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THE EXTRACTION AND SEPARATION OF COPPER AND CADMIUM CHELATES BY THE USE OF POLYURETHANE FOAM

by

GERALD N.LYPKA

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GERALD N. LYPKA

A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

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Abstract

Open pore polyurethane foam was shown to act as a stationary phase for a modified solvent extraction process. Cupric and cadmium acetylacetonates were extracted from aqueous solution using untreated foams. Foams pretreated with benzoylacetone quantitatively absorbed copper and cadmium from aqueous solution. Separation of a copper / cadmium system was achieved using benzoylacetone treated foams.

The Extraction and Separation of Copper and Cadmium Chelates by the use of Polyurethane Foam

Introduction

The use of porous polymeric material as a rigid support in chromatography was first reported in 1966 by Hollis[1], who used porous polystyrene beads in gas-liquid chromatographic columns. Ross and Jefferson[2] next prepared 'in-situ' formed rigid open pore polyurethane for gas chromatograph columns. This type of column was subsequently used for separations of compounds such as alcohols, metal chelates, and aromatics[3]. Ross[4] has also studied the effects of altering synthetic conditions on the separation properties of rigid open pore polyurethane in gas chromatograph columns.

Lynn, Rushneck, and Cooper[5] have used 'in-situ' formed rigid open pore polyurethane in liquid chromatography for the separation of dichloroanilines using n-heptane or isopropanol as solvents.

Bowen[6] was the first to use flexible open pore polyurethane foam as a selective absorbant for a number of substances from dilute aqueous solutions. Flexible polyether-based foams were found to absorb substances which can be extracted from aqueous solution using diethyl ether, e.g. iodine, benzene, chloroform, and phenol from water; mercury (II) and gold (III) from 0.2 M hydrochloric acid; iron (III), antimony (V), thallium (III), molybdenum (VI), and rhenium (III) from 6 M hydrochloric

acid; and uranium (VI) from saturated aluminum nitrate solution. Subsequently Bowen used polyurethane foam for the extraction of gold from mine wastes at the 0.02 mg/kg level[7]. Recovery of the gold was determined using radiochemical methods. The extraction procedure consisted of shaking the solution with the foam, which effected a 38% recovery.

Schiller and Cook[8] have used flexible polyurethane foam in a preconcentration technique for analysis of trace amounts (ppb range) of gold in natural waters. Absorption was done from acid solution, both 6 M and 0.2 M hydrochloric acid, followed by activation analysis.

Flexible polyurethane foam has also been used for the extraction and recovery of polychlorinated biphenyls (PCB) by Gesser et al[9]. PCB in the ppb range was absorbed onto the foam from aqueous solution, and was then eluted with acetone and hexane, followed by gas chromatograph analysis using electron capture detectors. This method has also been applied to the analysis of raw river water for PCB and organochlorine pesticides[10].

Uthe, Reinke, and Gesser[11] have used porous polyurethane foams coated with chromatographic grade greases for the extraction of organochlorine pesticides from water. Reinke, Uthe, and O'Brodovich[12] used coated foams as field monitors for organochlorine pesticide and PCB contents of streams.

More recently, Musty and Nickless[13] have compared the ability of six polyurethane foams of different bulk densities and surface areas, both uncoated, and coated with silicon oil, to

recover organochlorine insecticides and PCB from water, under varying flow rates and pH's. It was shown that extraction efficiency was related to the surface area.

Braun et al have done extensive studies on the use of open pore polyurethane foam as a solid support for reverse phase partition chromatography[14].

A separation of nickel and palladium was achieved at the mg/ml level using tri-n-butyl phosphate as the stationary phase and polyurethane as the solid support[15]. Foams loaded with tri-n-butyl phosphate were also utilized in the separation of a palladium, bismuth, and nickel mixture[16]. The initial solvent was 0.1 M perchloric acid - 3% thiourea - 1% sodium perchlorate. Using this solvent, bismuth and palladium were retained on the foam, while the nickel passed through. The bismuth complex was then eluted with 0.5 M perchloric acid, and the palladium was recovered by elution with water. Recovery of milligram amounts of metal was quantitative.

Tri-n-butyl phosphate loaded foams have also been used for the chemical enrichment and separation of the gold-thiourea complex from acidic solutions[17][18]. It was shown that 100 μg of gold in one liter of a solution of 0.1 M perchloric acid, 3% thiourea, and 1% sodium perchlorate could be quantitatively retained by the column. It was also possible to quantitatively separate trace amounts of gold from high concentrations of Zn^{+2}, Co^{+2}, Ni^{+2}, Fe^{+3}, Sb^{+3}, Cu^{+2}, Bi^{+3}, and Pd^{+2}. The gold was recovered by dissolution of the foam in nitric acid.

Braun has used tri-n-butyl phosphate loaded foams for the separation of iron from copper, cobalt, and nickel in a hydrochloric acid system[19]. Iron (III) ions were retained on the foam in 4 M hydrochloric acid, whereas at this acid concentration nickel, copper, and cobalt pass through the column quantitatively. The iron can then be eluted with 0.01 M hydrochloric acid. Milligram amounts of iron were quantitatively recovered.

Foams pretreated with tri-n-octylamine have been used to separate trace amounts of cobalt from nickel in hydrochloric acid solution.[20] Separation was shown to be possible when the ratio of nickel to cobalt ranged from 1 to 10^8. The nickel was eluted from the column with 8 M hydrochloric acid, and the cobalt with 1 M hydrochloric acid.

Collection of trace amounts of silver on dithizone treated foams has been done by Braun[21]. Zinc dithizonate was dissolved in various plasticizers and loaded on polyurethane foam. The foams were then used successfully for rapid and quantitative collection of trace amounts of silver in batch and column experiments. The preconcentration of small amounts (0.01 μg) of silver from dilute aqueous solutions was also found to be possible. The effects of different plasticizers, pH of the aqueous phase, and dithizone concentration were critically investigated. It was found that the effect of the plasticizer decreases in the order α-dinonylphthalate > tri-n-butylphosphate > di-n-octylphthalate. The best pH range for extraction proved to be

4.5 to 6.5. The collection rate of silver was found to increase when the dithizone concentration decreased, probably due to the corresponding increase in the plasticizer/dithizone ratio.

A similar study was done for the collection of mercury traces on dithizone and diethyldithiocarbamate foams[22]. The effect of pH, plasticizer, and chelating agent concentration on the collection rate of mercury was critically investigated. The capacity for mercury (II) of a tri-n-butylphosphate plasticized zinc dithizone foam at pH 6 was found to be 2.34 μeq. g^{-1}. It was also shown that traces of mercury (II) could be collected rapidly and quantitatively by diethyldithiocarbamate foam[22].

Braun has loaded foams with tetrachlorohyroquinone, and used this system in redox columns[23][24]. Reduction of Ce (IV), V (V), and Fe (III) was carried out quantitatively and rapidly at the micro and semimicro levels. The effects of flow rates and temperature on extraction efficiency were also determined. For 5 ml of a 0.0851 N $Ce(SO_4)_2$, the cerium was completely reduced at flow rates from 2 to 13 ml/min. at room temperature. The reduction of 5 ml of 0.0853 N ammonium vanadate was only complete at flow rates between 2 and 4 ml/min. at room temperature. An increase to 35° C gave complete reduction at flow rates as high as 9 ml/min. Iron (III) reduction at room temperature was only complete for flow rates up to 2 ml/min. , but at 35° C the rate could be increased to 6 ml/min.

Braun has also prepared ion-exchange foams by the direct and indirect introduction of functional groups/ionogenic groups

in the foamed backbone structure of the polymer[25]. Commercially available phenol-formaldehyde foam was sulphonated to give sulphonic acid groups bound to the foam, the ion exchange capacity being 1.85 meq/g. Indirect introduction of the ionogenic groups was done by carrying out a polymer analogue reaction after joining the foam to an easily transformable polymer. Styrene-polyurethane interpolymer foam was thus prepared, and anion exchange groups introduced by chloromethylation and amination. Radiation grafting of open cell polyurethane and closed cell polyurethane foams with methacrylic acid was also investigated[25].

Polyurethane - Varion KS heterogenous cation exchange foam was then used for separation of Cd (II), Zn (II), Fe (III), and Cu (II) in aqueous and alcoholic solutions, and the corresponding distribution ratios were determined and compared to values obtained for the conventional bead exchanger[26]. It was found that the cation exchange foam columns seem to work more efficiently than the common cation-exchange bead columns for separation, though the exchange distribution coefficients were similar.

Polyurethane foam has been used by Braun as an enert support for isotope exchange separation[27]. A very fine precipitate of silver sulphide was immobilized on the foam, and the extraction of various concentrations of radiosilver from 0.1 M nitric acid solution at 20 ml cm^{-2} min^{-1} flow rates studied. It was found that the radiosilver was quantitatively retained.

Braun has recently developed 'Chromofoams', which consist of chromogenic organic reagents immobilized in plasticized open

cell polyurethane foams[28]. These foams have been shown to have comparable or superior qualities to normal spot tests when batch techniques are used. Foam columns can be used for the detection and semiquantitative determination of trace amounts of metal ion, as shown by the use of these foams for the detection of zinc (II) and lead (II) with dithizone, copper (II) with rubeanic acid, and cobalt (III) with thiocyanate-Amberlite LA-1.

Mazurski, Chow, and Gesser have studied the extraction of mercury from aqueous solution using sulfide-treated polyurethane foam[29]. Sulfhydryl groups were generated in the foam by an electrical discharge in a hydrogen sulfide atmosphere. It was shown that the adsorption of mercury (II) chloride in the 4.0 to 0.0004 ppm range, and methylmercury (II) chloride in the 2.0 to 0.0004 ppm range was generally quantitative. Recovery of the mercury was done by elution with 2 M hydrochloric acid.

Chow and Buksak [30] have used diphenylthiocarbazone treated polyurethane foams for the extraction of mercury and methylmercury from aqueous solution. Extraction is quantitative over a pH range from 1 to 10 for mercury concentrations below 10 ppm. The absorbed mercury can be recovered by elution with acetone. This method was also shown to be acceptable for recovery of both mercury (II) and methylmercury from domestic water, river water, raw sewage, and secondary sewage.

Polyester polyurethane foam has been found to be a suitable matrix for the immunoadsorption of cells[31]. It was found that untreated foams had a high affinity for erythro-

cytes, but that this nonspecific affinity could be reduced by pretreating the foam with various polyanions. Immunospecific binding was achieved by adding anti-erythrocyte antibody to a gum arabic solution used to protect the foam.

Polyurethane foam could also be used in the preparation of an immobilized (insolubilized) cholinesterase [32][33]. The enzyme was immobilized by the use of a starch matrix, and placed on a urethane foam pad. This system had the advantage over a free enzyme system of lengthening the time the enzyme retained its activity.

Grégoire and Chow[34] have used silicone rubber foam in a system analogous to that for polyurethane foam. Dimethylglyoxime treated silicon foam was used in the separation of platinum and palladium in 10^{-4} M hydrochloric acid, the palladium being retained while the platinum passed through. The palladium could be recovered by elution with 8 M nitric acid.

There have been numerous reports on the use of solvent extraction methods on metal systems, as indicated by the large number of papers, reviews, and books published on the subject[35][36][37]. In view of the wide applicability of solvent extraction systems, it was considered desirable to determine whether an open pore polyurethane foam system could act as a stationary phase for a modified solvent extraction process.

The compound 2,4-pentanedione (acetylacetone) was first used as a chelating agent by Steinbach, who studied the extractions

of the chelates of Cr(III), Co(III), Fe(III), Cu(II), Be, Al, Ga, In, V, Zn, and Zr as functions of pH, ionic strength, and temperature[38][39][40]. A similar study on other metals, including Cu(II), Bi(III), Hf(IV), Fe(III), La, Pb, Pr, Zn, and Zr was done by Krishen[41].

Brown Steibach, and Wagner have studied the distribution of Er, Yb, Ho, Pr, Dy, Tb, Gd, Sn, and Nd in water/acetylacetone systems[42]

Jaskolska, Wodkiewicz, and Minczewski have used acetylacetone as a chelating solvent in the determination of As, Sb, Cu, Ga, Mo, Zn, Sn, and Au trace impurities in semiconductor materials[43].

Stary and Hladky have done a systematic study of the extraction of Be, Mg, Ca, Sr, Ba, Sc, La, Ti, Zr, Th, Cr, Mo, U, Mn, Co, Fe, Ni, Pd, Cu, Zn, Ag, Cd, Hg, Al, Ga, In, Tl, Sn, Pb, and Bi by 0.100 M solutions of acetylacetone in benzene in relation to the pH values for extraction[44][45]. The extraction constants and two-phase stability constants were calculated.

The use of 1-phenyl-1,3-butanedione (benzoylacetone) for the solvent extraction of metals has also been extensively studied by Stary. The solvent extraction of 30 metal systems by 0.100 M benzoylacetone solutions in benzene as a function of pH has been reported [45][46]. Extraction of cadmium by benzoylacetone has also been reported by Rudenko and Stary[47][48], using 0.100 M solutions of benzoylacetone in carbon tetrachloride

and chloroform. It was found that the $pH_{1/2}$ values for 0.100 M solutions of benzoylacetone in benzene, chloroform, and carbon tetrachloride were 8.48, 8.93, and 8.48, respectively. The values of log K, where K is the extraction constant equal to :

$$\frac{[MA_n]_{org}\,[H]^n}{[M]\quad[HA]^n_{org}}$$

where M^{n+} is the metal ion

HA is the organic reagent

MA_n is the uncharged chelate

were found to be -14.92, -15.83, and -14.90, respectively[45][47][48].

