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THE EXTRACTION OF TIN AND ANTIMONY BY THE USE OF POLYURETHANE FOAM

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Psalm 33

Sing for joy in the Lord, O you righteous ones;
  Praise is becoming to the upright.
Give thanks to the Lord with the lyre;
  Sing praises to Him with a harp of ten strings.
Sing to Him a new song;
  Play skillfully with a shout of joy.
For the word of the Lord is upright;
  And all His work is done in faithfulness.
He loves righteousness and justice;
  The earth is full of the lovingkindness of the Lord.

By the word of the Lord the heavens were made,
  And by the breath of His mouth all their host.
He gathers the waters of the sea together as a heap;
  He lays up the deeps in storehouses.
Let all the earth fear the Lord;
  Let all the inhabitants of the world stand in awe of Him.
For He spoke, and it was done;
  He commanded, and it stood fast.
The Lord nullifies the counsel of the nations;
  He frustrates the plans of the peoples.
The counsel of the Lord stands forever,
  The plans of His heart from generation to generation.
Blessed is the nation whose God is the Lord,
  The people whom He has chosen for His own inheritance.

The Lord looks from heaven;
  He sees all the sons of men;
From His dwelling-place He looks out
  On all the inhabitants of the earth,

He who fashions the hearts of them all,
  He who understands all their works.
The king is not saved by a mighty army;
  A warrior is not delivered by great strength.
A horse is a false hope for victory;
  Nor does it deliver anyone by its great strength.

Behold, the eye of the Lord is on those who fear Him,
  On those who hope for His lovingkindness;
To deliver their soul from death,
  And to keep them alive in famine.
Our soul waits for the Lord;
  He is our help and our shield.
For our heart rejoices in Him,
  Because we trust in His holy name.
Let Thy lovingkindness, O Lord, be upon us,
  According as we have hoped in Thee.

(P.788-9, New American Standard Bible, Gospel Light Publications, Glendale, California, U.S.A., 1971)

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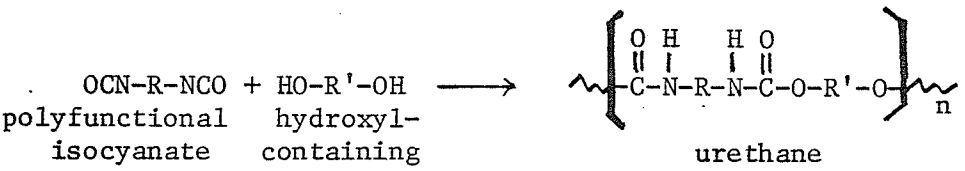
Abstract

Three types of polyurethane foams were studied for the extraction of tin and antimony. Static and flow-through systems were used for tin. The amount of metal extracted varied with the type of foam, acid strength, chloride concentration, concentration of metal ion and volume of metal ion solution. Quantitative extraction and recovery of tin and antimony were achieved. Open cell polyurethane foam is thought to act as a "solvent extractor" for tin and antimony from aqueous solution. The capacity of the foam (up to 8% tin by weight) was much higher than that due to surface adsorption.

The Extraction of Tin and Antimony by the use of Polyurethane Foam

Introduction

Polyurethane foam is also known as urethane foam and belongs to the family of cellular plastics. In 1947, Bayer[1] was the first to report the development of rigid polyurethane foam and later in 1952, Höchtlen[2] reported the preparation of a flexible urethane foam. The chemical ingredients of a urethane foam system are a polyfunctional isocyanate and a hydroxyl-containing polymer[3], along with the catalysts necessary to control the rate and type of reaction and other additives to control the surface chemistry of the process. A number of competing reactions can occur when the polyfunctional isocyanate and hydroxyl-containing polymer are brought together, but the main product, is a urethane.



