium and thorium on a column of hydrophobized kieselguhr, Celite 545, supporting a solution of N-benzoyl-N-phenylhydroxylamine in chloroform. The separations of Zn-Cu, Co-Fe, Co-Cu-Fe, U-Th and Th-Pa were reported.

The possibility of the separation of Hf, Nb, Ta and Pa using N-benzoyl-N-phenylhydroxylamine in chloroform was studied by Šebesta and Pošta¹⁶. They used granular Teflon for the support.

It was mentioned in 4.1.1 that neo-tridecano-hydroxamic acid had been suggested as a new extractant. Delle Site¹⁸ reported the analytical applications of the reagent supported

on microthene in extraction chromatographic columns. He reported separations of Am-U-Th and Np-Pu.

More recently, Vernon and Eccles²⁰ impregnated XAD-2 with stearohydroxamic acid. Although they concluded that stearohydroxamic acid was not suitable for extraction chromatography because the impregnated resin was unstable, they nevertheless found it to be very selective for iron (III) and proposed a separation of iron (III) from copper.

The previous work done has shown that hydroxamic acids are selective for a vast number of metals and that many separations are possible. However, previous workers used unsuitable microporous supports. Some also mentioned the fact that the columns were unstable^{17,20}. The aim of the work reported in this chapter was to test a series of hydroxamic acids as stationary phases in extraction chromatography. A series of long-chain hydroxamic acids were synthesised and characterised. They were tested for capacity and kinetics when supported on XAD-7. The distribution coefficients for several metals were measured using the most promising resins. The information regarding the distribution coefficients enabled column separations to be predicted. The rapid separation of copper from a series of other metals and of iron (III) from copper were carried out in columns. Some consideration was given to the stability of the column since this appeared to be a problem encountered by other workers.

4.1.4 Nomenclature of Hydroxamic Acids

For the sake of clarity, it is necessary to include some reference to the nomenclature of hydroxamic acids. There are two possible ways of naming this group of compounds. The one is based on the parent carboxylic acid and is called a hydroxamic acid. The other way is to regard the compound as a substituted hydroxylamine. In the text, the mono-substituted derivatives are named as hydroxamic acids. N-benzoyl-N-phenylhydroxylamine was the only di-substituted derivative dealt with, and is called by its more common name of a substituted hydroxylamine. Table 4.1 lists the names under both systems of some of the hydroxamic acids used.

Table 4.1: Nomenclature of some hydroxamic acids.

Parent Carboxylic Acid	Substituted Hydroxamic acid	Substituted Hydroxylamine
oleic acid (cis-9-octadecenoic acid)	oleohydroxamic acid	N-oleoylhydroxylamine
erucic acid (13-docosenoic acid)	erucohydroxamic	N-erucoylhydroxylamine
stearic acid (octadecanoic acid)	stearohydroxamic acid	N-stearoylhydroxylamine

4.2 EXPERIMENTAL

4.2.1 Synthesis of Hydroxamic Acids

1 Erucohydroxamic acid

The method described by Takeshi Sakai⁶⁷ was followed. Methyl Eruceate (Fluka AG) was used as received. Hydroxylamine hydrochloride (A.R.) was recrystallised from alcohol before use. 0,75 g hydroxylamine hydrochloride in 5 ml absolute alcohol was treated with a solution of 0,46 g sodium in 15 ml absolute alcohol. The mixture was added to a solution of 3,4 g methyl eruceate in 10 ml absolute alcohol. After standing at room temperature for 48 hours, the mixture was acidified with 10% concentrated hydrochloric acid in ethanol. The ethanol was removed on a rotary evaporator at a temperature below 40°C. Ice-cold water was added to dissolve the sodium chloride and to precipitate the hydroxamic acid. The erucohydroxamic acid was filtered and recrystallised from an ether-petroleum ether mixture (yield 0,84 g). The melting point agreed with the literature value (69,5 - 70,5°C)⁶⁷.

The presence of the hydroxamic acid group was verified by formation of a red-brown precipitate with ferric chloride, and by the expected peaks in the u.v. and i.r. spectra. The spectral results were as follows: i.r. (ν) (KCl) 3265, 3040, 3000, 2910, 2840, 1655, 1615, 1460, 1422, 1120, 1070,

1050, 1000, 965, 720, 645, 540 cm^{-1}), u.v. (λ_{max} (EtOH) 209 nm; $\log \epsilon_{\text{max}}$ 3,17). These results were very similar to those obtained for the commercially available N-benzoyl-N-phenylhydroxylamine (A.R., E. Merck) and stearylhydroxamic acid (Eastman).

2 Oleohydroxamic acid

The synthesis of oleohydroxamic acid was initially carried out using the method described by Nicolet and Pelc⁶⁸.

Ethyl oleate (Eastman) was used as received. Two products were obtained, both containing the hydroxamic acid functional group. One product had a melting point close to the expected literature value for oleohydroxamic acid (61°C)⁶⁸ and was soluble in most organic solvents.

The n.m.r. spectrum had a triplet at 4,6 τ , the expected shift for olefinic protons. The u.v. and i.r. spectra had the peaks expected for an hydroxamic acid. The i.r. spectrum is shown in Figure 4.2 and the n.m.r. spectrum in Figure 4.3. The results were as follows: i.r. (ν (KCl) 3410 (sh), 3260, 3045, 3000, 2910, 2840, 1655, 1615, 1460, 1420, 1110, 1090, 1060, 1045 (sh), 960, 730, 580 cm^{-1}), u.v. (λ_{max} (EtOH) 210 nm; $\log \epsilon_{\text{max}}$ 3,20), n.m.r. (τ (CCl_4) 1,2 (s), 4,6 (tr), 7,7 - 9,3 (multiplet)).

The other product, which was more readily isolated, had a higher melting point (92°C) and was practically insoluble in most organic solvents. The n.m.r. spectrum, which was run in deuterated dimethylsulphoxide, showed the

absence of a double bond and suggested a saturated compound (see Figure 4.4). Samples of the two products were sent to the National Chemical Laboratory, C.S.I.R. for analysis. The results were as follows. The lower melting solid had the composition: 4,67% N; 70,29% C; 11,62% H (expected for oleohydroxamic acid: 4,71% N; 72,73% C; 11,78% H) and the higher melting solid the composition: 5,16% N; 71,32% C; 12,27% H (expected for palmitohydroxamic acid: 5,17% N; 70,85% C; 12,18% H).

The results suggested that the ethyl oleate used as starting material was impure and that the more insoluble palmitohydroxamic acid was being isolated. In an attempt to purify the crude ethyl oleate, the ester was fractionally distilled under a pressure of 0,5 mm and a sand bath temperature of approximately 390°C. Four fractions were collected, the last fraction distilling over the temperature range 144 - 156°C. (b.p. of ethyl oleate 217-9⁴⁷).

Gas chromatograms were run of the crude ethyl oleate and of each of the four fractions collected. 0,5 µl of sample were injected onto a column, 5% SE-30 on Fluoropak 80 (135 cm x 0,5 cm), at a temperature of 220°C and carrier gas pressure of 20 psi. The area of each peak was determined by triangulation and the approximate percentage of each component in the sample calculated. The crude sample contained 72% ethyl oleate and 16% palmitate ester as well as four smaller fractions. The fourth fraction

Figure 4.2: The infra-red spectrum of oleohydroxamic acid.

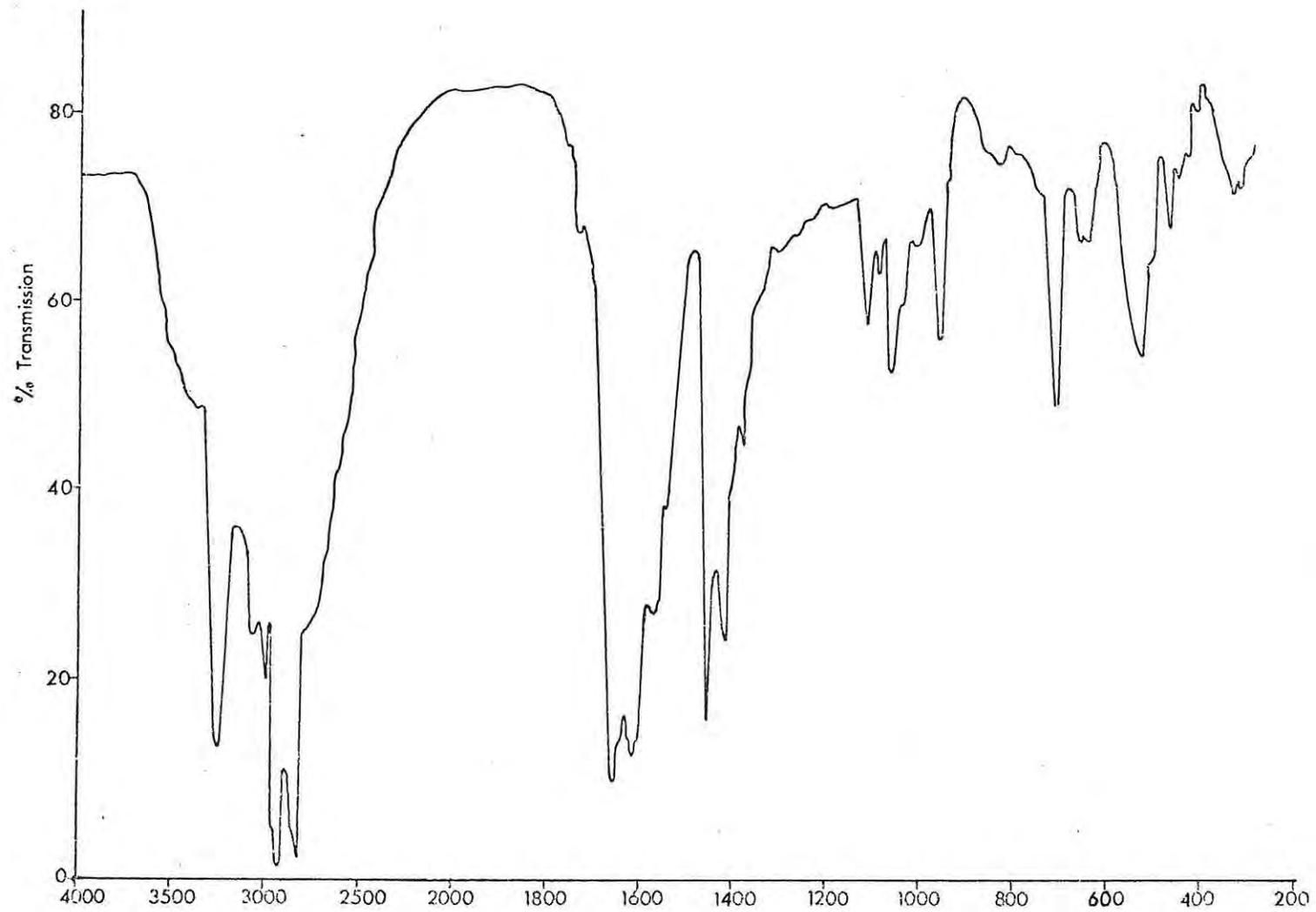


Figure 4.3: The n.m.r. spectrum of oleohydroxamic acid.