Stary has also investigated the solvent extractions of Be, Mg, Ca, Sr, Ba, Sc, La, Ti, Zr, Th, V, Nb, Cr, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Cd, Hg, Al, Ga, In, Tl, Pb, and Bi with 0.100 M oxine in chloroform[49][45]. The effects of pH and oxine concentration were studied, and the extraction constants and stability constants of the metal complexes calculated.

The unpublished work in this laboratory on the extraction and recovery of gallium by open cell polyurethane foam systems seemed to indicate that the foam could act as a solid organic phase for solvent extraction.

It is recognized that the "solvent" effect of a polyurethane foam system for metal chelates will be different than that for benzene, carbon tetrachloride, or ether, but it was believed that some parallel trends would occur if the foam acted in an analogous fashion to an organic phase in solvent extraction.

Polyurethanes are produced by the step growth polymerization of polyisocyanates and polyols. The mode of propagation involves the addition of a hydroxyl group to an isocyanate to yield a substituted amide ester of carbonic acid, i.e. polyurethane.

Equation 1)

$$R-NCO + R'-OH \longrightarrow R-\overset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R'$$

It was thought that the polyester or polyether backbone might exhibit similar properties to free esters or ethers in solution, and thus act as a solid organic phase for a metal chelate extraction process.

Experimental:

Apparatus and Reagents

Model 306 Perkin Elmer Atomic Absorption Spectrophotometer

Varian Techtron Hollow Cathode Lamps

Fisher Accumet Model 520 Digital pH Meter

Varian E-3 Electron Paramagnetic Resonance Spectrophotometer

Unicam SP 500 Series 2 U.V. and Visible Spectrophotometer

Fisher Scientific Certified Buffer Solutions

Acetylacetone, Fisher Scientific Company

Benzoylacetone, J.T. Baker Chemical Company

8-hydroxyquinoline, May and Baker Ltd., Dagenham, England

Cupric acetylacetonate, MacKenzie Chemical Works, Inc., New York

Cadmium acetylacetonate, Research Organic/Inorganic Chem. Co.

Gallium metal, 99.9999%, Research Inorganic Chemical Co.

Beryllium sulphate · $4H_2O$, Analar (British Drug Houses Ltd.)

Silver nitrate, J.T. Baker Chemical Co.

Foams were obtained from the B.F. Goodrich Company, Canada, in the form of 2-inch thick sheets, code number 1338, density 1.20 - 1.35 lb/cu. ft.

"diSPo" plugs were obtained from Canlab, Winnipeg, and were 2.2 cm. long and 4.0 cm. in diameter.

Pyrex columns, 40 mm. outside diameter and 50 cm. in length were made, and fitted with teflon stopcocks.

All chemicals used were of reagent grade unless otherwise specified. The water was doubly-distilled, and passed through an ion exchanger; Research Model I , Illinois Water Treatment Company.

Preparation of Standard and Sample Solutions

A 1169 ppm Cu^{2+} stock solution was prepared by dissolving copper wire, 99.9 % A.C.S. (Matheson, Coleman, and Bell) in nitric acid, evaporating to dryness, then dissolving the residue in 0.1 M hydrochloric acid.

A 1000 ppm Cd^{2+} stock solution was prepared by dissolving cadmium metal, 99.9 % (J.T. Baker) in a minimum amount of hydrochloric acid, then making the solution to volume using 0.1 M hydrochloric acid.

Sample solutions were brought to the desired pH with potassium hydroxide solution or hydrochloric acid as required. The pH values given are accurate to $\pm$ 0.02 pH units.

General Procedure

Foam plugs, 40 mm. in diameter and 50 mm. in length, average weight 1.4590 $\pm$ 0.0095 gm., were cut from the foam sheets. Prior to use, the plugs were soxhlet extracted with acetone for six hours, then air dried.

Acetylacetone was purified according to the procedure used by Steinbach and Freiser [38]. Two hundred ml. of acetylacetone was shaken with 100 ml. of dilute 1:10 ammonia, followed by two successive 100 ml. portions of distilled water. The acetylacetone was then distilled, and the portion which came off at 135-137° C was collected.

Experiments were done by placing the foams at the bottom of the column, adding the trial solution, then compressing the foam with a glass rod to 'open' it. After air bubbles no longer emerged, the rod was removed, and the foams allowed to expand to their normal size.

For static system experiments, 50.0 ml. of metal solution was used,normally either 3.51 ppm. copper or 2.50 ppm. cadmium. The fluid capacity of a single foam was about 60 ml., ensuring that all the sample solution was in contact with the foam. Contact time was two hours, after which the column was squeezed dry.

The amount of metal extracted was usually determined by measuring the concentration of the metal solution before and

after exposure to the foam. In cases where very dilute metal solutions were used, the original concentration was determined by dilution of a solution of known concentration. Solutions were analyzed under standard conditions as listed in the Perkin Elmer Handbook [50]. A two second integration mode was normally used, and the average of three or more of such instrumental readings reported.Where deviations are reported, the deviation is an average of three or more separate solutions. Matrix matching between standard and sample solutions was done whenever necessary.

Flow-through systems consisted of wetting the foam with water at the desired pH, then passing 50.0 ml. of trial solution through the foam, followed by a pH adjusted water solution again. One hundred ml. aliquots of effluent were collected and analyzed until no more metal was detected in the solution.

Metal recovery from the foam was normally done using the following procedure: The metal was first absorbed by the system, using either a flow-through or static process, and the foam squeezed as dry as possible, using a glass rod. The amount of solution left on the foam was calculated by measuring the amount which could be recovered by squeezing the foam. The amount left would be the difference between the amount put on and the amount recovered. The metal concentration of the solution left on the foam was assumed to be the same as the metal solution that passed through the foam system. Fifty ml. of 1.5 N hydrochloric acid

was then placed in contact with the foam for two hours, in a static system, after which the foam was again squeezed dry. The total volume of acid was then calculated to be the 50.0 ml. of acid added plus whatever amount of original solution that had remained on the foam. The acid remaining on the column was assumed to have the same concentration of metal as the acid which came off the column. The total amount of metal recovered was calculated by using the concentration of the metal in the acid, and the total volume of the acid.

Pretreatment of the foams with ligand was achieved by soaking the foams in an acetone solution of ligand, draining them, and then drying under vacuum.

Part I : The Extraction of Copper and Cadmium Acetylacetonates by Open Pore Polyurethane Foam

1) Extraction of Copper and Cadmium Acetylacetonates by Untreated Polyurethane Foam

Introduction

Various metal acetylacetonates in aqueous solution were passed through foam plugs in an attempt to determine which, if any, would be extracted by the foam. Metals studied were Fe(III), Fe(II), Co(II), Al(III), Zn(II), Zr(IV), Mn(II), and Ni(II). It was found that copper, ferric, cadmium, aluminum, and possibly zinc acetylacetonates were partially absorbed by the foam. Of these, copper and cadmium were studied more extensively, as extraction seemed to be more effective for these two.

Experimental

A saturated solution of copper acetylacetonate, $(Cu(acac)_2)$, was prepared by allowing distilled water to stand over excess $Cu(acac)_2$ for 48 hours, after which the solution was filtered through Whatman #42 filter paper, and the pH adjusted. The copper concentration was determined by atomic absorption analysis to be 2.32 ppm.

A similar procedure was followed for preparation of a saturated cadmium acetylacetonate solution, except that the concentration of the filtered solution was diluted to 2.65 ppm in cadmium.

The solutions were placed on the foam using a static system, with results shown in Figure 1.

Results and Discussion

Figure 1 indicates that absorption of acetylacetonates onto the foam is a pH dependent phenomena. The curves for both the copper and cadmium systems seem to reach a maximum at pH 10.0. The equilibrium reactions in solution are:

Equation 2) $Cu^{+2} + (acac)^{-1} \rightleftharpoons Cu(acac)^{+1}$ $\log K_1(20°)$ 8.31[51]

Equation 3) $Cu(acac)^{+1} + (acac)^{-1} \rightleftharpoons Cu(acac)_2$ $\log K_2(20°)$ 6.85[52]

Equation 4) $(acac)^{-1} + H^{+} \rightleftharpoons$ acetylacetone $\log K\ (20°)$ 9.02[52]

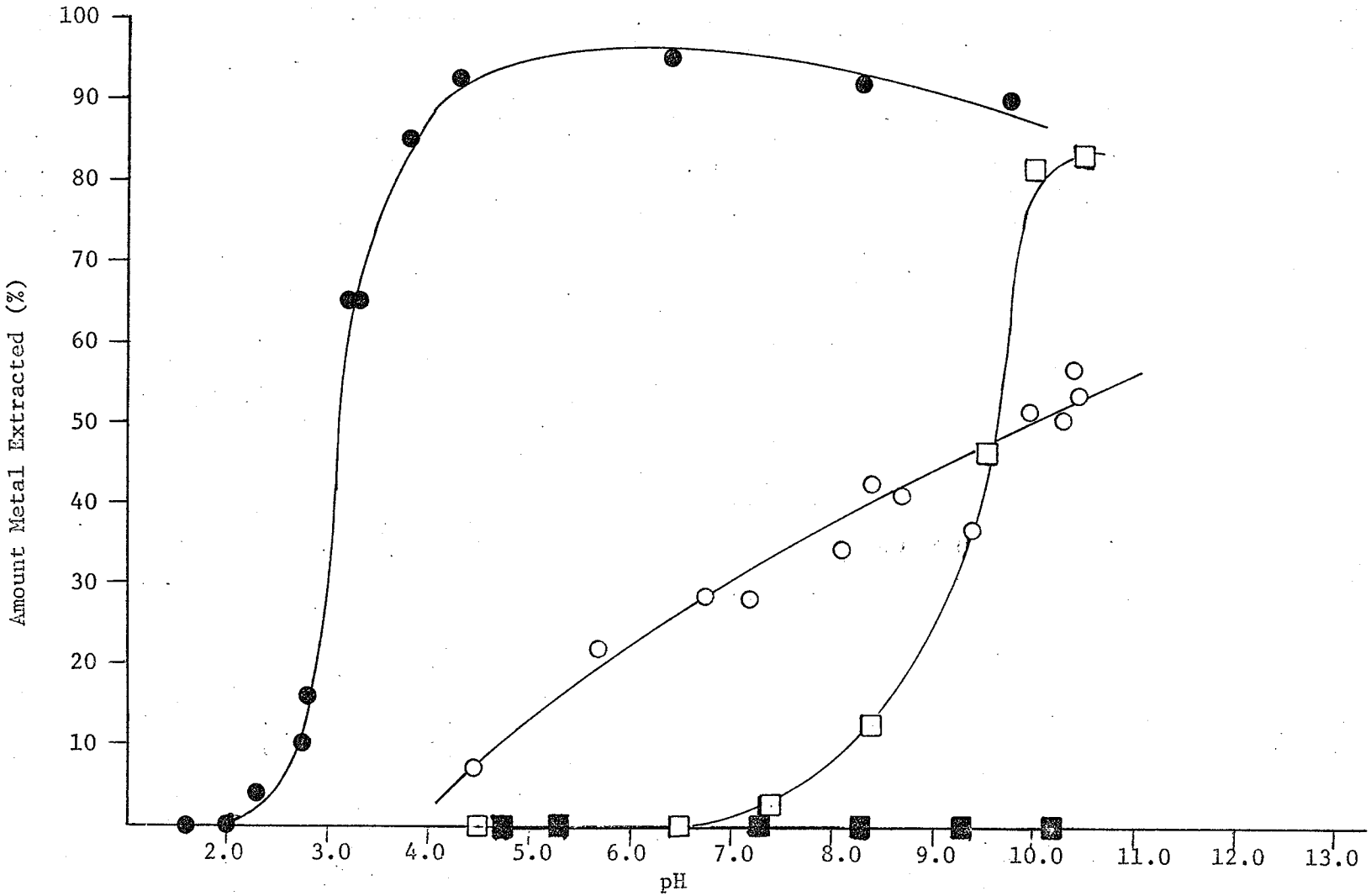
Increasing the pH would tend to favour the formation of $(acac)^{-1}$, Equation 4, by decreasing the H^{+} concentration. This in turn would shift the equilibrium in Equation 3 in favour of $Cu(acac)_2$ formation.

The results indicate that the species retained by the foam is the metal acetylacetonate, rather than the metal itself.

A comparison with the solvent extraction systems[44][45] for the extraction of copper and cadmium by acetylacetone in benzene indicates that, in the case of cadmium acetylacetonate, extraction is much greater for the foam system. Extraction of copper acetylacetonate, on the other hand, has a reverse trend. Extraction has decreased for the foam system, compared to the solvent extraction system. Extraction seems to start at approximately the same pH for both, but the foam system has a smaller amount of extraction at its optimum pH, and has a much higher optimum pH.

Figure 1

The pH Dependent Curves for Extraction of Copper and Cadmium Acetylacetonates into Polyurethane Foam Compared to the Corresponding Solvent Extraction Systems


Amount Metal Extracted (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
pH
Copper, Foam System
Copper, Solvent Extraction System (44)
Cadmium, Foam System
Cadmium, Solvent Extraction System (44)

2) Extraction of Copper and Cadmium by Untreated Polyurethane Foam

Introduction

The absorption of copper and cadmium in aqueous solution by untreated foam was run as a check to determine whether the retention of the metal by the foam was due to interaction between the foam and the metal ion, or if the ligand was the factor causing retention.