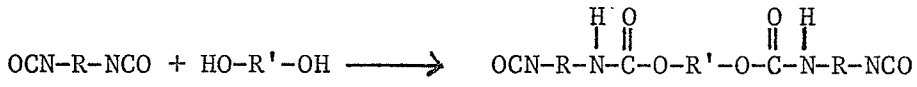
Carbon dioxide is generated *in situ* (by the reaction of isocyanate with water) as a blowing agent for both rigid and flexible urethane foams. The polyfunctional isocyanate can be a tolylene diisocyanate and the hydroxyl-containing polymer can be a polyester or a polyether. The physical properties are dependent on the structure of the R and R' groups. There are only 6 or 8 commercially available diisocyanates; therefore, the variation of

the composition of the foam is normally obtained by varying the structure of the polyhydroxy resin component. The equivalent weights for rigid foams vary from 100 to 150 and for flexible foams vary from 1,000 to 10,000. The equivalent weight is defined as the ratio of molecular weight to the number of hydroxyl groups of the hydroxy resin. The rigid foams have a higher cross-link density and a higher degree of branching than the flexible foams.

Producing polyurethane foam on a commercial scale is usually done by:

(1) One-shot process - all the ingredients for producing the foam are mixed together and then discharged from the mixer onto a suitable surface.

(2) Prepolymer process - the polyhydroxyl component is reacted with enough polyisocyanate to result in formation of a prepolymer with isocyanate groups plus excess isocyanate.



prepolymer

The prepolymer mixture is then reacted with water to simultaneously release carbon dioxide for expansion and to link to chains together in a cross-linked matrix. Foams made in this way could be open-celled or closed-celled. These cells may be interconnected in a manner such that gas may pass from one to another, in which case the material is termed open-celled. If the cells are discrete and the gas phase of each is independent of that of the other cells, the material is termed closed-celled.

The physical phenomena and chemical principles in the production of polyurethane foams have been studied. Bailey[4] studied the principles of hydrogen bonding, steric hindrance, simultaneous and consecutive reactions, equilibrium and polymerization as applied to polyurethanes. A method of measuring the surface area of polyurethane foams using stearic acid-1-^{14}C in n-heptane was described by Bowen[5].

The chemical properties of polyurethane foam were also investigated [6,7]. The foams remained unchanged except for swelling reversibly, in water, hydrochloric acid up to 10 M, hydrobromic acid up to 8 M, hydriodic acid up to 4 M, sulfuric acid up to 4 M, nitric acid up to 2 M, glacial acetic acid, 2 M ammonia, 2 M sodium hydroxide, and in the following solvents, light petroleum, benzene, carbon tetrachloride, chloroform, diethyl ether, di-isopropyl ether, acetone, isobutyl methyl ketone, ethyl acetate, isopentyl acetate and alcohols.

Since 1970, there has been an increasing interest in the study of polyurethane foam for the extraction and separation of inorganic and organic species from aqueous solution. In these studies, both flexible and rigid polyurethane foams have been used. The flexible foams could be used untreated or treated either physically by the coating with reagents or chemically by the introduction of a functional group into the foam backbone structure. The rigid foams were merely used as a solid inert support in chromatography.

Untreated Flexible Polyurethane Foams

In 1970, Bowen[7] began the use of flexible polyurethane foams as an absorbent for a number of substances from dilute aqueous solutions. The extraction of mercury (II) and gold (III) from 0.3 M hydrochloric acid, iron (III), antimony (V), thallium (III), molybdenum (VI) and rhenium (III) from 6 M hydrochloric acid; and uranium (VI) from saturated aluminium nitrate solution was found to be successful. The foams also removed iodine, benzene, chloroform, and phenol from water. Desorption of most of these species was obtained without difficulty.