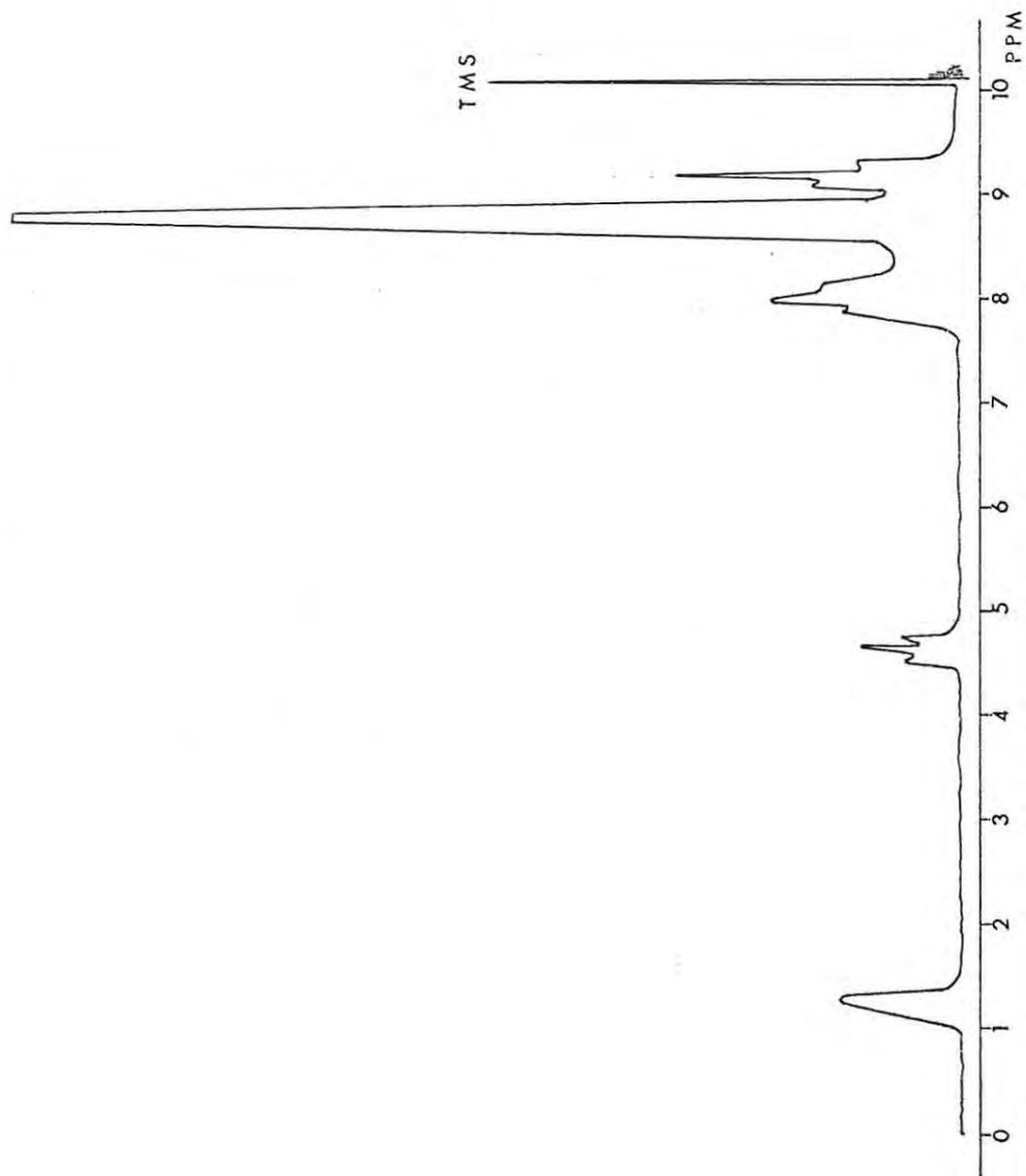
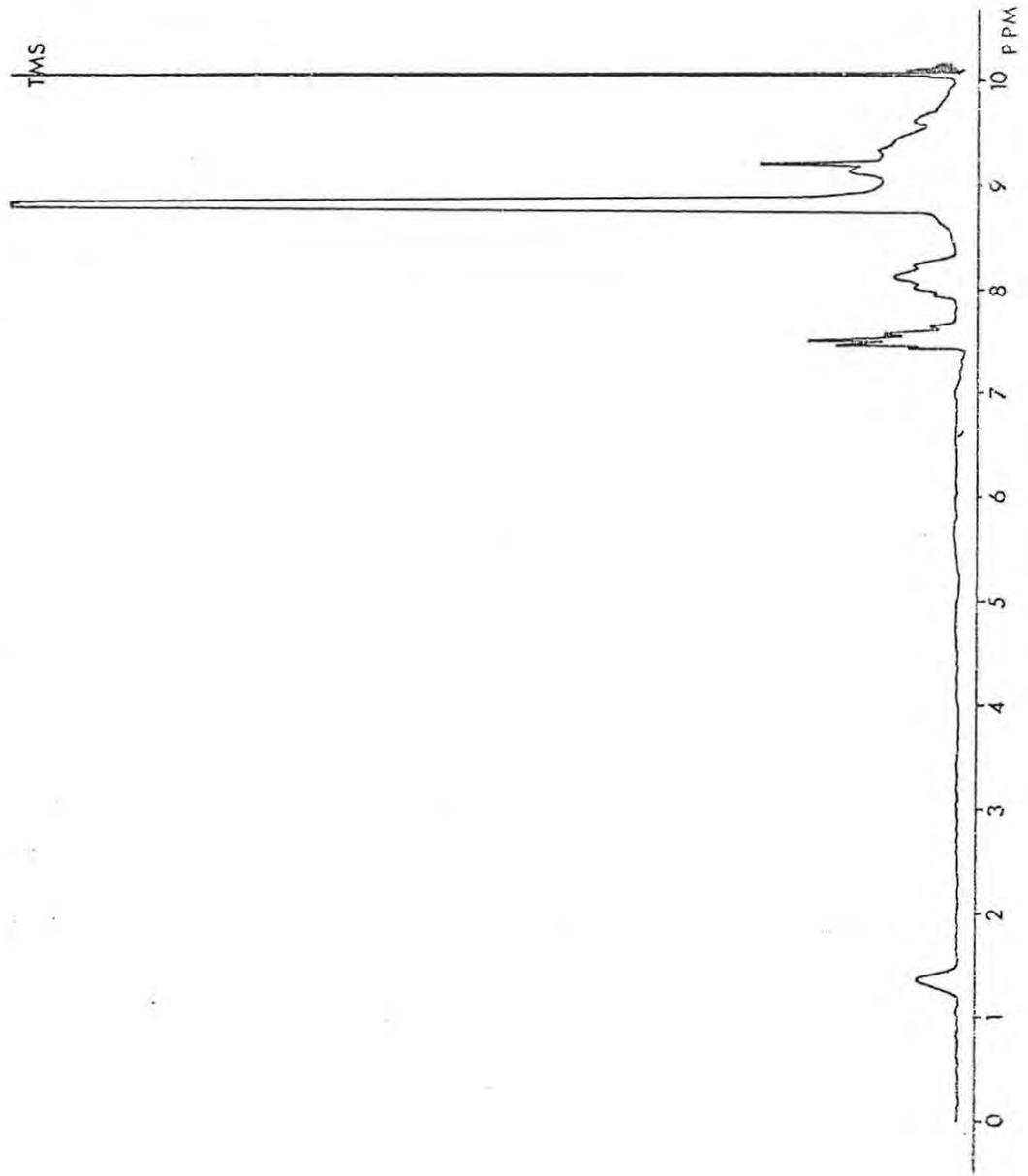


Figure 4.4: The n.m.r. spectrum of palmitohydroxamic acid.



collected contained 93% ethyl oleate and 7% palmitate ester. In subsequent syntheses, 93% ethyl oleate was used. The gas chromatograms are shown in Figures 4.5 and 4.6.

The following method was found to give the best yield of oleohydroxamic acid (50%). The method is based on syntheses reported in the literature^{69,70}. 2 g hydroxylamine hydrochloride (recrystallised from ethanol) was dissolved in 20 ml boiling methanol. 2,5 g potassium hydroxide was dissolved in 15 ml methanol. Both solutions were allowed to cool to room temperature before adding the alkaline solution slowly to the hydroxylamine hydrochloride solution with constant stirring. To ensure complete precipitation of potassium chloride, the mixture was allowed to stand in an ice-bath for 5 min. The potassium chloride was filtered off immediately after the addition of 3,5 g ethyl oleate in 10 ml ethanol. The filtrate was left stirring in a stoppered round-bottomed flask for 20 hours to ensure complete precipitation of the potassium salt of the hydroxamic acid. The potassium salt was filtered off, washed with ice-cold absolute ethanol and air-dried. In order to convert the salt to the free acid, the salt was dissolved in a minimum of ethanol. 15 ml 1,25M acetic acid was added to the solution and the mixture heated until a clear solution was obtained. The solution was cooled to room temperature before chilling in an ice-bath. The free acid was filtered off, dried and recrystallised from petroleum ether. The method described in 4.2.1.1 for obtaining the free acid was also followed and gave a similar yield.

Figure 4.5: Gas chromatogram of crude ethyl oleate.