Experimental

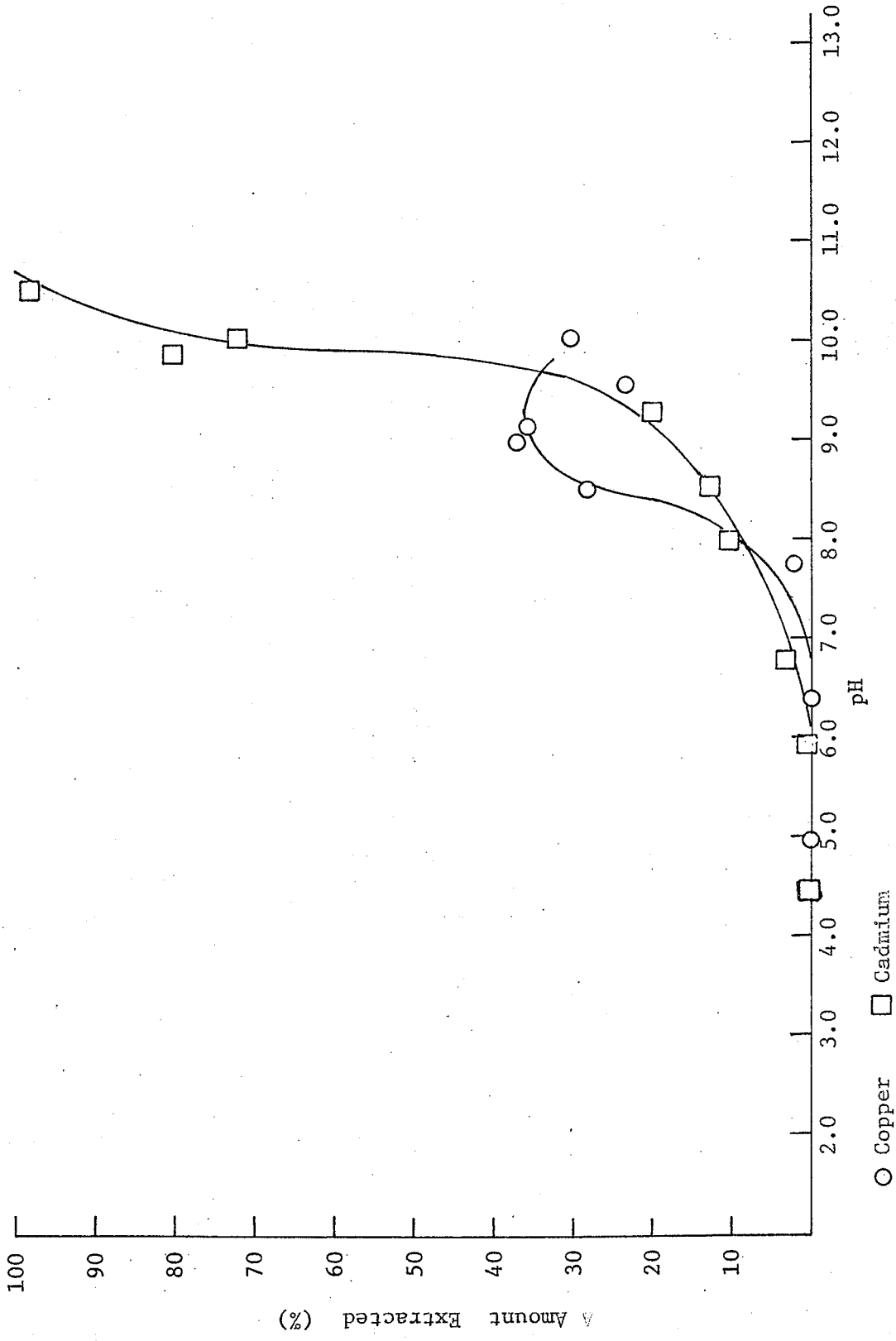
Copper and cadmium standard solutions were made up, 3.51 ppm. Cu and 2.50 ppm. Cd, and the pH's adjusted. Static absorption conditions were used, with results shown in Figure 2.

Results and Discussion

Copper and cadmium pH dependent extraction curves were somewhat similar to those obtained for the acetylacetonate systems, Figure 1. The copper acetylacetonate curve does have a higher maximum than the curve for copper ions, as well as starting at a lower pH, indicating some ligand effect. The cadmium extraction curves are almost identical, suggesting that absorption in this case is not determined by the same factors affecting copper absorption. Absorption in this case seems to be due to a factor inherent in the foam itself, rather than retention of a metal chelate.

Figure 2

The pH Dependent Curves for Extraction of Copper and Cadmium Ions by Untreated Polyurethane Foam


% Amount Extracted (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
pH
O Copper
□ Cadmium

3) Effect of Excess Acetylacetone on the Extraction of Copper by Untreated Polyurethane Foam

Introduction

As previously indicated, the species retained by the foam seems to be the copper acetylacetonate, rather than the metal ion. As verification, experiments were done using copper acetylacetonate solutions with excess acetylacetone present, and also copper solutions to which acetylacetone was added. Absorption should be consistent with equilibrium shifts.

Experimental

Acetylacetone in various concentrations was added to solutions of $Cu(acac)_2$, 2.34 ppm. in copper. A flow-through system, rate 2 ml./min., was used, with results shown in Table 1.

Various concentrations of acetylacetone were added to dilute solutions of copper, 0.117 ppm., and the solutions allowed to stand for two hours to equilibrate. One hundred ml. of solution was then passed through the foam, using a flow-through system with a flow rate of 2 ml./min. Results are tabulated in Table 2.

Results and Discussion

Data from Table 1 shows that as the concentration of acetylacetone increases, absorption of copper decreases. A large excess of acetylacetone results in no detectable absorption of copper. Addition of even a small amount of acetylacetone

Table 1 : The Effect of Excess Acetylacetone on Extraction of Copper Acetylacetonate by Polyurethane Foam

Copper Concentration of Sample Solution	Volume of Sample Solution (ml)	Concentration of Acetylacetone	pH	Amount of Cu Absorbed (moles)	Percent Cu Absorbed
3.23×10^{-5} M	100	0.0975 M	8.00	nil	--
3.23×10^{-5} M	100	0.292 M	8.00	nil	--
3.23×10^{-5} M	100	0.682 M	8.00	nil	--
3.68×10^{-5} M	100	9.75×10^{-5} M	8.50	7.71×10^{-7}	20.9
3.68×10^{-5} M	100	9.75×10^{-4} M	7.90	6.92×10^{-7}	18.8
3.68×10^{-5} M	100	4.87×10^{-3} M	7.50	5.43×10^{-7}	13.2
3.68×10^{-5} M	100	9.75×10^{-3} M	7.30	4.09×10^{-7}	11.1

Table 2 : The Effect of Addition of Acetylacetone to Solutions of Copper Prior to Absorption by Polyurethane Foam

Concentration of Acetylacetone	Stoichiometric Ratio of Acetylacetone to Copper	pH	Amount of Copper Extracted (moles)	Percent Copper Extracted
nil	0:1	10.01	$1.31 \pm 0.02 \times 10^{-7}$	71.3 ± 1.3
nil	0.1	9.80	$1.26 \pm 0.02 \times 10^{-7}$	68.5 ± 1.5
2.18×10^{-5} M	5.9:1	10.04	$1.60 \pm 0.01 \times 10^{-7}$	86.7 ± 0.7
2.18×10^{-5} M	5.9:1	9.81	$1.61 \pm 0.15 \times 10^{-7}$	86.5 ± 9.5
4.37×10^{-5} M	11.9:1	10.03	$1.15 \pm 0.15 \times 10^{-7}$	62.5 ± 8.1
4.37×10^{-5} M	11.9:1	9.95	$1.48 \pm 0.05 \times 10^{-7}$	80.5 ± 3.3
4.37×10^{-5} M	11.9:1	9.82	$1.38 \pm 0.12 \times 10^{-7}$	75.0 ± 7.0
8.73×10^{-5} M	23.7:1	10.06	$1.34 \pm 0.20 \times 10^{-7}$	72.9 ± 10.8
2.20×10^{-4} M	60:1	10.01	$1.05 \pm 0.23 \times 10^{-7}$	56.8 ± 12.5

average of two trials for each pH

decreases absorption from what would be expected at that pH. A possible explanation is that the acetylacetone in solution is competing for sites on the foam with the metal acetylacetonate. This is consistent with the idea that it is the ligand which is responsible for copper retention.

Table 2 illustrates the effect of adding acetylacetone to copper solutions. Absorption of copper ions would be expected from the results in Figure 2, but addition of small amounts of acetylacetone does increase copper absorption. This is probably due to chelate formation in solution. Absorption in the presence of a six - fold excess of acetylacetone gives the greatest absorption of the concentrations of acetylacetone studied. As the concentration of acetylacetone increases, there is a decrease in absorption, most noticeable when a sixty - fold excess was used. At this concentration, copper absorption is less than that for only copper ions in solution. It appears that at even these low concentrations of ligand, there is competition for binding sites on the foam between the free ligand and the metal chelate.

4) Extraction of Acetylacetone By Polyurethane Foam

Introduction

The decrease in copper absorption in the presence of excess acetylacetone was thought to be caused by competition for binding sites on the foam between the free ligand and the metal chelate. In order to justify this assumption, the absorption of acetylacetone onto polyurethane foam was studied to determine if the foam did show an affinity for the ligand.

Experimental

Fifty ml of a solution of acetylacetone in water, 9.75 x 10^{-5} M, was allowed to stand on the foams for two hours, after which the foams were squeezed dry. Duplicate samples were run, at pH's 4.25 and 7.19, and values corrected against water blanks. The absorbance maximum for a solution of acetylacetone in water was found to be 275 mμ, and all absorbance readings were taken at this value.

Results and Discussion

It was found that the foam did retain acetylacetone to some extent, absorbing 1.00 x 10^{-6} moles at pH 7.19 (20.5 $\pm$ 2.4%), and 0.96 $\pm$ 0.06 x 10^{-6} moles at pH 4.35 (19.7 $\pm$ 1.2%). The pH value did not seem to affect absorbance to any great degree.

These results show that acetylacetone is retained by the foam, independent of any metal being present. When compared to

the values shown in Table 2 it can be seen that the amount of copper bound to the foam is less than the amount of acetylacetone which can be bound, approximately 0.15×10^{-6} moles of copper compared to 1.00×10^{-6} moles of acetylacetone. Despite this, the copper was at best only 87% extracted, probably due to the six - fold stoichiometric ratio of acetylacetone to copper, the excess acetylacetone inhibiting copper absorption by competition for binding sites on the foam.

5) Extraction and Recovery of Copper Acetylacetonate From Polyurethane Foam

Introduction

The use of the foam as a preconcentrator for trace analysis would only be feasable if the metal in solution was both quantitatively absorbed onto the foam, and quantitatively recovered from the foam. The pH dependent extraction curves indicated that extraction decreased as the pH was lowered, so acid elution of the foam seemed possible.

Experimental

Copper was first extracted by the foams from copper acetylacetonate solutions. Recovery of the copper from the foams was initially done by elution with water, using different pH's, or by elution with hydrochloric acid at different normalities. Flow-through systems were used, with a flow rate of 4 ml/min (Table 3).

Once it was determined that an acid wash could be used for recovery of the copper, a system combining quantitative retention of copper from dilute solutions plus quantitative recovery was attempted. Dilute solutions of copper acetylacetonate were passed through the foam, using flow-through systems at different flow rates. Recovery of the copper was achieved by elution with 1.5 M hydrochloric, using either flow-through or static systems (Tables 4 and 5).

Results and Discussion

Elution of the foams with water at a low pH did not give quantitative recovery of the copper. If the elution curve was the reverse of the extraction curve, one would have expected a quantitative recovery at pH 1.86, as this pH is too low for copper absorption to occur (see Figure 1). Recovery was achieved, but was not quantitative until 1.0 M hydrochloric acid was used.

The percentage of copper absorbed, using the 0.23 ppm copper solution (Table 4) was not consistent, indicating that extraction conditions were not optimized. Extraction also was not quantitative, but was more consistent.

Conditions for quantitative absorption and recovery of dilute copper acetylacetonate solutions were determined to be the following: a flow rate of 2 ml/min. with a pH of 10.2, for absorption, followed by a static acid wash system using 1.5 M hydrochloric acid. At faster flow rates absorption was not quantitative, as shown in Table 4. The static acid wash system was also more effective than the flow-through system, as shown by a comparison of the recovery efficiencies in Tables 4 and 5.

Table 5 indicates that, under optimum conditions, quantitative preconcentration and recovery of trace amounts of copper acetylacetonate is possible.