In 1971, Gesser, Chow, Davis, Uthe and Reinke[8] examined the removal of polychlorinated biphenyls (PCB) and other pesticides from water by a column filled with open-pore polyurethane foam; PCB at the ppb level was extracted into the foam from aqueous solution and 93 to 100% of PCB could be recovered from the foam by sequential elution with acetone and hexane. Polyurethane foams were also used to monitor organics in river and drinking water[9]. Water was passed through the foam column at 2-4 ml cm^{-2} min^{-1} flow-rate. The extracted organic compounds were removed from the foam with hexane in a soxhlet extractor and then analyzed by gas chromatography. It was reported that organic contaminants were found and their concentration was estimated to be 0.005 to 0.010 ppb in drinking and river water. Musty and Nickless[10] also used six different types of polyurethane foams for the extraction and recovery of PCB from water. The extracted species were quantitatively recovered.

Polyurethane foams were used by Bindleman and Olney[11] to monitor PCB, DDT and chlordane levels in the atmosphere above the Sargasso Sea. Several million cubic meters of air was drawn in at a rate of 0.4 to 0.8 m^3/min through the foam plug measuring 15 cm long and 10 cm diameter. PCB, DDT and chlordane concentrations were measured in the 0.005 to 100 ng/m^3 range. Subsequently, Bindleman and Olney[12] used PCB coated on glass beads as a known source contaminant and put them in front of the collection system. Samples of 550 to 987 m^3 of air were drawn through foams of 8.9 cm in diameter at a flow-rate of 0.57 to 1.13 m^3/min, 0.22 to 0.65 ng/m^3 of PCB was collected. Porous polyurethane foam with a polyester backbone was tested by Turner and Glotfelty[13] as adsorbers for pesticide vapour in air. It was reported that a single cylindrical foam plug measuring 4.5 cm in diameter and 5 cm in length could trap 98% or more of the total pesticide vapour added at a flow-rate of 5 m^3/hour. The pesticides tested were easily removed by soxhlet extraction with acetone and hexane. The highest amount of pesticide tested was 300 µg and was retained by the foam even when pesticide-free air was drawn through the exposed foam for an additional 18 hours. If this is true, then, it would appear that absorption would be more likely than adsorption.

Schiller and Cook[14] suggested the use of flexible polyurethane foam for the preconcentration of gold (III) (ppb range) from tap water acidified with hydrochloric acid. An extraction of 99.4% of the gold

from solution was achieved. Bowen[15] also reported the extraction of gold (III) with polyurethane foam from liquid mine waste. A 0.02 mg of gold was taken up by 10 g of foam from 1 kg of liquid waste. Sukiman[16] also reported the extraction of gold chloride. The gold-198 tracer at a concentration of 0.02 ppm and unlabelled gold chloride solution at a concentration of 20 ppm in 1 M hydrochloric acid were passed through a foam column of 20 mm internal diameter at 30-40 ml/min. Gold chloride was recovered quantitatively from the same column with 20-50 ml of acetone at 3 ml/min. Braun and Earag [66] investigated the retention of gold thiourea complexes with untreated and treated foams. Various samples of foam material of different cell size, chemical composition and manufacture were used. Results showed that the uptake of gold-thiourea complex decreased as the cell size decreased for the unloaded foam. Furthermore, the absorption capacities of gold-thiourea complex on the polyether type foams were found to be generally better than on the polyester type. Palladium (II) thiourea complex was also found to be completely retained by untreated foam. However, it could not be completely eluted even by 300 ml of distilled water.

Lypka[17] described the extraction of copper (II) and cadmium acetylacetonates from dilute aqueous solution by untreated open pore polyurethane foam. Copper was quantitatively extracted at pH 10.2 and recovered with 1.5 M hydrochloric acid at a flow-rate of 2 ml/min through a column of 4.0 cm outside diameter. The

extraction and recovery of copper acetylacetonate were found to be very different at various pHs and acidities.

Gesser and co-workers described the use of polyurethane foam with the polyether backbone in the extraction and recovery of gallium from hydrochloric acid[18]. Gallium was absorbed into the foam by three passes of 100 ml solution of 7.5 N hydrochloric acid containing 50 ppm gallium. It was then removed by passing 50 ml of water or weakly basic solution at a flow rate of 64 ml/min through a column of 32 mm internal diameter. Quantitative extraction and recovery was possible. Iron (III) was also absorbed in the foam at 7.5 N hydrochloric acid.