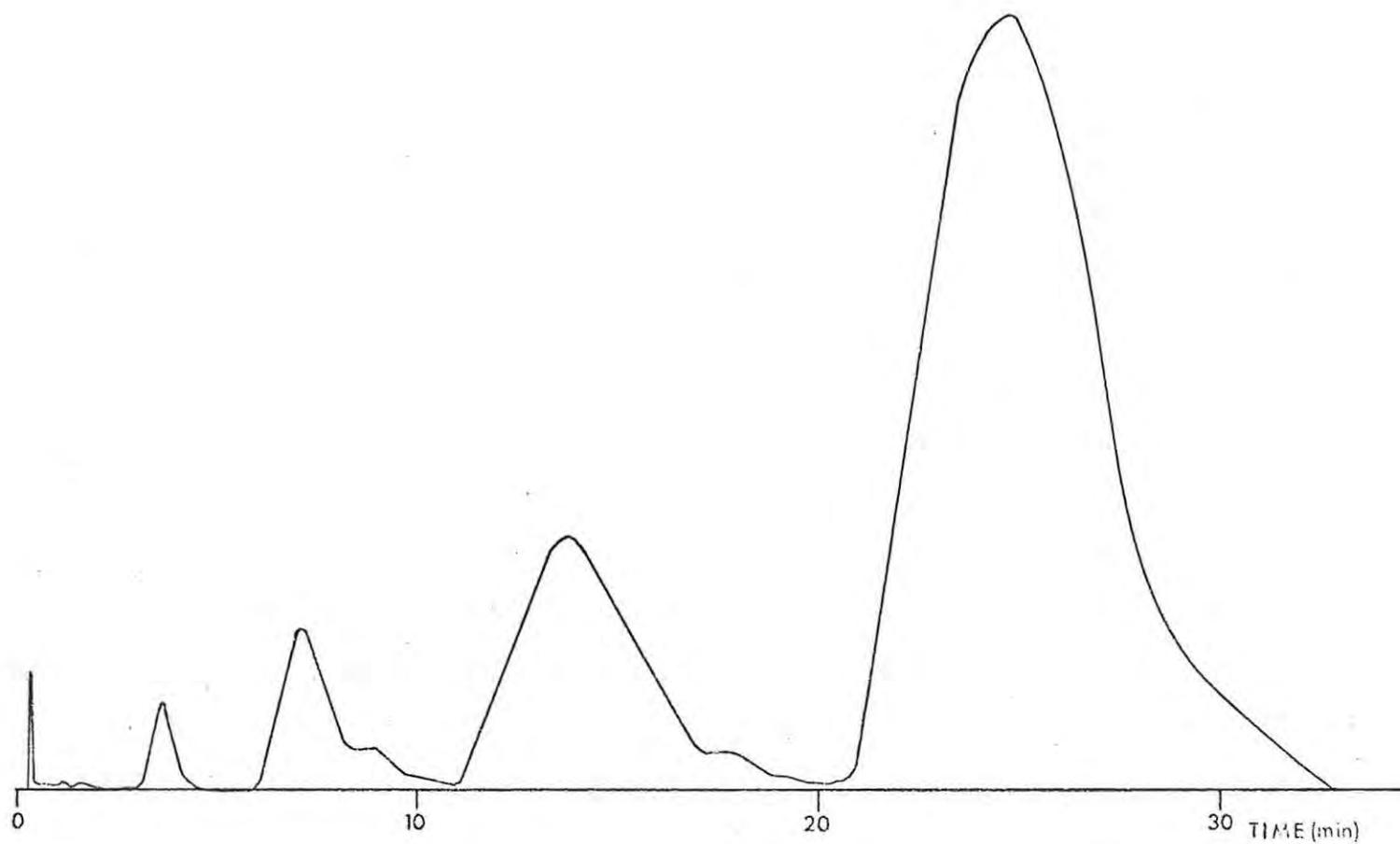
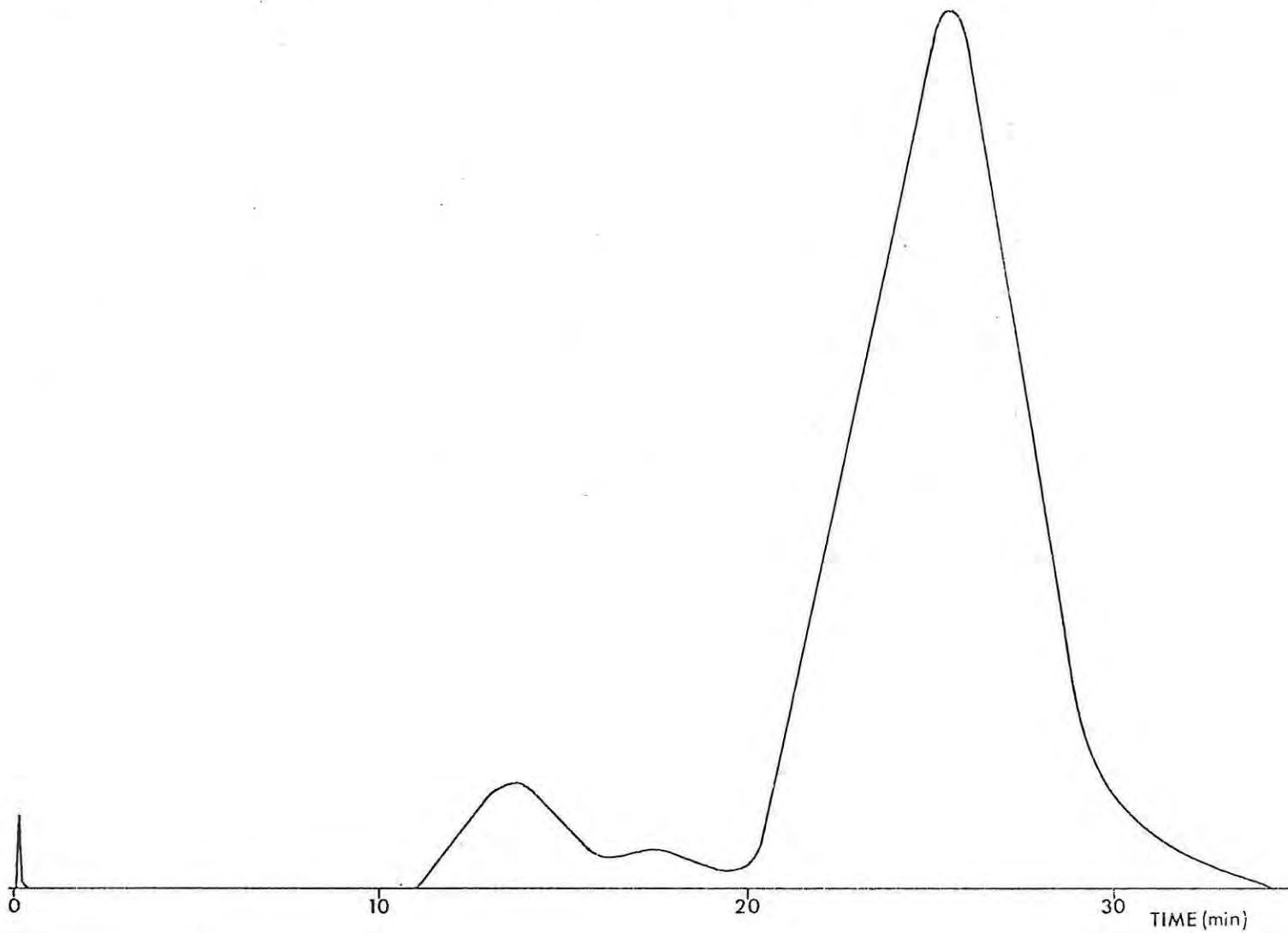


Figure 4.6: Gas chromatogram of partially pure ethyl oleate.



There appears to be no explanation in the literature for the fact that a molar excess of alkali was used for the synthesis of oleohydroxamic acid^{68,69,70}. It was thought that the poor yield (only 50%) could be due to the hydrolysis of the ester by the excess base, and thus attempted the synthesis without using an excess of base. The reaction was followed by TLC, and small amounts of excess potassium hydroxide were gradually added. With no excess potassium hydroxide, no reaction occurred even under reflux. In order for all the ester to react, a molar excess of base was found to be necessary. Sykes⁷¹ mentions the conversion of NH_2OH to its conjugate base $^-\text{NHOH}$ at high pH. This could be a possible explanation of the mechanism of the hydroxamic acid synthesis.

The thin-layer system used to follow the course of the reaction was as follows: Microscope slides were coated with silica gel G in chloroform. A 1:1 mixture of ethyl acetate and toluene was used as the developing solvent. The spots were rendered visible by placing the plates in a jar of iodine crystals, and the spots due to hydroxamic acid were distinguished from any others by spraying with an ethanolic solution of ferric chloride. (R_F values, ethyl oleate: 0,79; oleohydroxamic acid: 0,39).

3 Naphthenohydroxamic acid

Naphthenohydroxamic acid was prepared following the method described by Lipowski and Finnegan⁶⁰. The first step in

the synthesis was the formation of naphthenic ester. Naphthenic acids (Practical, Eastman) were used as received. 100 ml methanol was added to 50 g naphthenic acid in a 500 ml round-bottomed flask fitted with a stirrer, thermometer and condensor. When the solution was clear, 3,5 g 98% sulphuric acid was added. The solution was heated to 68 - 69°C under reflux. After 5 hours the solution was cooled to 20°C and the methanol removed on a rotary evaporator below 40°C. The mixture was transferred to a separating funnel and allowed to stand undisturbed for 2 hours for phase separation. The two layers were then separated. The organic layer was washed with 100 ml water, twice with 20 ml 50% sodium bicarbonate solution and then dried over sodium sulphate. The saponification value was 218 and the acid value 10. These values were determined using the methods given in the British Pharmacopoeia⁷².

The saponification value is the number of mg of potassium hydroxide required to neutralise the fatty acids resulting from the complete hydrolysis of 1 g of the substance, when determined as follows. A 0,5N solution of potassium hydroxide was made up by dissolving the required amount of potassium hydroxide in 20 ml water and making up to volume (1000 ml) with 95% alcohol. After standing overnight, the clear liquid was poured off and standardised with 0,5N standard hydrochloric acid solution. 25 ml of the alcoholic solution of potassium hydroxide was added to an accurately known mass (1 g) of the product in a 200 ml round-bottomed flask and the solution heated under reflux for 1 hour. While

still hot, the excess alkali was titrated with standard 0,5N hydrochloric acid solution.