Table 3 : Recovery of Copper From Foams Loaded With Copper Acetylacetonate Using Acid Washes

pH	Volume of Wash Solution (ml)	Amount of Copper Recovered (μg)	Percent of Copper Recovered
1.86	100	65.2	90.5*
1.86	50	54.5	75.7*
2.50	100	43.0	59.7*
2.50	50	36.5	50.7*
3.00	100	18.0	25.0*
3.00	50	17.5	24.3*
1 M HCl	100	100	102+
1 M HCl	50	90	91.8+
2 M HCl	100	100	102+
2 M HCl	50	80	81.6+
3 M HCl	100	100	102+
3 M HCl	50	90	91.8+

* 72 μg originally on foam

+ 98 μg originally on foam

Table 4 : The Absorption and Recovery of Copper Acetylacetonate by Untreated Polyurethane Foam, Using Flow-Through Systems for Absorption and Recovery

Concentration of Copper (ppm)	Volume of Cu Solution Used* (ml)	pH	Amount Cu Absorbed (μg)	Percent Cu Absorbed	Volume of Acid Wash (ml)	Flow Rate (ml/min)	Amount Cu Recovered (μg)	Percent Cu Recovered (Of Amt. Absorbed)
0.23	100	9.39	17.3	75.3	100	4	14.0	80.9
0.23	200	9.39	10.6	24.6	100	4	7.1	67.0
0.23	150	9.39	34.5	100	100	4	29.3	85.0
0.23	100	9.39	17.0	74.0	50	4	14.0	82.5
0.23	100	9.39	16.3	71.0	50	4	14.0	85.9
0.049	300	10.88	N.D.	--	50	2	4.0	--
0.049	300	10.88	N.D.	--	50	2	6.5	--
0.049	300	10.88	N.D.	--	50	2	6.0	--
0.049	300	10.88	N.D.	--	50	2	7.0	--
0.049	300	10.88	N.D.	--	50	2	6.0	--
0.049	300	10.88	N.D.	--	50	2	5.5	--

* flow rate 4 ml/min

N.D. not detectable, Cu concentration <0.05 ppm

Table 5 : The Extraction of Trace Amounts of Copper Acetylacetonate by Untreated Polyurethane Foam Using 50 ml of a Static Acid Wash for Recovery

Concentration of Copper (ppm)	Volume of Sample Solution Extracted* (ml)	pH	Amount Copper Recovered (μg)	Percent Copper Recovered
0.049	400	8.80	21.5	109
0.049	300	8.80	14.5	98.5
0.049	300	8.80	13.0	88.5
0.049	300	8.80	13.5	91.8
				Average 96.5 ± 4.5
0.049	400	10.80	13.8	70.0
0.049	400	10.80	11.9	60.3
0.049	400	10.80	16.5	83.8
0.049	400	10.80	13.8	70.0
				Average 71.0 ± 6.5
0.058	300	10.20	16.5	94.0
0.058	300	10.20	17.3	98.6
0.058	300	10.20	17.3	98.6
0.058	300	10.20	16.7	95.0
				Average 96.6 ± 2.0

* flow rate 2 ml/min

6) Determination of Copper Species Absorbed by Polyurethane Foam

Introduction

The mechanism for retention of metals, or metal chelates by untreated polyurethane foam is not fully understood. Bowen[6] has suggested that the absorption process may be ion-exchange, chelation by oxygen atoms in the polymer, or a combination of the two effects, or something entirely different. In order to determine the species of copper present when copper acetylacetonate was absorbed by the foam, E.S.R. spectra were run. By comparison of spectra for copper in a copper acetylacetonate/acetylacetone solution, it was hoped to determine whether or not the copper on the foam was still in the form of $Cu(acac)_2$, or if the copper was now bound to the foam, possibly coordinated to the amide ester linkage of the polyurethane.

Experimental, Results, and Discussion

Spectra were first obtained from clean foams. This was done by shredding the foam into small bits, and packing them in a quartz tube, outside diameter 11 mm. No peaks were observed. It was also noted that the microwave signal in the cavity was absorbed by the foam if the tube was packed too tightly. This factor restricted the amount of foam which could be used to generate a signal.

A spectrum of copper acetylacetonate was also run, using a solution of copper acetylacetonate in acetylacetone and

benzene. Four peaks were noted.

Foams were then used to extract copper from a solution of copper acetylacetonate, a stock solution of copper, and a solution of copper and acetylacetone, all approximately 2 ppm. in copper. The foams were dried, and then shredded and placed in the quartz tube and spectra run. No peaks were observed.

The lack of peaks was probably due to too low a concentration of copper on the foams, even though the maximum amount of copper was put on the foams in each case. Again, the amount of foam in the E.S.R. cavity could not be increased due to signal absorption. Detection would also be difficult due to a probable broadening of the signal peaks, which would make it difficult to separate the signal from the background noise. Results were inconclusive. The copper species may have been altered by absorption on the foam, but detection of any kind of signal was impossible under the conditions present.

7) Determination of the Active Sites on Polyurethane Foam

Introduction

The binding site of the ligand on the foam was assumed to be the amide ester linkage of the polyurethane. In order to test this theory, attempts were made to put blocking groups on the foam at this site, and to study the effect this would have on the absorption of metals.

Experimental

Acylation, methylation, and silanization were attempted. The procedure for acylation consisted of making a solution of 50 ml. of acetyl chloride in 450 ml. of dry toluene, and soaking the foams for 24 hours. Methylation was done using a modification of the procedure used by Icke, Wisegarver, and Alles [53]. The foams were placed in 200 ml. of formic acid, and then 100 ml. of 37% formaldehyde solution were added, and the reaction allowed to stand at room temperature for 24 hours.

The foams from these two reactions were washed first with toluene, then acetone, and then with distilled water. The distilled water wash was continued until the pH of the water did not change after contact with the foam.

Silanization was done using a modification of the procedure described by Corey and Venkateswarku [54]. One hundred and fifty ml. of dry (over molecular sieve) benzene was

used to dissolve 0.75 gm of t-butyl dimethylchlorosilane. The scavenger used was 1.4 ml. of dry (over KOH) triethylamine. Contact time was 20 hours, after which the foams were washed with chloroform, then acetone, and then distilled water. The water wash was again continued until the pH of the water did not change after contact with the foam.

Cadmium solutions in static adsorption systems were used to determine the effect of pretreatment.

Results and Discussion

Cadmium absorption was used to determine if the pretreatment of the foam was successful, as cadmium was previously extracted by untreated foams. If the active site on the foam was the amide ester linkage, and if the pretreatment was successful, a decrease in cadmium absorption would be expected. However, pretreatment did not seem to affect the retentive properties of the foam.

This may mean that the pretreatment was unsuccessful, and the blocking group was not put on the foam, or that the group was put on the foam but not at a site responsible for absorption, ie. the amide ester linkage was not responsible for absorption or the blocking group attacked at a different site. Infrared spectra could be used to determine if the blocking groups were present on the foam, and possibly the binding site, but this study was not done.

Part II : The Extraction of Copper and Cadmium by Benzoylacetone Treated Polyurethane Foam

1) Extraction of Copper Benzoylacetonate by Untreated Polyurethane Foam

Introduction

The extraction of copper benzoylacetonate by untreated polyurethane foam was studied to determine if this chelate acted in an analogous fashion to the acetlyacetonate.

Experimental

Copper benzoylacetonate was prepared according to Berg and Truemper [55]. The nitrate salt was made up as a 5 weight % solution and buffered immediately before use by adding five grams of sodium acetate for every 100 ml. of solution. The buffered metal ion solution was shaken with an alcoholic solution of the ligand until the reaction appeared complete. After precipitation the chelate was collected by filtration, and recrystallized twice from ethanol/water solutions. The melting point of the product was 196.5 - 197.5, and the literature value was 195 - 196°C [56].

A saturated solution of the benzoylacetonate in water was prepared by putting excess chelate in water, and allowing the solution to stand overnight. The solution was then filtered through Whatman #42 paper, and the copper concentration determined. The amount of copper in solution was found to be less than what could be determined by atomic absorption, ie.

less than 0.05 ppm., indicating that the copper benzoylacetonate was relatively insoluble in water.

In order to dissolve the benzoylacetonate, acetone was added to the solution prior to use. The solutions were then filtered and passed through the foam using a flow-through system with a flow rate of 2 ml./min. Data is shown in Table 6.

Results and Discussion

When acetone/water solutions of copper benzoylacetonate were used, copper was found to be retained by the foam. This would seem to indicate that the benzoyl chelate is absorbed by the foam preferentially to remaining in solution. This is also similar to absorption in the acetylacetonate system, implying a similar mechanism of absorption.

When pure acetone was used as the solvent, absorption decreased sharply. In an aqueous solution, the attractive ability of the foam is higher than the solvation properties of the solvent, and the chelate is bound preferentially to the foam. In pure acetone, the solvation of the chelate is greater than in acetone/water systems, and absorption onto the foam is not as great. An alternative explanation could be a decrease in absorption due to a change in the pH of the solution.

Table 6 : The Extraction of Copper Benzoylacetonate in Acetone Solution by Untreated Polyurethane Foam

Concentration of Acetone (per 100 ml of solution)	pH	Copper Concentration of Sample Solution (ppm)	Volume Sample Solution Extracted (ml)	Amount Cu Extracted (μg)	Percent Cu Extracted
0.5 ml	10.01	0.107	100	9.25	89.8
2.0 ml	10.02	0.107	100	9.62	86.4
10 ml	9.98	0.345	100	33.6 ± 0.0	97.5 ± 0.0
20 ml	9.97	0.435	100	41.9 ± 0.7	96.3 ± 1.6
30 ml	9.99	0.455	100	43.2 ± 1.3	94.9 ± 2.8
30 ml	9.97	0.530	100	52.1 ± 0.0	98.3 ± 0.0
pure acetone	--	0.173	50	4.82 ± 0.1	90.1 ± 2.1
pure acetone	--	0.864	50	16.0 ± 2.8	37.0 ± 6.4

2) Pretreatment of Polyurethane Foam with Benzoylacetone

Introduction

The relatively insoluble nature of copper benzoylacetonate in an aqueous system suggested a different type of extraction procedure. Rather than have the metal chelate in solution, an insoluble ligand could be put on the foam, and an aqueous solution of a metal passed through it.

Experimental

Pretreatment of the foam with benzoylacetone was achieved by soaking the foams in a solution of benzoylacetone in acetone, draining them, and drying under vacuum. The concentration of the benzoylacetone/acetone solution normally used was 0.00503 gm. per 100 ml. (50.3 ppm.). The foams retained 26 ± 2 ml. of this solution after draining, so that the foams contained 0.0013 ± 0.0001 gm. of benzoylacetone after treatment.

To determine if the concentration of the ligand solution changed upon contact with the foam, the absorbance peak at 329 millimicrons was used to determine absorbance increase or decrease. The normal concentration of ligand solution used was studied, as well as a solution 1/25 the normal concentration, before and after contact with the foam.

Results and Discussion

The benzoylacetone concentration of the regular soaking solution did not noticeably differ before and after contact with the foam. The dilute solution did show an increase in the benzoylacetone concentration, from 2.01×10^{-4} gm./1000 ml. to 2.44×10^{-4} gm./1000 ml. This indicates that the acetone was being absorbed into the foam (causing swelling), but the benzoylacetone remained at the surface of the foam, forming a surface coating of ligand. The slight increase in ligand concentration was considered negligible compared to the normal concentration of ligand used.

3) Extraction and Recovery of Copper and Cadmium by Benzoyl-Acetone Treated Polyurethane Foam

Introduction

Benzoylacetone treated foams were expected to retain metals by coordination of the metal with the ligand on the foam. The insoluble nature of the ligand, combined with an apparent ligand-foam interaction, would prevent the complex from being washed off the foam.

Experimental

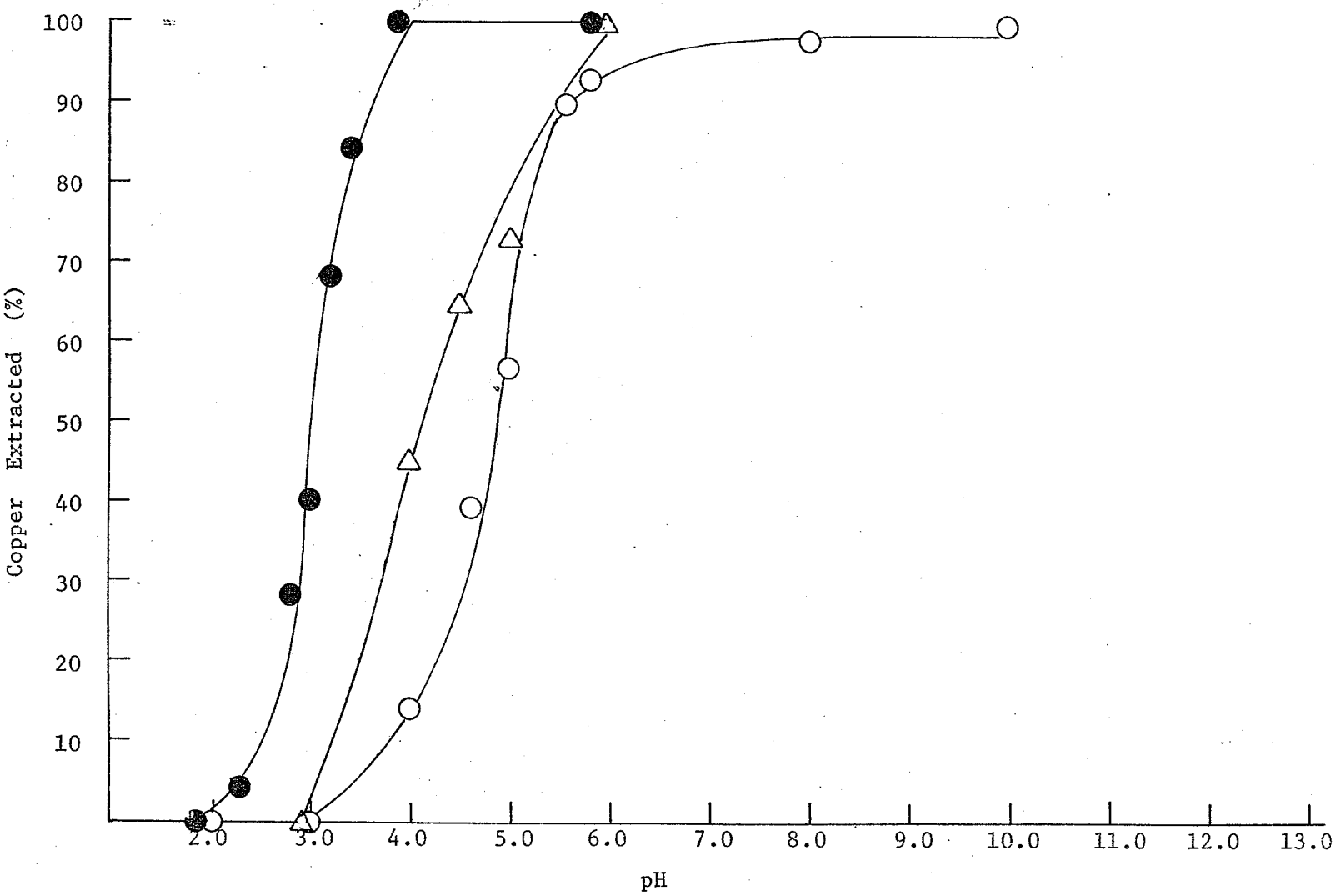
Normal static extraction procedures were used, using 3.51 ppm.copper and 2.50 ppm. cadmium solutions. Benzoylacetone treated foams were used, at normal and five times normal concentration of ligand. Results are shown in Figures 3 and 4.

