

THE UNIVERSITY OF MANITOBA

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

by

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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 μ g 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 \langle -dinonylphthalate \rangle tri-n-butylphosphate \rangle 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 $2.34 \mu\text{eq. g}^{-1}$. It was also shown that traces of mercury (II) could be collected rapidly and quantitatively by diethyldithiocarbamate foam⁽²²⁾.

Braun has loaded foams with tetrachlorohydroquinone, 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 $\text{Ce}(\text{SO}_4)_2$, 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 inert 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 $20 \text{ ml cm}^{-2} \text{ min}^{-1}$ flow rates studied. It was found that the radiosilver was quantitatively retained.

Braun has recently developed 'Chromofoms', 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 immunoabsorption 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 $\text{pH}_{1/2}$ 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 :

$$\frac{[\text{MA}_n]_{\text{org}} [\text{H}]^n}{[\text{M}] [\text{HA}]_{\text{org}}^n}$$

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⁾.

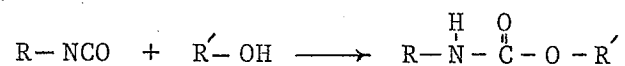
Starý has also investigated the solvent extractions of Be, Mg, Ca, Sr, Ba, Sc, La, Ti, Zr, Th, V, Nb, Cr, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Cd, Hg, Al, Ga, In, Tl, Pb, and Bi with 0.100 M oxine in chloroform⁽⁴⁹⁾⁽⁴⁵⁾. The effects of pH and oxine concentration were studied, and the extraction constants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



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 $\cdot 4\text{H}_2\text{O}$, 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 ± 0.02 pH units.

General Procedure

Foam plugs, 40 mm. in diameter and 50 mm. in length, average weight 1.4590 ± 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

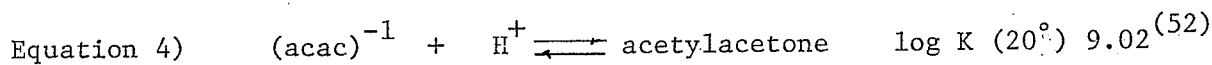
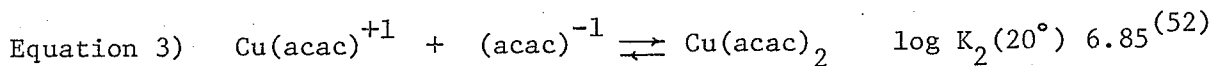
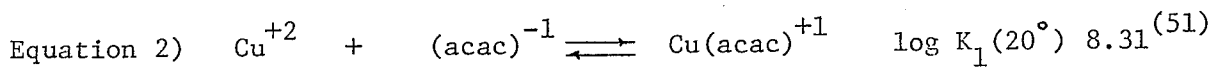
A saturated solution of copper acetylacetonate, $(\text{Cu}(\text{acac})_2)$, was prepared by allowing distilled water to stand over excess $\text{Cu}(\text{acac})_2$ for 48 hours, after which the solution was filtered through Whatman #42 filter paper, and the pH adjusted. The copper concentration was 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:



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