The acid value is the number of mg potassium hydroxide required to neutralise the free acid in 1 g of substance, when determined by the following method. To an accurately known mass of the product (1 g) in a 250 ml flask, 50 ml of a mixture of equal volumes of 95% ethanol and ether, which had been neutralised after the addition of 1 ml phenolphthalein solution, was added. The solution was titrated with standard aqueous potassium hydroxide (0,5N) until a pink colour persisted for 15 seconds.

The following procedure was used to synthesise the naphtheno-hydroxamic acid from the ester. A flask containing 10,6 g hydroxylamine hydrochloride in 100 ml methanol was placed in an ice-bath. 12,75 g potassium hydroxide in 75 ml methanol was added dropwise over an hour to the hydroxylamine hydrochloride solution. 20g methyl naphthenate was added to the mixture while still in the ice-bath. After addition of the ester, the mixture was stirred at room temperature for 5 hours. The methanol was removed on a rotary evaporator and 80ml water added to dissolve the potassium chloride. The aqueous layer was removed after allowing the layers to separate in a separating funnel over 2 hours. The organic layer was washed with 10% sodium sulphate solution. In order to isolate the free acid, 5 g glacial acetic acid in 10 ml methanol was added to the solution.

After separation and washing of the organic layer, 5 ml ethylene dichloride was added and the residual water removed by azeotropic distillation under vacuum (yield 11 g).

4.2.2 Copper Uptake by Oleohydroxamic Acid and Naphthenehydroxamic Acid Used as Liquid Ion-exchangers.

The method described by Lipowski and Finnegan⁶⁰ was followed. A solution of 0,5 g of the hydroxamic acid in 100 ml hexane was mixed with 50 ml 0,2M copper sulphate solution in a 250 ml flask. After 3 hours in a mechanical shaker, the mixture was allowed to stand undisturbed in a separating funnel until the two layers had separated. The upper layer containing the deep green solution of the copper complex was washed several times with a 10% (w/w) sodium sulphate solution. The chelated copper was recovered by extracting with 50 ml 5M hydrochloric acid solution. The acidic fractions of copper were collected and diluted to one litre in a volumetric flask and the total copper content determined by atomic absorption. There was a tendency for emulsions to form, but it was found that the metals could be recovered if sufficient time was allowed for the emulsions to break.

4.2.3 Impregnation of XAD-7

Because the hydroxamic acids used are generally insoluble in a variety of cold organic solvents, difficulty was experienced in coating the resin. When the method described in 2.2.2

was followed, the hydroxamic acids crystallised out from the solution as soon as reduced pressure was applied. Different procedures were tried, for example, using a higher boiling solvent like pentanol, refluxing in ethanol to allow adsorption of the hydroxamic acids and distillation of the solvent in order to maintain a high temperature. The following method was the most successful. A known mass of the dry XAD-7 resin was covered with a solution of the required amount of hydroxamic acid in butanol. The mixture was heated on a waterbath for approximately three hours and then left to stand overnight to allow for complete adsorption of the hydroxamic acid. The butanol was removed at 100°C on a rotary evaporator. The resin was wetted a second time with butanol and the butanol evaporated off under reduced pressure. The resin was wetted by covering with distilled water and applying water-pump suction. The resin was filtered and stored wet.

The above method was not successful for stearohydroxamic acid and N-Benzoyl-N-phenylhydroxylamine, since they crystallised out on evaporation of the solvent. Use of nonylphenol as diluent facilitated the coating of the resin, but the impregnated resins were not of much practical use. The N-Benzoyl-N-phenylhydroxylamine was too soluble (145 mg l⁻¹) in buffered water (pH 5.5), and the rate of uptake of copper was too slow for the resin coated with stearohydroxamic acid and nonylphenol. (See Tables 4.2 and 4.3). It was decided to use a polystyrene resin with similar porosity to XAD-7 instead of the polyacrylic resin. This resin

coated with steorhydroxamic acid would not wet, and coated with N-Benzoyl-N-phenylhydroxylamine gave a slow rate of uptake of copper. (See Table 4.4).

Another method of impregnating the resin was attempted. Dry XAD-7 was covered with a 10% solution of oleohydroxamic acid in amyl alcohol. The air was dispelled from the resin by applying water-pump suction. After standing overnight, the excess solution was filtered off and the resin blotted between pieces of filter paper. A kinetic experiment showed that the resin coated in this way gave a slow rate of uptake of copper. (See Table 4.3).

4.2.4 Solubility of Hydroxamic Acids

The solubility of oleohydroxamic acid and N-Benzoyl-N-phenylhydroxylamine in water, and the amount of the respective hydroxamic acid that leaches out of the resin during the course of a kinetic experiment, were determined in the following way. A known mass of the impregnated resin (or hydroxamic acid) was equilibrated with 50 ml buffered water (or 50 ml 5M hydrochloric acid) for 24 hours in a mechanical shaker. After filtering off the solid, any dissolved hydroxamic acid was converted into its iron complex by addition of 10 ml 0,1M ferric solution. The pH was adjusted to 2, and the iron complex extracted into chloroform. The combined extracts were made up to a volume of 50 ml and the concentration of the iron complex determined spectrophotometrically (λ_{\max} 450 nm; $\log \epsilon_{\max}$ 3,06 for

N-Benzoyl-N-phenylhydroxylamine and λ_{\max} 425 nm; $\log \epsilon_{\max}$ 2,91 for oleohydroxamic acid).

4.2.5 Determination of Loading of the Stationary Phase

The resin was stripped of the stationary phase using a Soxhlet extractor. The resin was weighed into a 20 mm sintered glass filter (porosity 1) from which one end had been cut off, instead of into a porous thimble. The coated resin and filter were dried at 110°C overnight and weighed after cooling in a desiccator. The hydroxamic acid was extracted with 95% ethanol for 1 hour, the minimum time required to get constant mass. After extraction, the resin and funnel were again dried overnight at 110°C and then weighed. The percentage loading was determined from the mass loss. The loading of the resin was determined before and after use.

4.2.6 Measurement of Distribution Coefficients

The buffer solutions required for the measurement of distribution coefficients were made up in the following way. For pH values 4 and 5, 1M hydrochloric acid was mixed with 1M sodium acetate in the required proportions. For pH values 2 and 3, 1M chloroacetic acid and 1M sodium hydroxide were used, and for pH values below 2, 1M sodium chloride solutions were acidified with 1M hydrochloric acid.

The distribution coefficients were measured in the following way. 10 ml appropriate buffer solution and 20 ml 0,001M metal ion solution were pipetted into a 150 ml flask containing a known mass of wet resin (1 g). The pH of the solution was adjusted to the required value and the volume of the solution made up to 50 ml. The flasks were stoppered and shaken on a mechanical shaker for 24 hours. The solutions were filtered into 100 ml volumetric flasks, the resins washed with water, and the solutions made up to volume. The metal ion content of the solutions was determined using accepted analytical techniques.

Copper, iron, lead and zinc were determined by atomic absorption spectrometry at the following wavelengths, 327,4 nm (copper); 248,3 nm (iron); 217,0 nm (lead); 213,9 nm (zinc). Nickel and cobalt were determined by EDTA titrations, since they were not taken up by the resin at pH 5. There was thus a large enough metal ion content in the filtrate for volumetric analysis.

Uranium was determined colorimetrically as the uranyl ion after extraction into a 1% solution of 8-hydroxyquinoline in chloroform at pH 8,8^{73,74}. The chloroform extracts were made up to volume (50 ml) with chloroform and the absorbance measured at 420 nm.

Vanadium was determined using the method described by Shome⁵⁴. The pH of the filtrate collected after equilibration was adjusted to 2,5 and 10 ml of a 0,2% solution

of N-benzoyl-N-phenylhydroxylamine in ethanol added. The solution was made up to volume (100 ml) with ethanol and the absorption measured at 510 nm.

The distribution coefficient was calculated from the formula⁷⁵

$$D = \frac{\text{mmoles adsorbed solute per gram dry resin}}{\text{mmoles solute in solution per ml solution.}}$$

4.2.7 Column Separations

A column was packed with XAD-7 coated with 25% oleohydroxamic acid as described in 3.2.5. The rapid separation of a mixture of two metals was carried out using the same procedure as before. However, difficulty was experienced in eluting the iron after the copper/iron separation. It was found necessary to use 75 ml 5M hydrochloric acid in order to recover the iron quantitatively. The capacity of the column decreased to such an extent that it was necessary to use freshly prepared resin for the copper/lead separation.

10 μmol of copper was taken up from 1 litre of solution at a flow rate of 45 ml min^{-1} , using the same column. The copper was recovered by elution with 25 ml hydrochloric acid at 10 ml min^{-1} .

Elution curves of a copper/nickel separation were obtained using a commercial chromatographic column (type LC-9MA;

Laboratory Data Control, Florida). 2ml fractions were collected and analysed by atomic absorption spectrometry.

4.2.8 Column Capacity

The capacity of the column for copper was determined at pH 5 by pumping an excess of copper through the column. 50 ml 0,2M copper sulphate solution and 15 ml pH 5 buffer were pumped through the column at a flow rate of 10 ml min⁻¹. The excess copper was washed through the column with 25 ml water. 30 ml 2M hydrochloric acid was used to elute the copper. The effluent was neutralised with 4M NaOH and buffer to pH 5, and the copper determined by titration with 0,01M EDTA solution.

4.2.9 Other Measurements

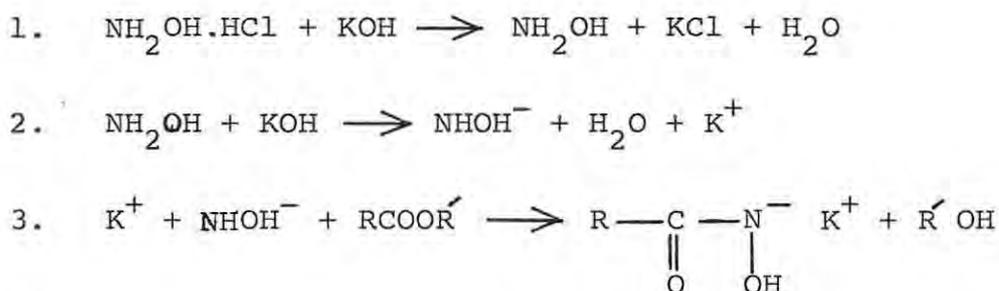
All other measurements on XAD-7 impregnated with hydroxamic acids were obtained using the procedures described in 2.2.