Copper and cadmium were recovered from the treated foams by elution with 1.5 M hydrochloric acid, using standard conditions.

Trace amounts of copper were recovered by passing 300 ml. of solution containing 17.5 μg of copper through the foam, using a flow-through system at pH 7.2. The acid wash recovered 17.2 $\pm$ 0.5 μg. A similar run with 300 ml. of a solution containing 15.0 μg of cadmium, pH 10.4, gave a recovery of 14.7 $\pm$ 0.3 μg.

Figure 3

The pH Dependent Curves for Extraction of Copper by Benzoyl-Acetone Treated Polyurethane Foam Compared to the Corresponding Solvent Extraction Process

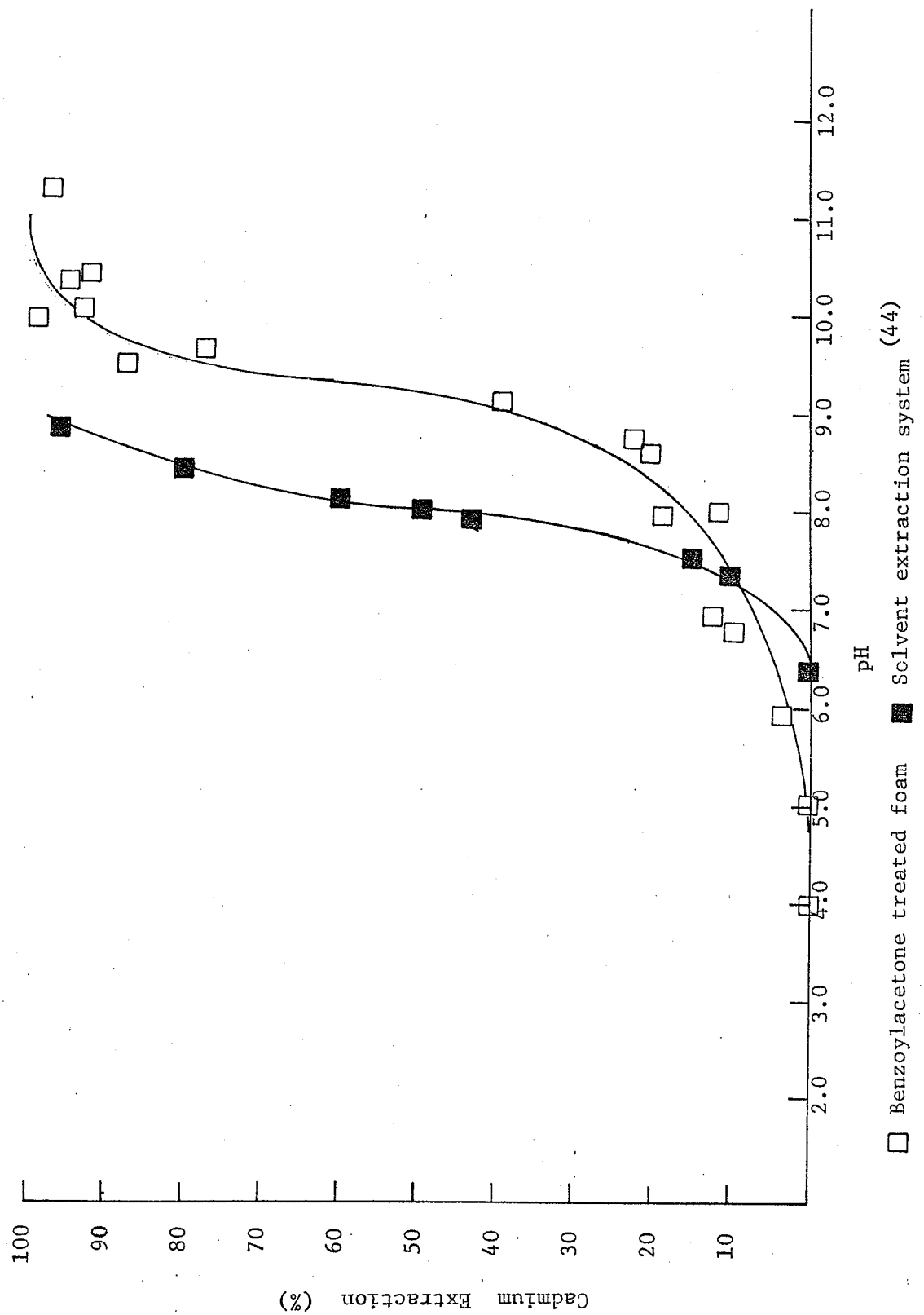


○ Benzoylacetone treated foam △ Foams with 5 times the normal amount of ligand

● Solvent extraction system (44)

Figure 4

The pH Dependent Curves for the Extraction of Cadmium by Benzoyl-Acetone Treated Polyurethane Foams Compared to the Corresponding Solvent Extraction System


Cadmium Extraction (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
pH
Benzoylacetone treated foam
Solvent extraction system (44)

Results and Discussion

The pH dependent extraction curves were very similar to those obtained by the use of a benzoylacetone/benzene solvent extraction system.[44] The major difference seems to be a shift to a slightly higher $pH_{1/2}$. The cadmium curves obtained from extraction by an untreated foam system (Figure 2), and the benzoylacetone pretreated foams are also similar, the only difference appearing to be a slight lowering of the pH required for maximum absorbance when pretreated foams are used.

Extraction of copper is much more efficient using the benzoylacetone pretreatment system, rather than the acetylacetonate or metal solutions on untreated foam. When the concentration of benzoylacetone on the foams was increased five-fold, the extraction curve shifted closer to the solvent extraction curve. The pH at which extraction began remained constant, but the pH for complete extraction decreased slightly.

Recovery of metals from the pretreated foams was quantitative. Of 171.6 ± 1.1 μg copper absorbed, 172.1 ± 1.4 μg was recovered, and of 100.5 ± 0.7 μg cadmium absorbed, 101.7 ± 5.0 μg was recovered.

Recovery of trace amounts of copper and cadmium was also quantitative, suggesting that this method may serve as a preconcentration technique for trace analysis.

4) A Flow Rate Study on the Extraction of Copper and Cadmium by Benzoylacetone Treated Polyurethane Foam

Introduction

The extraction of copper and cadmium was previously done using static systems. This technique would be more suitable as a preconcentration technique if flow-through systems proved to be efficient. The effectiveness of a flow-through system would depend on the rate at which the copper-ligand complex was formed.

Experimental

The dependence of absorption on flow rates was studied using 3.51 ppm copper and 2.50 ppm. cadmium solutions. Standard conditions for a flow-through system were used, with the exception of the use of two foams per column to prevent channeling. Results are shown in Table 7. The flow rate of 250 ml./min. was the maximum flow rate obtainable for the system.

Results and Discussion

Relatively fast flow rates gave quantitative extraction of metals from aqueous solution, providing the pH was optimized. At a less than optimum pH for copper, recovery was not quantitative. The decrease in absorption was proportional to the flow rate, regardless of the pH.

Cadmium extraction was more effective at faster flow rates than copper extraction, but as previously indicated, a different mechanism is probably responsible for extraction.

Table 7 : The Extraction of Copper and Cadmium by Benzoylacetone Treated Polyurethane Foam; A Flow Rate Study

Flow Rate (ml/min)	Amount Copper Extracted (μg)	Percent Copper Extracted	Amount Cadmium Extracted (μg)	Percent Cadmium Extracted
	pH 8.00		pH 10.53	
1.5	175.5	100	174.4	99.4
2.0	175.5	100		
3.0	175.5	100	174.1	99.2
6.0	170.5	97.2	174.1	99.2
12	158.5	90.4	174.1	99.2
18	152.5	87.0	174.1	99.2
250	123.5	70.4	160.1	91.2
	pH 6.02			
2.0	144.5	82.4		
6.0	131.5	74.9		
18	97.5	55.6		

5) Separation of Copper and Cadmium by Benzoylacetone Treated Polyurethane Foam

Introduction

The pH dependent extraction curves of copper and cadmium seemed to be sufficiently different to enable separation of the two by adjusting the pH of the sample solution. It appears that separation may be achieved by two methods. In the first, the absorption difference at specific pH's may be utilized. A pH may be chosen low enough so that cadmium is not absorbed, but yet high enough for quantitative recovery of the copper. The second method is based on elution differences. Both metals may be put on the foam, and eluted by water of too high a pH to remove the copper, but of low enough a pH to wash off the cadmium.

Experimental

Both static and flow-through systems were studied, under various conditions. The copper concentration was normally 3.51 ppm. , and the cadmium concentration was 3.50 ppm.

Results and Discussion

Table 8 shows that there is an overlap in the pH dependent extraction curves for copper and cadmium on benzoylacetone treated foam. There is no pH where copper extraction is complete and cadmium extraction is negligible.

Extraction using consecutive foams in static conditions

proved to be the most effective method for separating a copper/cadmium system by absorption. The system was run at pH 4.86, and after extraction of the solution with five consecutive foam plugs, 99.8 $\pm$ 0.2 % of the copper was extracted, and less than 1 % of the cadmium. The original amount of metal present was 175 μg of each.

Separation was probably more successful using consecutive foams because of an equilibrium effect between the copper on the foam and the copper still in solution. After each successive contact with the foam, the amount of copper left in the aqueous phase decreased, so that by the time five equilibrium distributions have occured, most of the copper is absorbed in the foam.

Separation by elution techniques proved to be less effective, as shown in Table 9. The foam was originally loaded with 175.5 μg of copper and 165.7 μg of cadmium, and eluted with water at various pH's. The recovery of cadmium off the foam was not what would be expected if the pH dependent elution curve was the reverse of the pH dependent extraction curve. Copper was beginning to come off the column before all the cadmium had been recovered, making separation by elution impossible.

Table 10 gives the data for flow-through extraction systems for copper/cadmium separations, run at pH 4.84. The fact that copper is washed off the foam again suggests that the extraction process is an equilibrium process. At less than optimum extraction pH, the copper involved in chelate formation

is in equilibrium with the free copper ions in solution. Subsequently, once the copper is bound to the foam, and copper-free water passed through it, copper is lost to the aqueous phase.

Subsequently, the best procedure for separation of copper and cadmium by benzoylacetone treated foams seems to be successive static extraction systems.

Table 8 : The Separation of Copper and Cadmium by Benzoylacetone Treated Polyurethane Foam in a Static System

pH	Amount Copper Extracted (μg)	Percent Copper Extracted	Amount Cadmium Extracted (μg)	Percent Cadmium Extracted
6.99	175.5	100	34.8 $\pm$ 2.8	19.6 $\pm$ 1.6
6.51	175.5	100	27.3 $\pm$ 3.0	15.6 $\pm$ 1.7
6.21	172.2 $\pm$ 1.6	98.1 $\pm$ 0.9	25.7 $\pm$ 1.2	14.7 $\pm$ 0.7
6.02	169.2 $\pm$ 0.4	96.4 $\pm$ 0.2	10.0 $\pm$ 3.4	5.7 $\pm$ 2.2

Table 9 : Elution of Copper and Cadmium After Absorption by Benzoylacetone Treated Foams

Elution pH	Volume of Effluent (ml)	Amount Cadmium* Extracted (μg)	Amount Copper** Extracted (μg)
7.15	100	37.8 $\pm$ 2.2	1.5 $\pm$ 0.5
	100***	12.2 $\pm$ 0.7	< 0.5
6.05	100	11.2 $\pm$ 1.2	< 0.5
4.44	100	8.0 $\pm$ 0.3	37.0 $\pm$ 2.7

* 165.7 μg originally on foam

** 175.5 μg originally on foam

*** second 100 ml of effluent

Table 10 : Separation of Copper and Cadmium by Benzoylacetone Treated Polyurethane Foam Using a Flow-Through System, pH 4.84

Portion of Wash Analyzed (ml)	Amount Cadmium* Detected (μg)	Amount Copper* Detected (μg)	Amount Cadmium** Detected (μg)	Amount Copper** Detected (μg)
0 - 100***	23.5 ± 0.5	8.5 ± 2.5	258 ± 6.0	10.5 ± 0.5
100 - 200	5.5 ± 0.5	7.0 ± 0.0	72.5 ± 3.5	7.0 ± 1.0
200 - 300	0.5	3.0 ± 0.0	8.5 ± 2.5	3.0 ± 1.0
total:	29.0 ± 1.0	18.5 ± 2.5	339 ± 12	20.5 ± 2.5
%	82.9 ± 2.9	52.9 ± 7.1	96.9 ± 3.4	58.6 ± 7.1

* original solution 0.35 ppm Cu and 0.35 ppm Cd

** original solution 0.35 ppm Cu and 3.50 ppm Cd

*** original solution volume

6) Elution of Absorbed Copper from a Benzoylacetone Treated Foam System by Acetyacetone

Introduction

It was previously shown that when a large excess of acetyacetone was present in the copper acetylacetonate system, retention of copper did not occur. This suggested that copper may be removed from the foam by a ligand exchange process,using acetylacetone in aqueous solution.

Experimental

Copper was first absorbed onto benzoylacetone treated foams at pH 8.00. An acetyacetone solution, 1 ml. per 100 ml. solution, pH 8.00, was placed on the foams using conditions for an acid wash.

Results and Discussion

Of the 172.4 ± 0.2 μg of copper put on the foam, 155.7 ± 3.1 μg were removed by the acetyacetone wash solution. The pH used was a high enough pH to prevent copper from coming off using a simple water wash, suggesting that a ligand exchange process may have occured. The copper coordinated to the benzoylacetone on the foam became bound to the aqueous acetylacetone which remained in solution. An alternative effect may be that the benzoylacetone became more soluble in the aqueous phase due to the acetyacetone, and the copper-coordinated benzoylacetone was washed off the foam.