4.3 RESULTS AND DISCUSSION

4.3.1 Synthesis of the Hydroxamic Acids

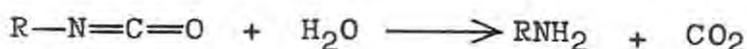
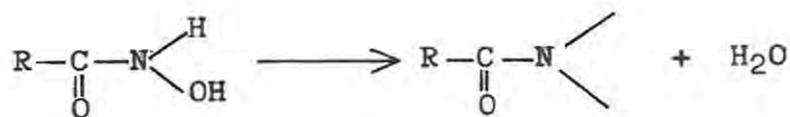
The most general method of preparation of hydroxamic acids is the reaction between an ester and hydroxylamine⁴⁷. In

the presence of base, the reaction proceeds readily and gives a yield of 50 - 60%.⁶² A molar excess of base was found to be necessary for the reaction. Sykes suggests⁷¹ that the alkali is necessary to convert the NH_2OH to the more reactive NHOH^- . Using this suggestion it is possible to write down the following reaction scheme for the synthesis.



The free hydroxamic acid is formed from the potassium salt by addition of mineral acid. Since water is a product of the reaction, the synthesis may be carried out in the presence of water, sodium carbonate replacing the sodium or potassium alkoxide⁴⁷.

Nicolet and Pelc⁶⁸ carried out the reaction under reflux, but later workers^{47,67,69,70,76} stated that the temperature should be kept below 40°C . In this laboratory it was found that the best yield was obtained when the reaction mixture was kept at room temperature. Since the Lossen rearrangement occurs at higher temperatures and in alkaline medium⁴⁷, it is possible that product is lost by rearrangement when the temperature is raised. The rearrangement occurs as follows⁴⁷:



The reaction was easily followed by thin-layer chromatography, the spots due to the hydroxamic acid being readily identified when the plates were sprayed with alcoholic iron (III) solution. Although the reaction mixture was left stirring at room temperature for 20 hours, there was hydroxamic acid present after a few minutes. Davenport⁶⁹ found that the reaction was usually complete within a few minutes, whereas earlier workers left the reaction mixture for 36⁷⁶ or 48⁶⁷ hours.

The hydroxamic acids were easily characterised by the formation of a brick-red precipitate with ferric chloride solution. They were further characterised by their melting points and i.r. and u.v. spectra. The peaks due to the hydroxamic acid function are listed below for erucohydroxamic acid. All the hydroxamic acids studied had similar peaks in their spectra. Infra-red: 3265 cm⁻¹ (ν O-H); 3040 cm⁻¹ (ν N-H); 1655 cm⁻¹ (amide I, ν C = O); 1615 cm⁻¹ (amide II, δ N - H); 965 cm⁻¹ (ν N - OH); 645 cm⁻¹ (δ CO-N). Ultra violet: λ_{max} 209 nm, log ε_{max} 3.17.

4.3.2 Solubility of Hydroxamic Acids

The limited solubility in organic solvents of some of the hydroxamic acids studied caused difficulty in the impregnation of the resins. The hydroxamic acid function exhibits an elevated solubility in water and insufficient solubility in non-polar solvents. Gasparini and Polidori⁵⁸ suggested increasing and branching the aliphatic chain in the "neo" structure to produce hydroxamic acids with higher solubility in organic solvents and a lower solubility in water. Vernon and Khorassani⁶¹ suppressed the hydrophilic nature of aliphatic hydroxamic acids by increasing the length of the alkyl chain and tested the products for use in the solvent extraction of metals. Because of its very low solubility in organic solvents, they discarded stearo-hydroxamic acid.

In this laboratory, the saturated long-chain aliphatic hydroxamic acids, stearo-, eruco- and palmitohydroxamic acids, were found to be too insoluble in organic solvents to be suitable for extraction chromatography. The aromatic N-benzoyl-N-phenylhydroxylamine and the unsaturated oleo-hydroxamic acid were more suitable although they exhibited slight solubility in water.

Tandon and Bhattacharyya⁷⁷ prepared a series of N-aryl hydroxamic acids and investigated their properties with a view to analytical use. Among the properties investigated was their solubility in water. The amount of hydroxamic acid dissolved was determined from the ultra-violet absorption.

They found the solubility of N-benzoyl-N-phenylhydroxylamine to be 400 mg l^{-1} at 25°C . Similar solubility tests were carried out in this laboratory on oleohydroxamic acid and N-benzoyl-N-phenylhydroxylamine. However, the concentration of hydroxamic acid in solution was determined by measuring the absorbance of the iron (III) chelate complex. The results listed in Table 4.2 show that the solubility of the hydroxamic acids decreased when coated on XAD-7 resin. When nonylphenol was used as a diluent, the solubility of N-benzoyl-N-phenylhydroxylamine was greater than when the resin was impregnated without using a diluent.

Table 4.2: Aqueous solubilities of hydroxamic acids.

Hydroxamic Acid	Solubility (mg l^{-1})
N-benzoyl-N-phenylhydroxylamine (BPHA)	498
60% BPHA on XAD-7	45
30% BPHA + 30% nonylphenol on XAD-7	145
oleohydroxamic acid	3
60% oleohydroxamic acid on XAD-7	0

4.3.3 Method of Impregnation

Warshawsky and Patchornik³⁵ found that hydrophobic phenolic oximes like LIX-64N were ineffective complexing agents if impregnated by the "dry method", but that they became very

efficient complexants if the "wet impregnation method" was used. In the "dry method" the excess solvent was removed by evaporation under vacuum whereas in the "wet method" the metal-ligand complex was formed in the presence of a residual amount of solvent. Since the dry method was used exclusively in this work, the wet method of impregnation was used for comparison. After equilibration of the resin with a 10% (w/w) solution of oleohydroxamic acid in amyl alcohol, the resin was filtered off and blotted between pieces of filter paper. From the results shown in Table 4.3, it can be seen that the resin impregnated by the wet method has a much slower rate of uptake of copper than the resin impregnated by the dry method. The rate was also retarded by the presence of nonylphenol as diluent. Parrish⁴² found that the use of nonylphenol reduced the rate of uptake of copper when XAD-7 was impregnated with LIX-64N, but increased the rate when XAD-7 was impregnated with KELEX 100¹³. Hanson et al³⁷ studied the effect of nonylphenol on the kinetics of the solvent extraction of copper (II) with the LIX reagents and found that the presence of the diluent had a deleterious effect on the rate.

Stearohydroxamic acid and N-benzoyl-N-phenylhydroxylamine did not coat successfully on XAD-7 since they crystallised out on evaporation of solvent. When nonylphenol was used as a diluent, the resin was easily impregnated with the liquid ion-exchanger. However, the rate of uptake of copper was slow for the resin coated with stearohydroxamic

Table 4.3: XAD-7 coated with hydroxamic acids and nonylphenol.

Stationary Liquid Phase	P_{2min} (%)	Capacity (meq g ⁻¹)	Water Regain
25% oleohydroxamic acid (OLHA)	87	1,02	1,64
25% OLHA + 25% nonulphenol	67	1,15	1,24
12½% OLHA + 12½% nonylphenol	58	0,48	2,04
10% OLHA	89	0,35	1,86
10% OLHA in amyl alcohol ^a	43	1,30	1,65
5% steorhydroxamic acid + 5% nonylphenol	66	0,42	1,68
10% steorhydroxamic acid	88	0,16	2,18

a. The "wet method" of impregnation was used.

acid (Table 4.3), and the N-benzoyl-N-phenylhydroxylamine was too soluble in the aqueous phase (Table 4.2). It was thought that the ion-exchangers would adsorb more readily on a non-polar resin, hence a polystyrene resin with a porosity similar to that of XAD-7 was used as the support. The resin coated well, but when impregnated with steorhydroxamic acid was too hydrophobic to wet and could not be used to take up copper. From Table 4.4 it can be seen that the polystyrene resin impregnated with N-benzoyl-N-phenylhydroxylamine has a slower rate of uptake of copper than when XAD-7 resin is used as support.

Table 4.4: Macroporous resins loaded with 60% N-benzoyl-N-phenylhydroxylamine.

Support	P _{2min} (%)	Capacity (meq g ⁻¹)	Water Regain
Polystyrene	78	0,47	1,87
XAD-7	84	0,43	1,80

4.3.4 Comparison of Hydroxamic Acids Supported on XAD-7

The results of kinetic experiments on XAD-7 resin impregnated with different hydroxamic acids are listed in Table 4.5. Oleohydroxamic acid, erucohydroxamic acid and naphthenohydroxamic acid were synthesised in the laboratory. N-benzoyl-N-phenylhydroxylamine and stearohydroxamic acid were obtained commercially and were used as received. The best results were obtained for XAD-7 loaded with 25% oleohydroxamic acid and for XAD-7 loaded with 60% naphthenohydroxamic acid, since these resins had a fast rate of uptake of copper as well as a high capacity for copper. It was decided to use these two resins for the determination of distribution coefficients and in columns for the rapid separation of metals.

Table 4.5: Comparison of XAD-7 resin impregnated with different hydroxamic acids.

Hydroxamic Acid	Loading (%)	P_{2min} (%)	Capacity (meq g ⁻¹)	Water Regain
N-benzoyl-N-phenylhydroxylamine	10	96	0,29	2,14
N-benzoyl-N-phenylhydroxylamine	25	98	0,29	2,14
N-benzoyl-N-phenylhydroxylamine	60	84	0,43	1,80
oleohydroxamic acid	10	89	0,35	1,86
oleohydroxamic acid	25	87	1,02	1,64
oleohydroxamic acid	60	53	1,96	1,21
erucohydroxamic acid	10	72	0,37	1,92
stearohydroxamic acid	10	88	0,16	2,18
naphthenohydroxamic acid	25	99	0,49	1,84
naphthenohydroxamic acid	60	83	0,98	1,67

4.3.5 Oleohydroxamic Acid and Naphthenohydroxamic Acid as Liquid Ion-exchangers

Clingman and Parrish tested oleohydroxamic acid for the solvent extraction of iron (III) and copper¹². When attempts were made to recover the metals with minerals acids, stable emulsions were formed with xylene as solvent. They found that chloroform or carbon tetrachloride gave better results and that the metals could be recovered if the emulsions were given sufficient time to break. Lipowski and Finnegan⁶⁰ determined the capacity for copper of naphtheno-

hydroxamic acid in solution in heptane. Their method⁶⁰ was followed in order to determine the capacity for copper of oleohydroxamic acid and naphthenohydroxamic acid. Although there was a tendency for stable emulsions to form, it was possible to obtain results provided sufficient time was allowed for the emulsions to break. However, neither oleohydroxamic acid nor naphthenohydroxamic acid can be recommended as liquid ion-exchangers in solvent extraction.