7) Determination of the Capacity of Benzoylacetone Treated Polyurethane Foam

Introduction

The use of pretreated foams for extraction would be limited by the amount of metal which could be retained by the foam. In order to study the relationship between the amount of ligand present on the foam, and the capacity of the foam, a saturation study was done.

Experimental

The capacity of the benzoylacetone treated foams was determined using a flow-through system, at a flow rate of 3 ml/min. A 3.51 ppm copper solution was used, pH 8.00, and foams having the normal amount of ligand, 0.0013 gm, and five times the normal amount of ligand were used. The copper solution was passed through the foam until no decrease in the copper concentration was detectable. Results were corrected against a foam blank, the amount of copper retained by an untreated foam being subtracted from the total amount of copper retained.

Results and Discussion

Untreated foams were found to retain 264 μg of copper, foams having five times the regular amount of benzoylacetone 407 μg, and regular pretreated foams 381 μg of copper. The amount of copper retained by the ligand was calculated to be the difference in copper absorption between pretreated foams

and untreated foams, which gave values of 117 μg for regular foams, and 143 μg for foams having five times the regular amount of ligand.

The molar absorption ratio of copper/benzoylacetone for foams having the regular amount of ligand was found to be 1:5.6, and for foams having five times the regular amount of benzoylacetone, 1:23.1. A ratio of 1:2 would be expected for a normal solvent extraction system. A possible explanation for the variance may be the physical nature of the system, in that the metal ion could only interact with ligand at the ligand/liquid interface.

These results indicate that maximum extraction capacity is probably limited by the surface area of the foam, as absorption appears to be an interface reaction.

8) Possible Interferences Affecting Absorbance of Copper and Cadmium by Benzoylacetone Treated Polyurethane Foam

Introduction

The extraction of copper and cadmium was done in a system having the minimum of possible interferences. However, there will be a salt effect due to the pH adjustments, and separation studies could possibly be affected by competitive absorption of copper and cadmium.

Experimental

Potassium chloride in various concentrations was added to copper standard solutions to determine the salt effect. KCl was chosen as the pH adjustments were accomplished by the addition of KOH and HCl solutions. The original copper stock solution could not be used, as the pH was too low, the metal being dissolved in acid. A new stock solution of $CuCl_2 \cdot 4H_2O$ was made up, and dilutions made from this.

Cadmium and copper selective absorption effects were studied using standard solutions.

Normal static conditions were used in all trials.

Results and Discussion

Extraction of copper by pretreated foams was shown to be slightly affected by the ionic strength of the solution, as illustrated in Table 11, but at low concentrations of salt, as could occur during pH adjustment, the effect was negligible.

Table 11 : The Effect of the Ionic Strength of the Solution on Copper Extraction by Benzoylacetone Treated Polyurethane Foam

pH	KCl Concentration (ppm)	Amount Copper* Extracted (μg)	Percent Copper Extracted
5.39	7.0	68.1 $\pm$ 1.7	38.8 $\pm$ 0.5
5.47	14.0	85.6 $\pm$ 2.4	48.8 $\pm$ 1.4
5.87	100	67.6	38.5
6.23	2096	66.0	37.6
6.33	10480	70.0	39.8

* original Cu concentration 3.51 ppm

volume of sample solution 50 ml

Table 12 : The Effect of Cadmium on Copper Extraction and the Effect of Copper on Cadmium Extraction by Benzoylacetone Treated Polyurethane Foam

pH	Volume of Solution (ml)	Copper Concentration (ppm)	Cadmium Concentration (ppm)	Percent Copper Extracted	Percent Cadmium Extracted
7.00	50	3.51	0.35	98.4 $\pm$ 0.2	
7.00	50	3.51	3.50	98.5 $\pm$ 0.2	
7.00	50	3.51	35.0	98.4 $\pm$ 0.3	
7.00	50	3.51	175	98.8 $\pm$ 0.2	
7.00	50	3.51	350	97.1 $\pm$ 1.0	
10.00	50	0.25	2.50		88.8 $\pm$ 0.4
10.00	50	2.50	2.50		70.7 $\pm$ 0.5
10.00	50	25.0	2.50		53.9 $\pm$ 1.6

It was also found that potassium was not absorbed by the foam.

The extraction of copper in the presence of cadmium was relatively unaffected (Table 12). This would be expected as the pH was too low for cadmium extraction. Cadmium extraction was affected by the presence of copper, probably due to competition for the ligand sites, as copper as well as cadmium would be expected to be extracted at the pH used.

Part 3 : Use of Different Types of Polyurethane Foam for Extraction of Copper and Cadmium

Introduction

The use of different types of polyurethane foam was studied to check if the observed absorption properties were unique to the original polyurethane studied, or would be characteristic in general to polyurethane foam as a class of compounds.

A second type of foam, Type II, was obtained from the same source under the same specifications, but the physical properties of the foam were found to be different. The size was slightly larger, the foams having a diameter of 40 mm. and a length of 53 mm., average weight 1.6566 ± 0.0253 gm. The larger size resulted in a greater amount of ligand solution being retained, 33.2 ± 1.0 ml. The foams did not yellow with age, maintaining a white colour even when exposed to light over long periods of time. The original foams yellowed fairly rapidly upon exposure to light.

A third type of polyurethane foam used was obtained in the form of " diSPo " plugs, 22mm. long and 40 mm. in diameter.

Experimental

The foams were pretreated with acetone solutions of benzoylacetonate in a similar fashion to pretreatment of the original foams. The pH dependent extraction curves were run under standard conditions for a static system, using both treated and untreated foams. Results are shown in Figures 5 and 6, and in Tables 13 and 14.

Table 13 : Extraction of Copper by Untreated and Benzoylacetone Treated "diSPo" Plugs, Using Static Extraction Systems

pH	Type of Foam	Amount Copper Extracted (μg)	Percent Copper Extracted
3.04	treated	4.5	2.6
4.30	"	58.5	33.4
5.03	"	108.0	61.5
5.82	"	136.5	77.7
7.31	"	164.5	93.8
3.04	untreated	9.0	5.12
4.30	"	9.0	5.12
7.31	"	45.5	25.9

original copper concentration 3.51 ppm, volume of trial solution 50 ml

Table 14 : Extraction of Cadmium by Untreated and Benzoylacetone Treated "diSPo" Plugs, Using Static Extraction Systems.

pH	Type of Foam	Amount Cadmium Extracted (μg)	Percent Cadmium Extracted
5.66	treated	18.0	14.4
8.57	"	8.0	6.4
9.50	"	23.0	18.4
10.02	"	86.0	68.8
5.66	untreated	26.0	20.8
8.57	"	14.0	11.2
9.50	"	22.5	18.0
10.02	"	59.0	47.2

original cadmium concentration 2.50 ppm, volume of trial solution 50 ml

Figure 5

The pH Dependent Curves for the Extraction of Copper by Type II Polyurethane Foam, Using Untreated and Benzoylacetone Treated Systems

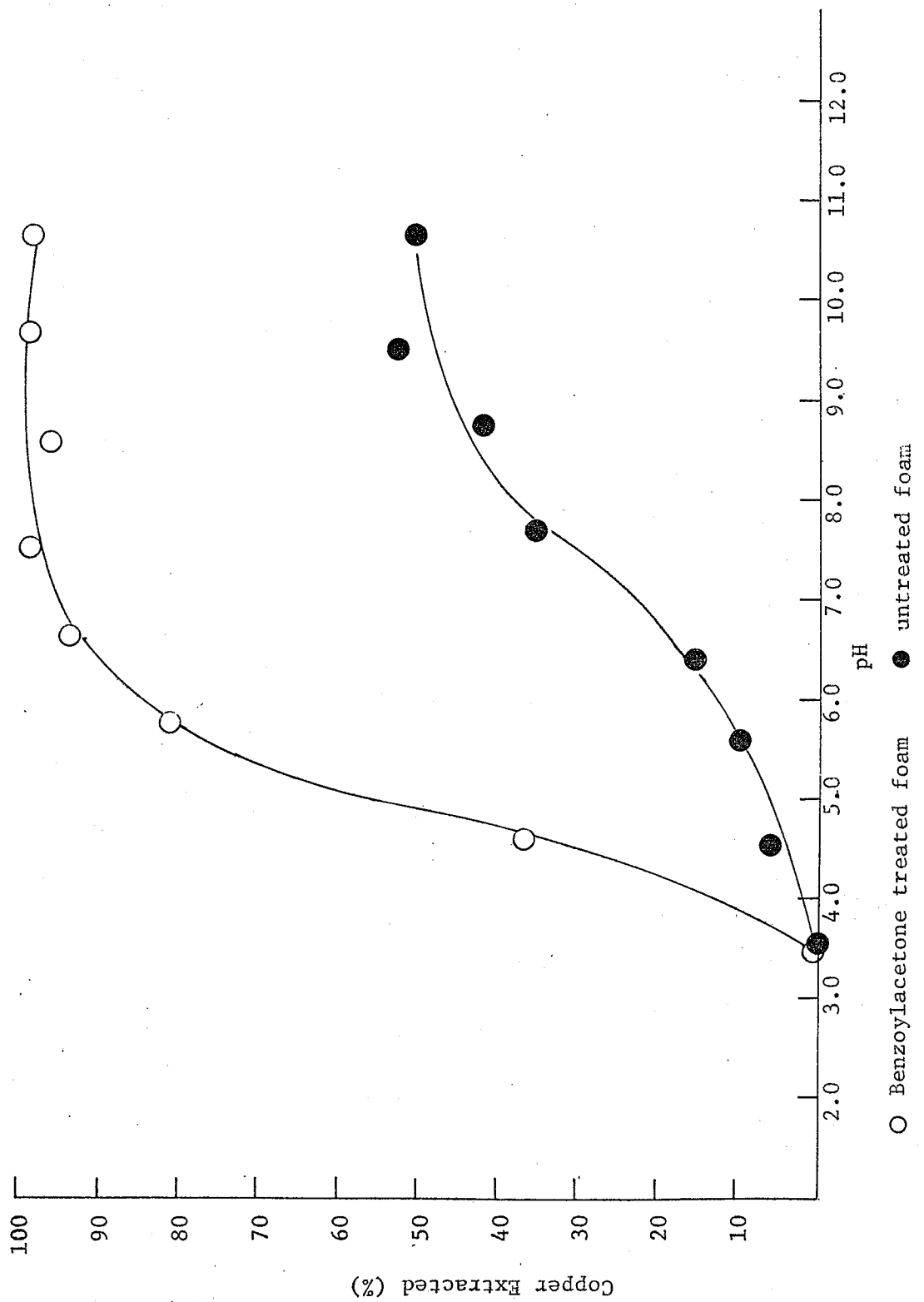
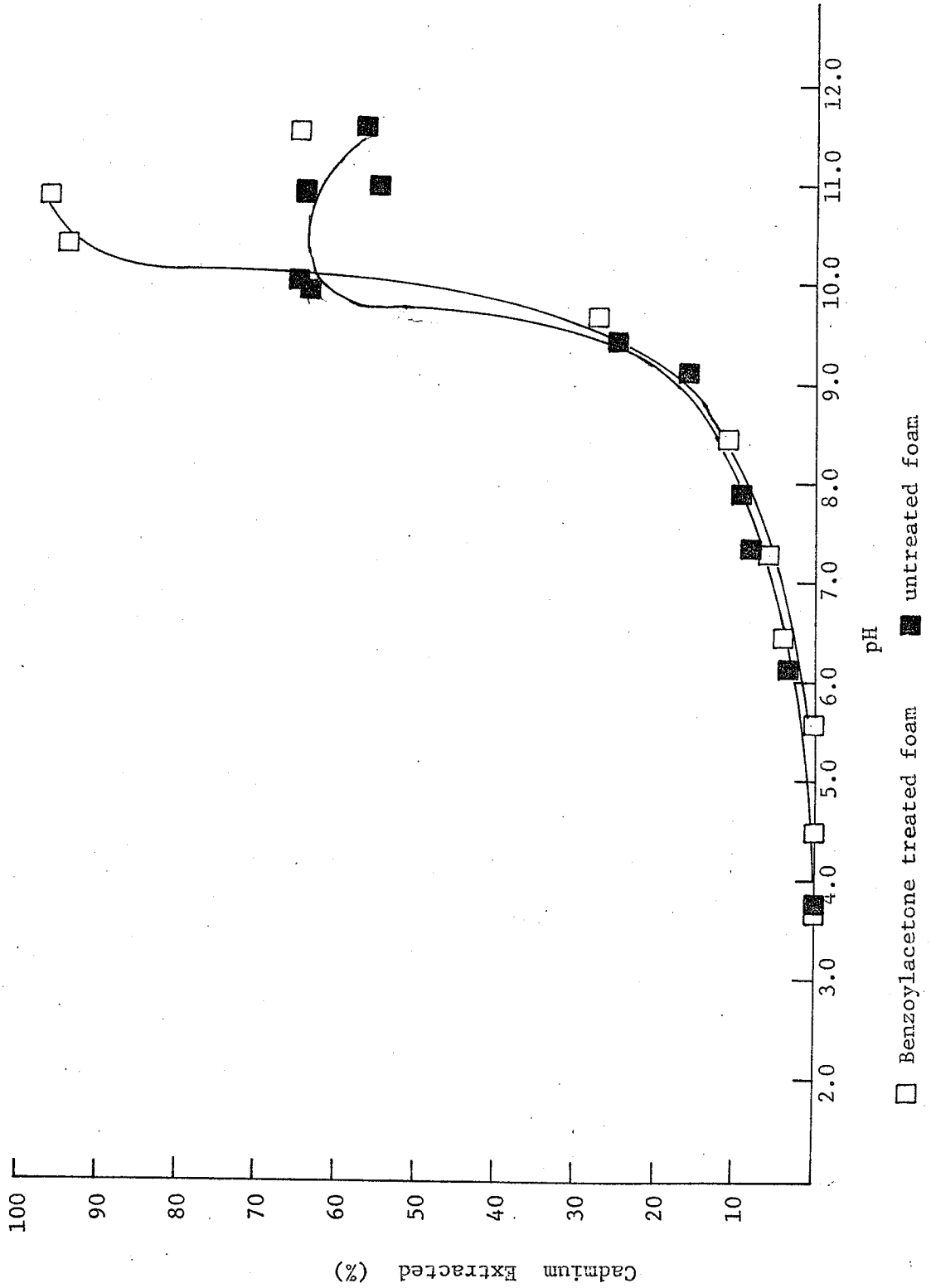

Copper Extracted (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
pH
○ Benzoylacetone treated foam
● untreated foam

Figure 6

The pH Dependent Curves for the Extraction of Cadmium by Type II Polyurethane Foam, Using Untreated and Benzoylacetone Treated Systems


Cadmium Extracted (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
pH
Benzoylacetone treated foam
untreated foam

Results and Discussion

The pH dependent extraction curves for the Type II foam were compared to the corresponding curves for the original foam. The cadmium extraction by untreated foams shows a decrease from 100% for Type I foams to close to 70% for Type II foams. The chelate effect is now noticeable in cadmium extraction, as pretreated foams still showed 100% extraction at the optimum pH. Extraction of copper seems to differ little between the two types of foam, either before or after treatment.