The capacity of oleohydroxamic acid for copper was 7,74 milliequivalents per gram of oleohydroxamic acid (or 3,87 mmole g^{-1}). Oleohydroxamic acid has a molecular mass of 297 $g\ mole^{-1}$, hence, from its capacity, it can be suggested that a 1:1 complex with copper is formed. Naphthenohydroxamic acid has a copper capacity of 2,52 meq g^{-1} (or 1,26 mmole g^{-1}), which is one third that of oleohydroxamic acid.

From capacity measurements of the hydroxamic acids coated on the XAD-7 resin, it can be seen that the copper capacity is less than that of the hydroxamic acids used in solvent extraction. The capacity for copper of oleohydroxamic acid is approximately halved when the reagent is coated on the resin, whereas the copper capacity of naphthenohydroxamic acid is only slightly reduced. This suggests that the functional group is more readily available to form a complex with copper when naphthenohydroxamic acid is coated on the resin than when oleohydroxamic acid is coated on the resin.

In 4.3.7 it will be seen that naphthenohydroxamic acid is lost from the column packed with impregnated XAD-7. It can thus be concluded that naphthenohydroxamic acid is not as strongly adsorbed to the resin as oleohydroxamic acid. In Table 4.6 the capacities of the resins coated with hydroxamic acids are expressed as milliequivalents of copper per gram of hydroxamic acid, instead of per gram resin, for comparison with the hydroxamic acids used in solvent extraction.

Table 4.6: Copper capacities of oleohydroxamic acid and naphthenohydroxamic acid used in solvent extraction and coated on XAD-7 resin.

Hydroxamic Acid	Capacity (meq g ⁻¹) ^a
(a) Oleohydroxamic Acid:	
0,5 g in 100 ml hexane	7,74
10% on XAD-7	3,50
25% on XAD-7	4,08
60% on XAD-7	3,27
(b) Naphthenohydroxamic Acid:	
0,5 g in 100 ml hexane	2,52
25% on XAD-7	1,96
60% on XAD-7	1,63

a. Capacity is expressed as meq copper per gram of hydroxamic acid.

4.3.6 Measurement of Distribution Coefficients

The equilibrium distribution coefficients of several metal ions were measured using the XAD-7 resin loaded with either 25% oleohydroxamic acid or 60% naphthenohydroxamic acid. There was no significant difference between the results obtained for the same metal using different resins, hence only one set of results is given. The metals tested were copper, iron (III), vanadium, uranium, zinc, lead, cobalt and nickel, and the method used for determining the distribution coefficients was that described by Strelow⁷⁸. The measurements were made at pH values ranging from 0 to 5 since that was the pH range in which the metals were selectively taken up by the impregnated resins. At higher acid concentrations, the resins should become selective for heavy radio-isotopes^{16,17}.

The results of the distribution coefficient measurements are given in Figure 4.7 as a plot of the log of the distribution coefficient against the pH. From these contours it was possible to predict which metal pairs could be separated using a column packed with the impregnated resin. It was thought that the measurement of distribution coefficients was a more practical measure than measurement of capacity since column separations involved small amounts of metal ion and excess resin. Capacity measurements were made using an excess of metal ion and it was found that copper was taken up at a lower pH than in the distribution coefficient measurements. Figure 4.8 shows the capacity against pH contours for copper taken up by XAD-7 coated

Figure 4.7: Distribution coefficients as a function of pH.

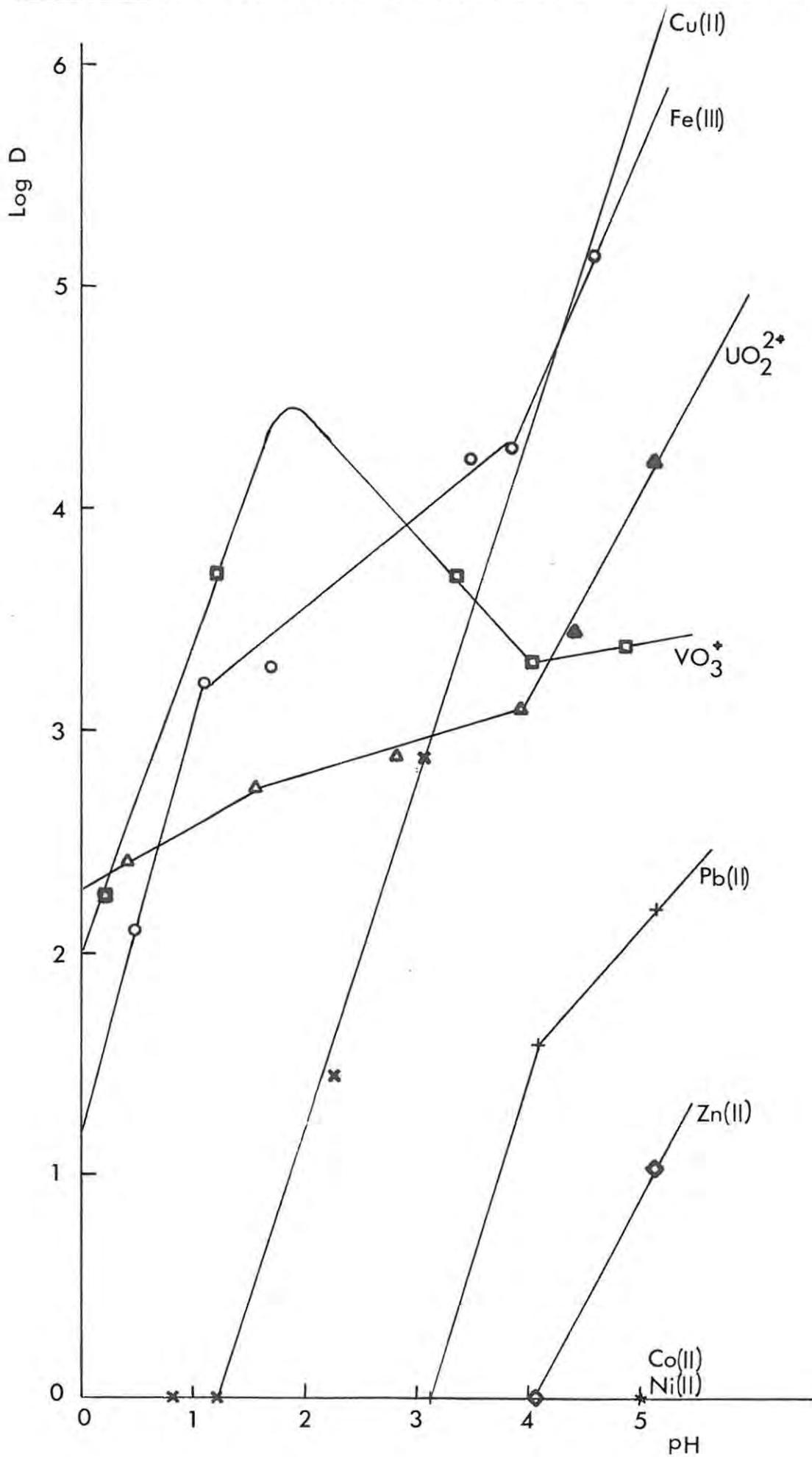
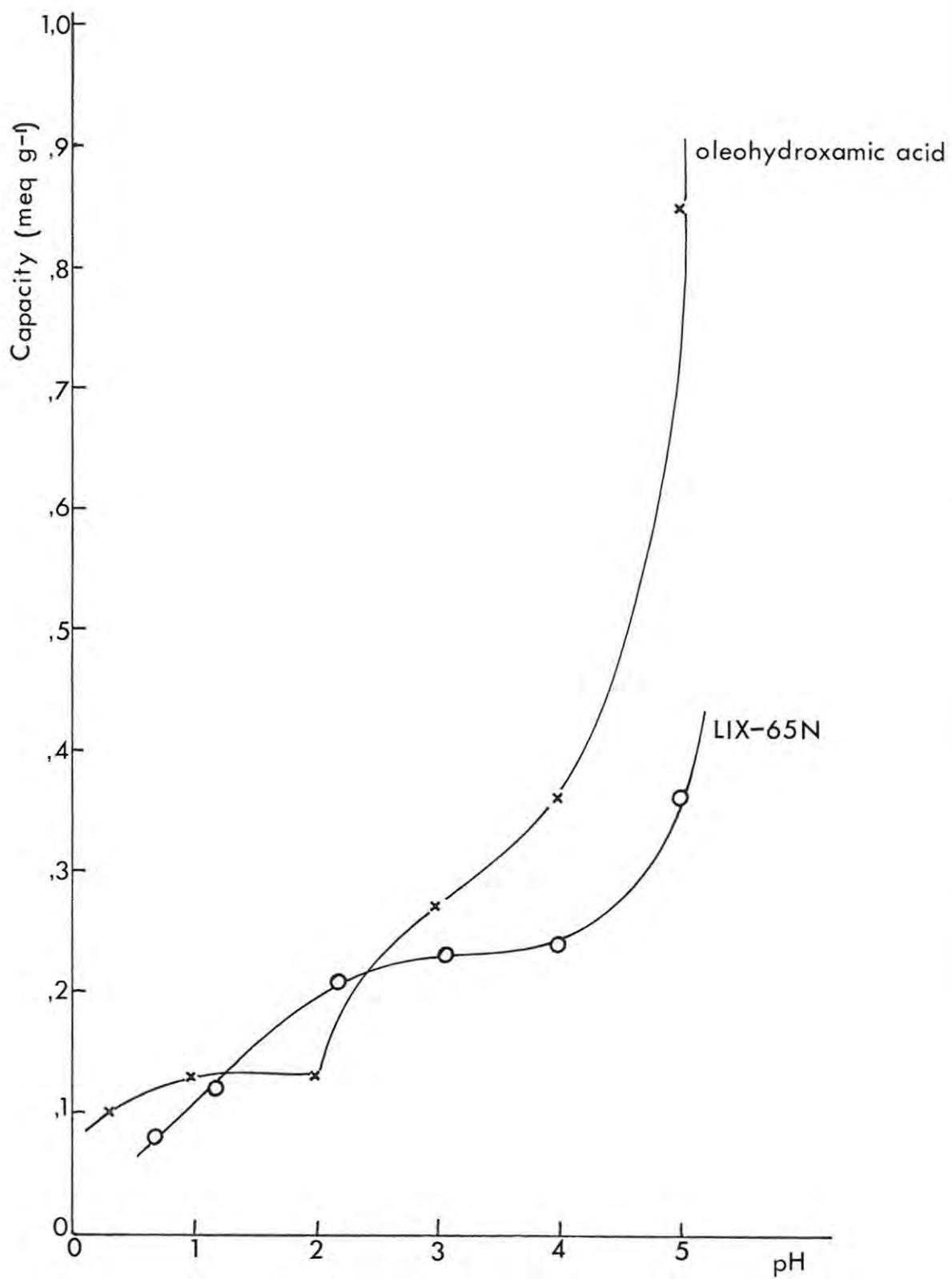


Figure 4.8: Copper capacities as a function of pH.



respectively with 25% LIX-65N and 25% oleohydroxamic acid. Comparison of the contours in Figure 4.8 with the curve for copper in Figure 4.7 shows that no copper is taken up below pH 1 for the distribution coefficient measurement, but certainly is for the capacity measurement. This can be explained in terms of mass action.