Extraction by "diSPo" plugs could be expected to be lower than for the original foams, due to their smaller size. About 10 ml of the 50 ml of metal solution used in the static system was not in direct contact with the plugs, as the liquid capacity was only about 40 ml. Pretreatment would also result in a less than normal amount of ligand left on the foam, again due to the smaller size of the foam.

Copper extraction of the treated plugs is similar to the extraction noted in the other foam systems, suggesting that the ligand is responsible for metal absorption (Table 13). Extraction of cadmium does show a definite increase after pretreatment with benzoylacetone. Untreated "diSPo" plugs also tend to absorb less cadmium than the other types of foam studied.

Part 4 : Extraction of Beryllium, Silver, and Gallium by Benzoylacetone Treated Polyurethane Foam.

Introduction

The extraction of metals other than copper and cadmium by benzoylacetone treated foams was studied to determine the applicability of this type of system to a more generalized metal extraction process. The effect of the charge on the metal ion was also under study.

Experimental

Standard conditions for a static system, using 2.50 ppm. metal solutions, were used in all cases. The silver standard solutions were adjusted by the addition of nitric acid and potassium hydroxide, rather than hydrochloric acid, to prevent formation of the insoluble silver salt.

Results and Discussion

Beryllium was studied, as this metal is a very toxic potential pollutant, even in trace quantities. A preconcentration technique would be useful for analysis.

Pretreatment of the foam with benzoylacetone did result in an increase in absorption, but quantitative retention was not achieved at the concentration of ligand used. (Figure 7) The $pH_{1/2}$ was found to be higher than in the corresponding solvent extraction process.

The extraction of a monovalent ion, Ag^{+}, gave a

different type of extraction curve (Figure 8) than previously obtained for other metals. Absorption never decreased to zero, but seemed to have two maxima, at pH's 3 and 10.5. The shape of the curves for both the treated and untreated systems are similar, the noticeable difference being that absorption was consistently higher for the pretreated foam. Comparison with the solvent extraction of a benzoylacetone in benzene solution[44] shows that the increased absorption at pH 10.5 tends to follow the curve for absorption for the solvent extraction system, even though the rest of the curve does not.

Results from the trivalent ion system, Ga^{+3} (Figure 9), gave curves vaguely resembling the benzoylacetone/benzene solvent extraction system[44]. Again, absorption by the treated foam increased over that by the untreated foam. The fluctuating results are partially caused by working near the detection limit of analysis, but may also be inherent in the solvation of the trivalent ion.

Figure 7

The pH Dependent Curves for the Extraction of Beryllium by Benzoylacetone Treated Polyurethane Foams Compared to the Corresponding Solvent Extraction System

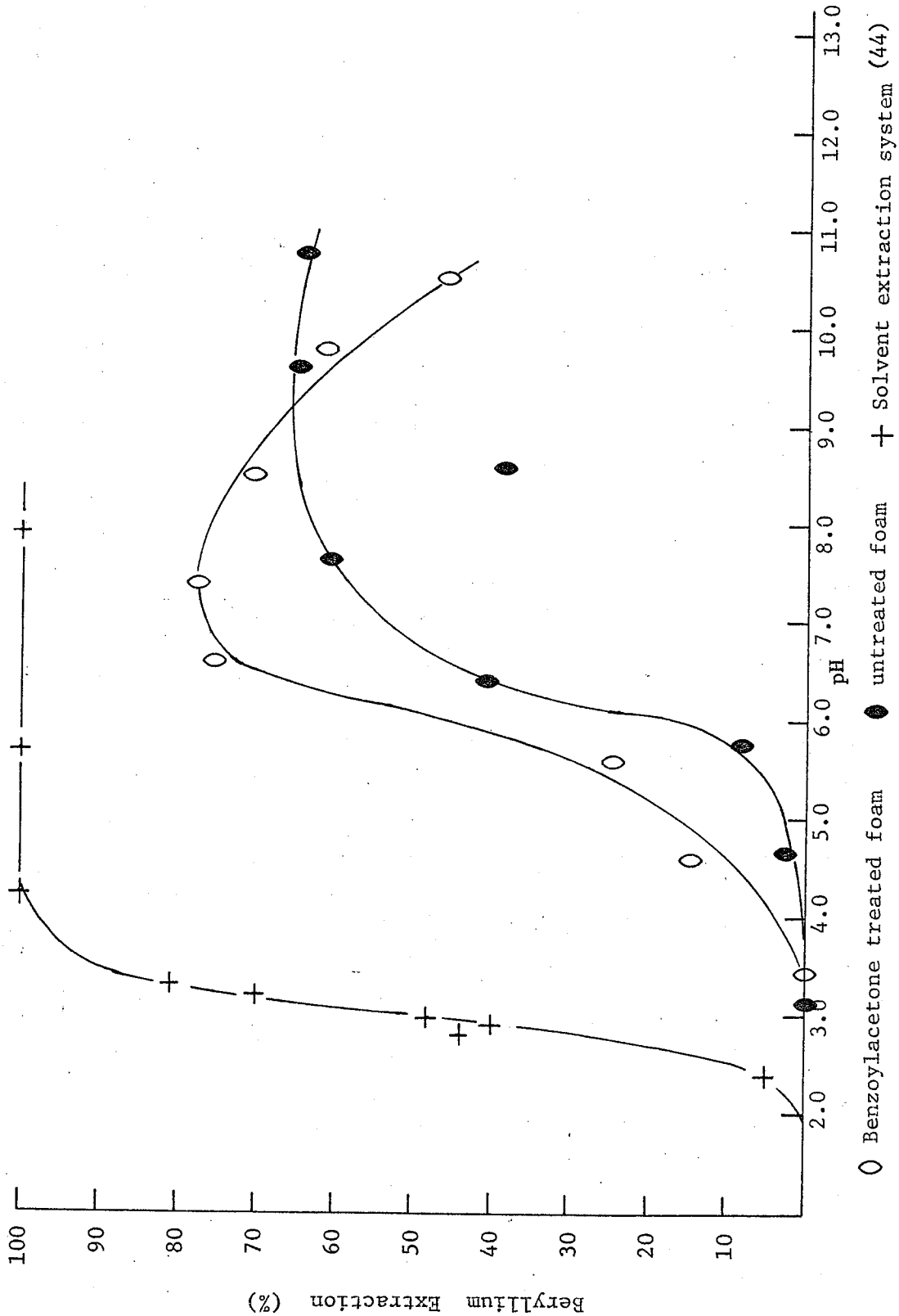

Beryllium Extraction (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
pH
O Benzoylacetone treated foam
● untreated foam
+ Solvent extraction system (44)

Figure 8

The pH Dependent Curves for the Extraction of Silver by Benzoyl-Acetone Treated Polyurethane Foams Compared to the Corresponding Solvent Extraction System

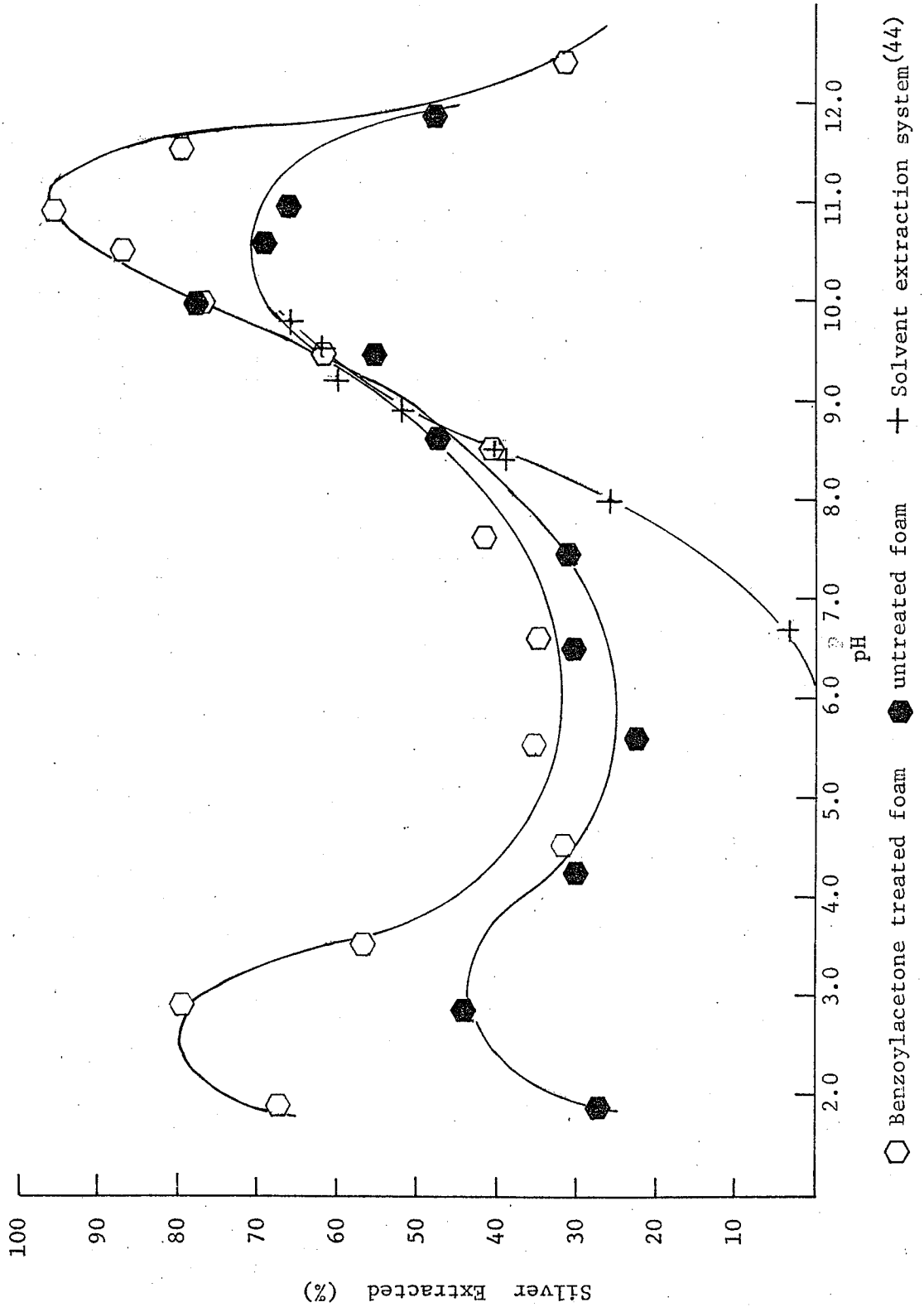
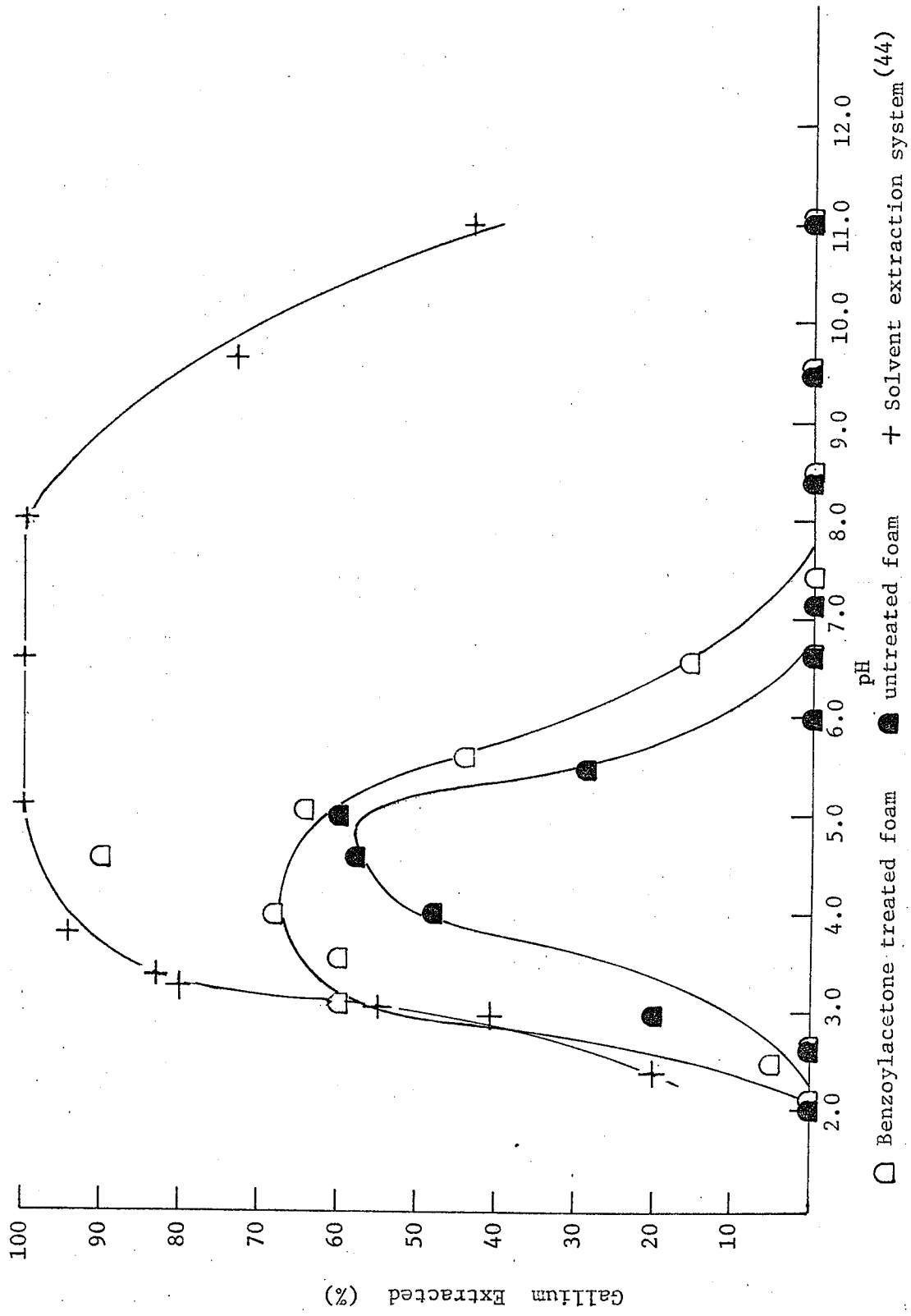

Silver Extracted (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
pH
Benzoylacetone treated foam
untreated foam
Solvent extraction system(44)

Figure 9

The pH Dependent Curves for the Extraction of Gallium by Benzoyl-Acetone Treated Polyurethane Foams Compared to the Corresponding Solvent Extraction System


Gallium Extracted (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
pH
Benzoylacetone treated foam
untreated foam
Solvent extraction system (44)

Part 5 : Extraction of Copper and Cadmium by Oxine Treated Polyurethane Foam

Introduction

The use of foams pretreated with oxine (8-hydroxyquinoline) was studied to determine if the modified solvent extraction process established to this point could be applied to other ligands.

Experimental

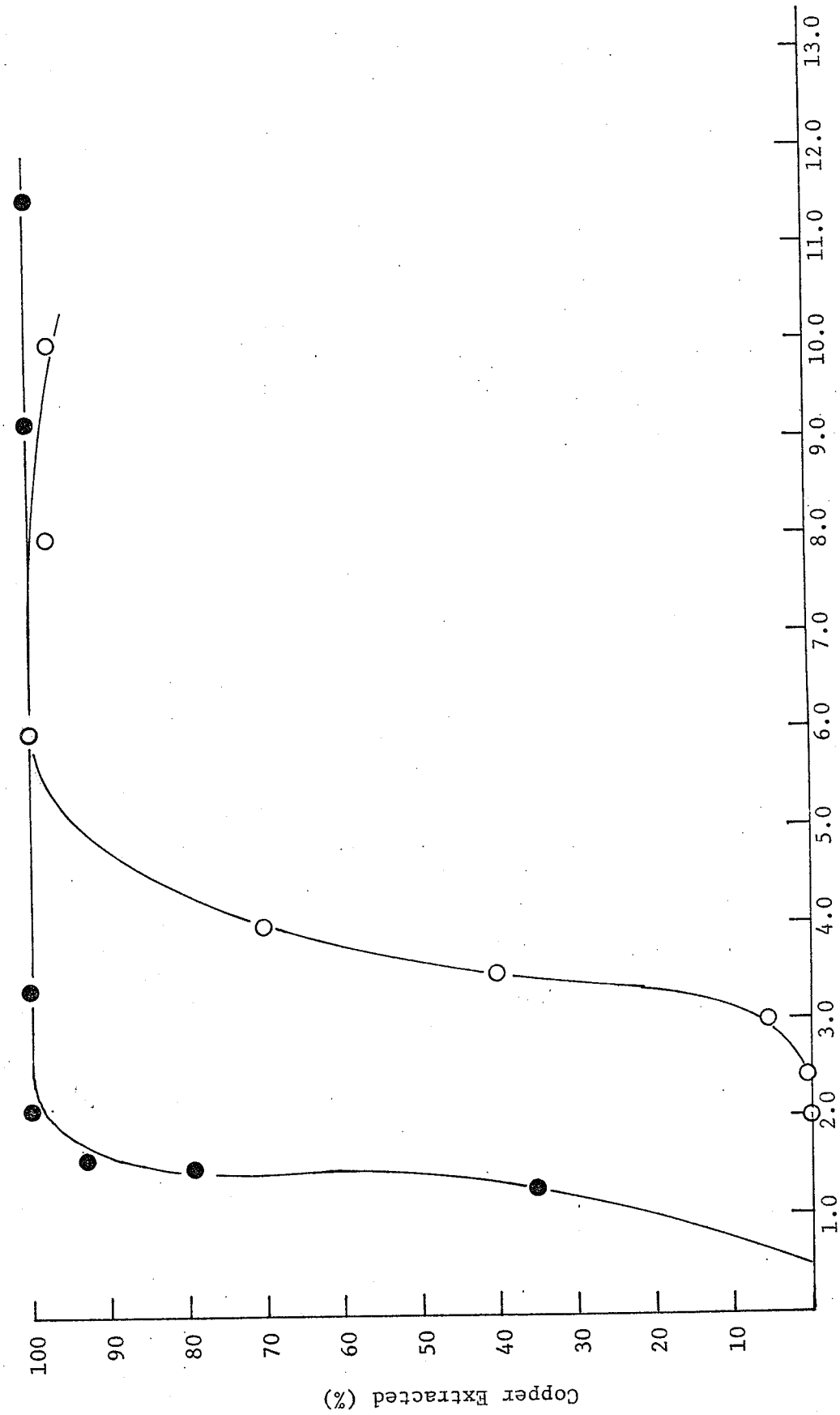
Foams were pretreated with acetone solutions of oxine in a similar manner used for pretreatment by benzoylacetone. The soaking solution normally contained 0.00318 gm oxine per 100 ml. of acetone solution, which would result in 0.00086 $\pm$ 0.00003 gm. of oxine being left on the foam.

The pH dependent extraction curves are shown in Figures 10 and 11, using foams with both the regular amount of oxine, and 10 times the regular amount.

It was found that the oxine treated foams were light sensitive, as extractive properties decreased if the foams were not used as soon as possible after pretreatment. The decrease in absorption was also accompanied by a slight discolourization of the material on the foam.

Figure 10

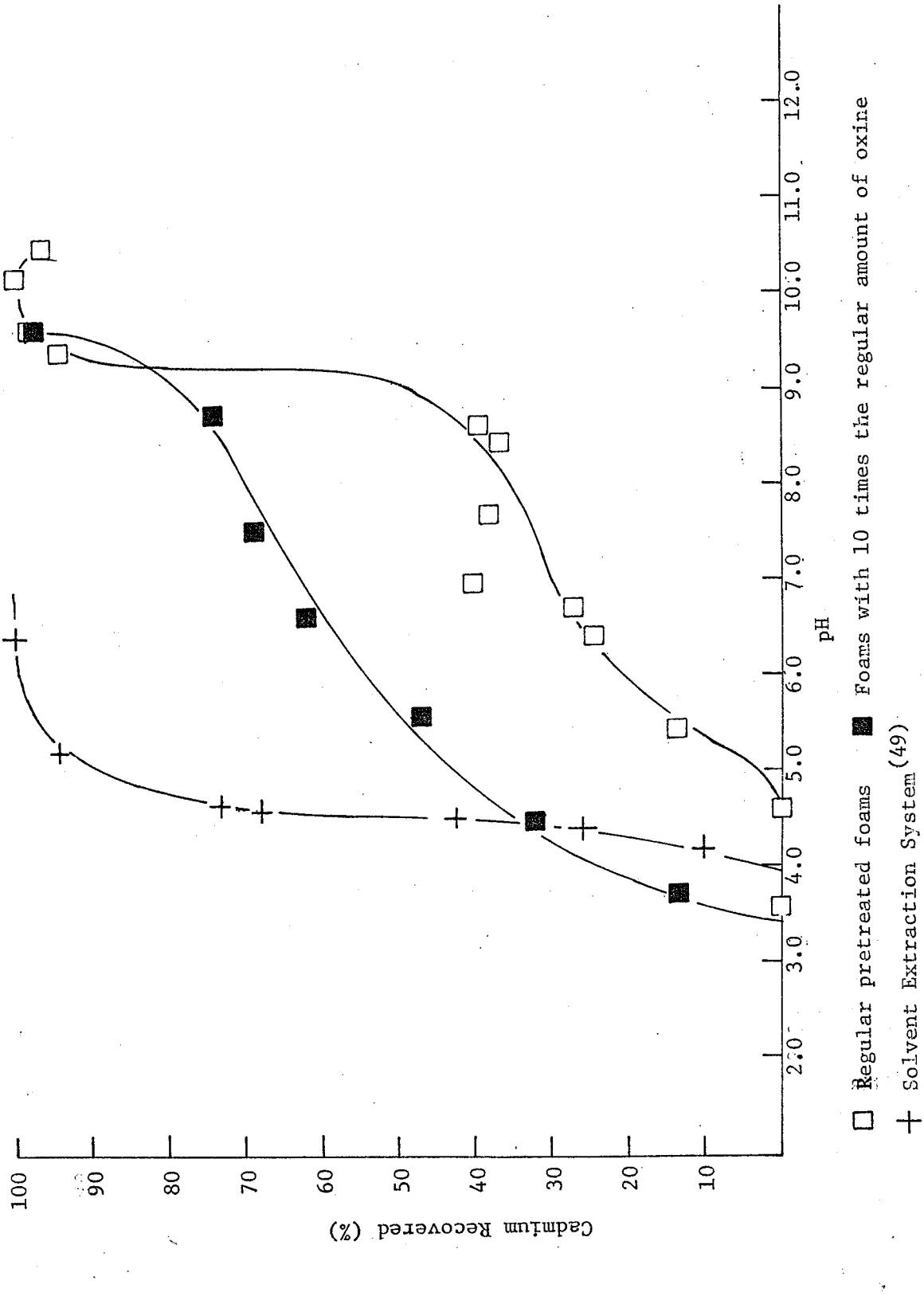
The pH Dependent Curves for the Extraction of Copper by Oxine Treated Polyurethane Foam Compared to the Corresponding Solvent Extraction System


Copper Extracted (%)
100
90
80
70
60
50
40
30
20
10
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
pH
○ Foam System
● Solvent Extraction System

(49)

Figure 11

The pH Dependent Curves for the Extraction of Cadmium by Oxine Treated Polyurethane Foam Compared to the Corresponding Solvent Extraction System


Cadmium Recovered (%)
100
90
80
70
60
50
40
30
20
10
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
pH
Regular pretreated foams
Foams with 10 times the regular amount of oxine
Solvent Extraction System (49)

Results and Discussion

The copper extraction curve for oxine treated foams has a higher $pH_{1/2}$ than the corresponding solvent extraction system using an oxine/chloroform solution[49], but seems to correspond almost exactly to the curve from benzoylacetone treated foams, suggesting a similar mechanism of retention.

Cadmium extraction seems to correspond to the extraction curve for cadmium onto untreated foam, except in the region from pH 5 to pH 9, where absorption is higher for the oxine treated foams. When foams containing ten times the regular amount of oxine were used, a marked change in the absorption curve occurred. Absorption increased even more at the lower pH range, resembling the solvent extraction curve to a greater extent. Absorption in this case was probably due to ligand effects, as well as retention of the metal by the foam itself.

Conclusion:

This work has shown that an open pore polyurethane foam system could act as a stationary support phase for a modified solvent extraction process for the extraction of metal chelates.

Soluble chelates such as copper and cadmium acetylacetonates could be extracted from aqueous solution due to retention of the ligand by the foam. The actual site of retention could not be determined, nor could the metal species present on the foam after absorption, but evidence suggests that it is a ligand effect and not a metal effect.

This type of system could be used as a preconcentration technique for trace analysis, by addition of the ligand to the aqueous phase prior to passing the solution through the foam. However, this type of system would not be particularly adaptable to preconcentration of large volumes of solution, or to field analysis.

Pretreatment of the foam with an insoluble ligand is a more useful technique, suitable to the preconcentration of large volumes. There is probably a dual effect keeping the ligand on the foam, both the insoluble nature of the ligand, and a ligand/foam interaction. Extraction and recovery of trace amounts of copper and cadmium utilizing this type of system was found to be quantitative.

The separation of copper and cadmium was proven to be possible, though the system used, consecutive static extractions,

would not be very practical for routine analysis, due to the time involved.

The technique of pretreatment of the foam with an insoluble ligand seems to be applicable to polyurethane foams as a general class, and is not dependent on one specific type, though interferences from the extraction of the metal by the foam itself may be a problem.

The benzoylacetone system was found to be practical for copper and cadmium, but as only a limited number of other metals were studied, it seems probable that it would also be applicable to other metals.

The analogous behaviour of the oxine system indicates that pretreatment of the foam may serve as a general method for preconcentration and analysis, providing the proper ligand/metal system can be established.

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