However, Vernon and his co-workers^{45,65} plotted capacity versus pH contours and used them for predicting feasible column separations. Vernon and Eccles⁴⁵ measured the capacity for copper, iron, uranium, vanadium, lead, mercury, cobalt and nickel using a poly (hydroxamic acid) ion-exchange resin. They found that the resin was highly selective for vanadium and mercury, and that the capacity against pH contours suggested three different forms of vanadium resinate depending on the pH. The results obtained here for XAD-7 coated with 25% oleohydroxamic acid showed that the resin was highly selective for uranium and iron (III) as well as vanadium. The shapes of the contours in Figure 4.1 suggest three different types of chelate formation, depending on pH, for vanadium and iron (III). Christian and co-workers⁷⁹ postulated the existence of a 1:1 complex of iron (III) with benzohydroxamic acid at low pH, a 1:2 complex at higher pH values and a 1:3 complex at pH values above 3. The formation of a 1:3 complex suggests that the reagent is adsorbed to the resin in such a way as to allow sufficient flexibility for three hydroxamic acid groups to fit around one metal ion. It is to be expected that the 1:3 complex would only form in the presence of excess reagent.

Vernon and Khorassani⁶¹ investigated the solvent extraction of metals with benzohydroxamic acid, caprylohydroxamic acid, stearohydroxamic acid and p-cresoxyacetohydroxamic acid. Their results showed that the hydroxamic acid group is selective for molybdenum and chromium as well as the metals mentioned above.

Vernon and Eccles^{45,64}, using a poly (hydroxamic acid) resin, found that the only way to recover all the vanadium was to destroy the resin. They tried a wide variety of eluting systems, but did not manage to find a suitable eluent. A similar problem was encountered here when an attempt was made to elute the vanadium from the resin after the measurement of distribution coefficients. Even concentrated hydrochloric acid would not remove the metal from the resin. A possible solution might be to strip the resin of the vanadium-hydroxamic acid complex with an organic solvent like ethanol. It should then be possible to determine the vanadium directly by measuring the visible absorbance of the vanadium hydroxamate complex. Grieser and Pietrzyk⁸⁰ measured the adsorption of various organic reagents on XAD-2 resin from water-ethanol mixtures. They found that the degree of retention by the resin decreased as the ethanol concentration increased. Their results suggest that the resin can be stripped of the metal-hydroxamic acid complex by eluting with ethanol.

4.3.7 Column Separations

In Table 4.7 are listed the separations achieved using a column packed with XAD-7 loaded with 25% oleohydroxamic acid. The pH of the separation was chosen with reference to Figure 4.1, so that one metal was selectively absorbed while the other was eluted with buffer of the appropriate pH. Provided the column had sufficient capacity for the absorbed metal, no difficulty was experienced in obtaining quantitative separations. Since most metals form coloured complexes with hydroxamic acids, it was possible to see visually if the column had sufficient capacity for the metal and to see if all the metal had been eluted from the column. Copper formed a tight green band at the top of the column, but when the capacity for copper was reduced, the band spread down the length of the column. Iron (III) formed a dull red complex with the hydroxamic acid. Even a slight trace of iron gave the distinctive colour, hence it was possible to judge when all the iron had been eluted. The separation of copper from iron was easily achieved without using a complexing agent, but it was found that the iron was strongly held on the column and needed to be eluted with 50 - 70 ml of 5M hydrochloric acid. For the separation of lead from copper it was necessary to use a mixture of copper nitrate and lead nitrate solutions. For other separations, copper sulphate solution was used. However, if used for the copper-lead separation, lead sulphate precipitated out.

Table 4.7: Rapid separations of metals using XAD-7 resin impregnated with 25% oleohydroxamic acid. Flow rate, 10 ml min⁻¹. Column dimensions, 11 mm x 130 mm. Copper was eluted with 2M HCL, iron (III) with 5M HCl.

pH	Metal	Taken (mmole)	Found (mmole)	Recovery (%)
4,0	Ni	0,2495	0,2490	99,8
	Cu	0,0998	0,0998	100,0
4,0	Ni	0,2495	0,2495	100,0
	Cu	0,2495	0,2502	100,3
4,0	Co	0,2540	0,2541	100,0
	Cu	0,0998	0,1000	100,2
4,0	Co	0,2540	0,2535	99,8
	Cu	0,2495	0,2501	100,2
3,5	Zn	0,1031	0,1029	99,8
	Cu	0,0998	0,1001	100,3
3,5	Zn	0,2555	0,2550	99,8
	Cu	0,0998	0,1002	100,4
3,0	Pb	0,1003	0,0998	99,5
	Cu	0,1018	0,1021	100,3
3,0	Pb	0,2508	0,2500	99,7
	Cu	0,1018	0,1027	100,9
1,0	Cu	0,2495	0,2485	99,6
	Fe	0,0998	0,0995	99,7
1,0	Cu	0,1000	0,1005	100,5
	Fe	0,0998	0,0993	99,5

Vernon and Eccles⁶⁴ achieved separations of small amounts of metal ions (0.01 mmole) at slow flow rates (1 ml min⁻¹) using a hydroxamic acid chelating resin. The separations in Table 4.6 were achieved at a flow rate of 10 ml min⁻¹ and involved much larger amounts of metal ion.

Separations were attempted using a column packed with XAD-7 resin coated with 60% naphthenohydroxamic acid. However, a precipitate of the metal-hydroxamate complex was present in the effluent and made determination of the eluted metals difficult. Because of the physical loss of hydroxamic acid, the column lost capacity. It is possible that a resin with 25% loading of naphthenohydroxamic acid would be more stable, but the capacity would be too low for the column to be of much practical use.

The separation of iron from vanadium and uranium was not attempted, although Vernon and his co-workers^{64,65} have reported such separations on hydroxamic acid-type resins. Vernon and Eccles⁶⁴ separated iron from vanadium by passing a mixture of the metals in 2M hydrochloric acid through a column of poly (hydroxamic acid) resin. 99% recovery of iron was achieved by elution with 2M hydrochloric acid. They were, however, unable to remove the vanadium from the resin. Because of this difficulty, the separation was not attempted. Since hydroxamic acids have such a high affinity for vanadium, the resin could be used for the removal of vanadium from strong acid solutions. In order to recover the vanadium, the resin would have to be stripped

of the organic layer. Vernon and Kyffin⁶⁵ separated iron from uranyl ions by taking up both metals at pH 3 and selectively eluting the uranyl ions with 2M sodium carbonate. Since this separation does not rely on the selectivity of the hydroxamic acid for one metal over the other, the separation was not attempted, although there should be no difficulty in achieving it.

The column packed with XAD-7 resin loaded with 25% oleohydroxamic acid was also used to concentrate copper from very dilute solution. One ℓ of water containing 0,623 mg of copper was adjusted to pH 5 and was pumped through the column at 45 ml min^{-1} . A faster flow rate could have been achieved if a shorter column had been used. The recovery of copper was 100,8%.

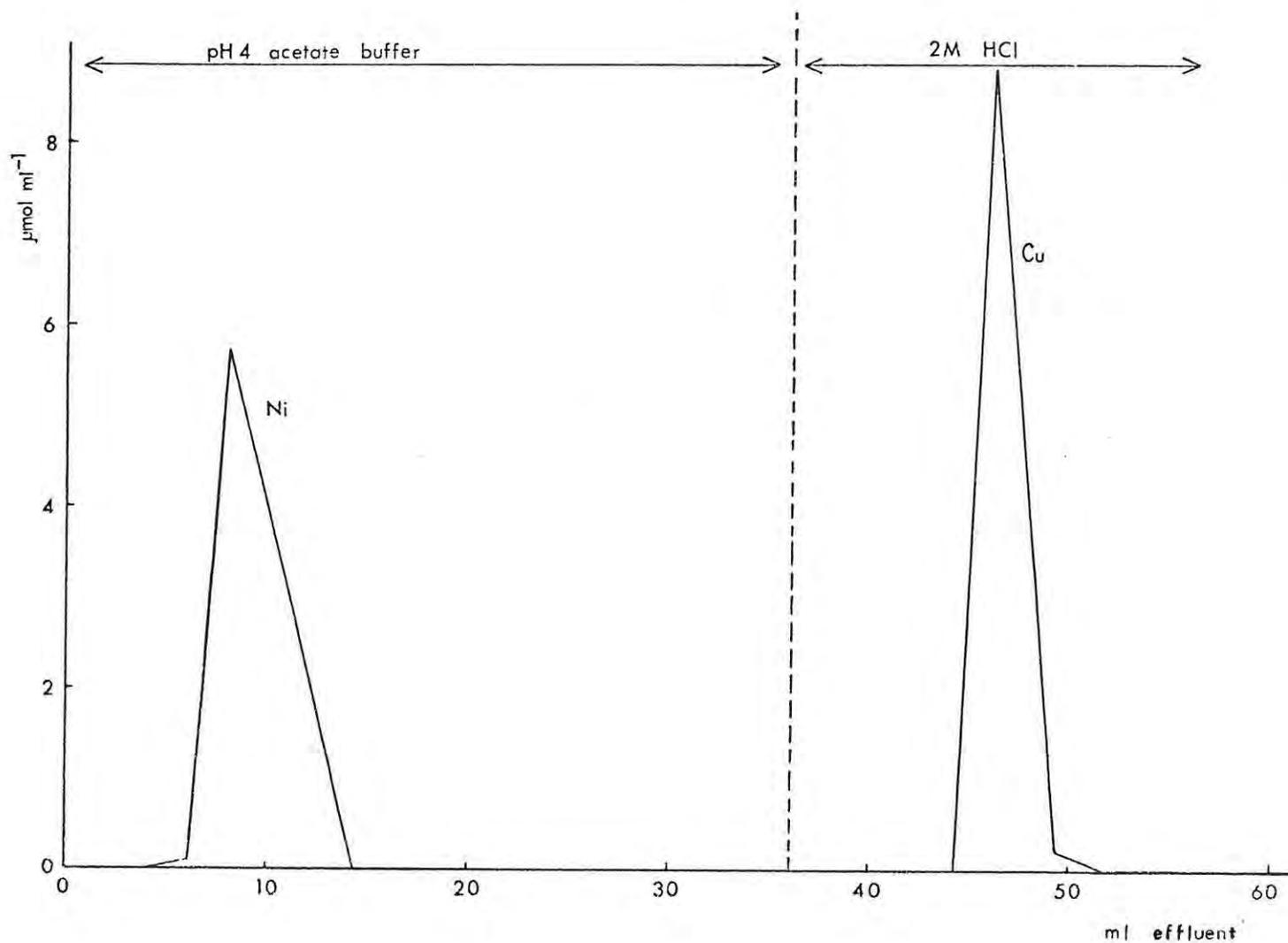
4.3.8 Elution Curves

Selective elution was also possible with the metals listed in Table 4.7. Figure 4.9 shows the selective elution of nickel and copper after both metals were absorbed on the resin at pH 5. The nickel was eluted with pH 4 acetate buffer and the copper with 2M hydrochloric acid. No copper appeared in the effluent until the eluent was changed.

4.3.9 Stability of Macroporous Resins Impregnated with Hydroxamic Acids

Although resins coated with hydroxamic acids have potential for use in columns for the rapid separation of metals, it

Figure 4.9: Selective elution of nickel and copper.
Selective elution of 0,01 mmol nickel and 0,01 mmol copper with pH 4 acetate buffer and 2M HCl from XAD-7 resin loaded with 25% (w/w) of oleohydroxamic acid. Column dimensions: 9 mm x 170 mm. Flow Rate: 1 ml min⁻¹. Particle size of resin: 75 - 150 μm



must be mentioned that difficulty was encountered with the stability of the impregnated resins. The problem was first encountered with the measurement of distribution coefficients. It was noted that the results were not reproducible if a resin was used more than once. To overcome this difficulty, each distribution coefficient measurement was carried out using freshly coated resin. Physical loss of the hydroxamic acid occurred when XAD-7 resin impregnated with N-benzoyl-N-phenylhydroxylamine was used for the measurement of distribution coefficients, since it was noted that a fine precipitate due to the hydroxamic acid-metal chelate complex was present after equilibrium had been achieved. It was thus decided to determine the loading on the resin after equilibration with different solutions. The results are given in Table 4.8. The method of determination of loading was described in 4.2.5.

The physical and chemical stability of the resin poses a problem if the resin is to be of analytical use. It was found that the impregnated resins lost capacity when used in columns for the rapid separation of metals. XAD-7 resin loaded with 60% naphthenohydroxamic acid was physically unstable, since the hydroxamic acid-metal chelate complex was evident as a precipitate in the effluent. The XAD-7 resin impregnated with oleohydroxamic acid appeared to be only slightly physically unstable since determination of the loading after use showed that the percentage loading had decreased from 25 to 20%. However, as can be seen from the results in Table 4.9, the final capacity was only 25%

Table 4.8: The loading of hydroxamic acid on the resin after use.

Resin	Hydroxamic Acid	Initial Loading (%)	Final Loading (%)	Treatment
XAD-7	N-benzoyl-N-phenylhydroxylamine	25	21	Distribution coefficient measurement for copper
Polystyrene	N-benzoyl-N-phenylhydroxylamine	25	3	Copper D measurement
XAD-7	Oleohydroxamic acid	15	11	D measurement
XAD-7	Oleohydroxamic acid	15	8	3 capacity cycles ^a

- a. A capacity cycle refers to equilibration of the resin with excess copper, followed by elution of the absorbed copper with 2M hydrochloric acid.

of the original column capacity. It would thus appear as if the hydroxamic acid functional group was not chemically stable, and was decomposed under the acidic conditions used for the column separations.

Some of the resin that had been used in the column was stripped of its stationary phase by immersing in ethanol. The ethanolic solution was tested by TLC (for method, see 4.2.1.2). Two spots were visible with iodine at R_F values of 0,68 and 0,89. Neither of these values correspond to that obtained for oleohydroxamic acid (R_F 0,39), and neither

spot was visible when the plate was sprayed with iron (III) solution. Although these results clearly show the absence of hydroxamic acid, it is not possible to say definitely that decomposition occurred on the column, since the resin had been dried overnight at 110°C after use in the column.

Very little reference has been made in the literature to chemical stability in acid media.

Table 4.9: Loss of capacity for copper by columns packed with XAD-7 resin loaded with hydroxamic acids.

Hydroxamic acid	Loading (%)	Initial Capacity (meq g ⁻¹)	Number of Cycles ^a	Final Capacity (meq g ⁻¹)
Oleohydroxamic acid	25	1,21	13 17	0,44 0,30
Naphthenohydroxamic acid	60	0,85	7	0,60

- a. A cycle refers to the absorption of a metal on the resin, followed by elution of the metal.

According to the Italian workers, Gasparini and Polidori⁵⁸, the hydroxamic acid function exhibits poor stability with respect to acidic and oxidant solutions. Unfortunately they do not quote a reference to support their statement. They did, however, perform a series of studies on the chemical

stability of hydroxamic acids in different acid concentrations in order to show that the branched-chain trialkylacetohydroxamic acids were stable. They compared the results obtained for the branched-chain hydroxamic acids with those obtained for the straight-chain n-dodecanohydroxamic acid, and showed that the straight-chain hydroxamic acid decomposed far more rapidly than the trialkylacetohydroxamic acids. The increased chemical stability is believed to be due to the steric hindrance of the substitutions at the hydroxamic group. Although the branched-chain hydroxamic acids have the advantages of increased stability and increased solubility in organic solvents, one would expect the formation of the metal chelate to be hindered and the kinetics of extraction to be slower. Baroncelli and Grossi⁵⁹ investigated the solvent extraction of uranium (VI) with neotridecano-hydroxamic acid, but ignored the kinetics of extraction. They assumed that equilibrium was reached extremely rapidly.

Reference to the chemical stability of N-benzoyl-N-phenylhydroxylamine was made by Šebesta and Pošta¹⁶. They used a column of teflon impregnated with N-benzoyl-N-phenylhydroxylamine in chloroform for only one separation because they thought that the concentration of the hydroxamic acid in chloroform might decrease due to decomposition in concentrated mineral acid solutions. The two references which they quoted^{81,82} to support their assumption make no mention of the acid decomposition of N-benzoyl-N-phenylhydroxylamine. Both the papers mentioned deal with the

extraction of hafnium and other actinides from concentrated acid solutions. Reference is made to the fact that the solubility of the metal-hydroxamic acid complex in the aqueous phase increased as the acid concentration was increased.

Vernon and Eccles, in their paper describing the synthesis of a poly (hydroxamic acid) resin⁴⁵, made the claim that their resin was vastly superior to previous ones which were unstable toward relatively concentrated acids.

The physical instability of impregnated resins has tended to be a weakness in extraction chromatography, although some resins appear to be reasonably stable^{2,35}. Vernon and Eccles²⁰ found that the capacity of the resin coated with steorohydroxamic acid decreased from 9,3 mg g⁻¹ to 5,7 mg g⁻¹ after five 24 hour loading-acid washing cycles. They came to the conclusion that it was not suitable to use a crystalline solid such as steorohydroxamic acid for extraction chromatography. This is obviously an area in which more work must be done.

5. CONCLUSION

In this research, XAD-7 loaded with LIX-64N was found to be the most suitable support of the Amberlite XAD series. The rapid uptake of copper correlated with the high water regains of the bare and coated resins. It was found that the rate decreased with increased loading, but that the rate of uptake of copper was satisfactory up to 60% loading (w/w) for XAD-7.

XAD-7 coated with 25% LIX-65N can be recommended for use in columns. The resin was stable and separations of copper from iron (III), nickel, cobalt and magnesium were achieved at flow rates of 10 ml min^{-1} . Each separation was completed in 15 min. Since the use of purified LIX-65N or the addition of LIX-63 had no noticeable effect on the rate of uptake of copper, the use of the commercial LIX-65N can be recommended.

The reaction between hydroxylamine and a long-chain ester was used to synthesise hydroxamic acids. It was found that the reaction was complete within a few minutes, and that it was not necessary to let the reaction go for several days. In order to get maximum yield, it was necessary to keep the temperature low and to use a molar excess of base. The saturated stearo- and erucohydroxamic acids were too insoluble in organic solvents to be coated on the resin. Use of a diluent facilitated impregnation, but was deleterious

to the rate of uptake of copper. N-benzoyl-N-phenyl-hydroxylamine coated more easily on a macroporous polystyrene-type resin than on XAD-7, but had a slower rate of uptake of copper.

XAD-7 loaded with 25% oleohydroxamic acid was used to measure the distribution coefficients at varying pH values for eight different metals. The hydroxamic acid was particularly selective for iron (III), uranium and vanadium. The resin had such affinity for vanadium that the metal ions could not be eluted from the resin. It might be possible to develop an analytical procedure for determining vanadium using this resin. Vanadium could be taken up exclusively by the resin from strong acid solutions. The resin could then be stripped of the vanadium-hydroxamate complex using ethanol. The concentration of the vanadium-hydroxamate complex in ethanol could then be determined spectrophotometrically.

Although the XAD-7 resin loaded with oleohydroxamic acid was successfully used in columns for several separations, the resin was chemically unstable and lost capacity. It is possible that the branched-chain trialkylacetohydroxamic acids recommended by Gasparini and Polidori⁵⁹ will be more stable. Before hydroxamic acids can be recommended for use as stationary phase in extraction chromatography, more research will have to be done into their chemical stability.

6. BIBLIOGRAPHY

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