The Canadian Plant and Process Engineering Ltd.[19] demonstrated that polyurethane foam could be used as an oil filter to clean up oil spills in both fresh and salt water. It was reported that flexible polyurethane foam was effective in the removal of 99% for "Bunker C" oil, 70% for marine diesel oil, 60% for crude oil and less than 5% for phenol at flow rate of 407 $l/min/m^2$.

Gough et al.[20] reported the removal of phthalate esters from water by polyurethane foam. Five types of foam and phthalates with side-chains varying in length from one to ten carbons were investigated. A 100 ml of water spiked with 0.1 μg of phthalate was run on a column of 5 foam plugs at 10 ml/min through a column of 15 mm internal diameter. The absorption of the phthalates was found to be dependent on the size of the phthalate and its structure. In her thesis[21], Gough reported that open pore polyurethane foam

was used to remove phthalates from air at the ppb level. Five foam plugs were put into a column and air was drawn through. Phthalates were then recovered with hexane and analyzed by gas chromatography.

Treated Flexible Polyurethane Foams

Polyurethane foams can be treated either physically with immobilized reagents and extractants by coating or soaking the foam or chemically by the introduction of functional groups into the foam structure before or after foaming.

Physically Treated Polyurethane Foams

In 1972, Braun and Farag[22] reported that foam polymer was loaded with tributyl phosphate (TBP) as a stationary phase and compressed into a chromatographic column which would give flow-rates of 1-4 ml/min through a column of 1.5 cm internal diameter. A solution containing both palladium (II) and nickel (II) each at a concentration of 1 mg/ml was first passed into the column. Then nickel was eluted first with 0.1 M perchloric acid containing 0.39 M thiourea and 0.08 M sodium perchlorate in water saturated with TBP. Palladium was then eluted with water saturated with TBP. Open cell polyurethane foam was reported to have the advantage of taking up TBP better than other inert supports in granular form, thus giving a higher capacity for the foam. Braun et al.[23] continued their investigation of TBP-treated foam as a column filling on

reverse-phase foam chromatography. Separation of nickel (II), bismuth (II) and palladium (II) was achieved. The metals were prepared in 0.2 M perchloric acid containing 0.78 M thiourea and 0.16 M sodium perchlorate. Nickel was then eluted with 0.1 M perchloric acid, 0.39 M thiourea and 0.08 M sodium perchlorate. Bismuth was eluted with 0.5 M perchloric acid and palladium eluted with water.

Braun et al.[24] separated gold (III) quantitatively from Zn (II), Co (II), Ni (II), Fe (III), Sb (III), Cu (II), Bi (III), and Pd (II) using polyurethane foam loaded with TBP. The extraction of gold-thiourea complex was later examined with different polyether and polyester types of polyurethane foams loaded with TBP. Polyurethane foams of the polyether type were found to retain TBP much more efficiently than the polyester foam and hence gave a better extraction. It was confirmed that the foam material behaved as an inert support in the loaded state. Braun and co-workers[25] continued to use TBP-loaded polyurethane foam and separated iron (III) from copper (II), cobalt (II) and nickel (II). The distribution of iron, copper, cobalt ions between the TBP-hydrochloric acid system on the foam was measured and found to be dependent on the concentration of the hydrochloric acid in the system. Separation was achieved because the different metals formed readily-extractable chloride complexes in aqueous solutions at different hydrochloric acid concentrations. Iron was eluted by 0.1 M hydrochloric acid, copper and nickel by 4 M

hydrochloric acid and cobalt by 5 M hydrochloric acid after all the metals had been loaded onto the foam.

Uthe et al.[26] used polyurethane foam coated with chromatographic grade greases for the extraction of organochlorine pesticides from water. Polyurethane coated with Dow Corning 200 oil was found to give better than 90% recovery of all ten pesticides tested. Musty and Nickless[10] also used silicone oil DC 200 coated porous polyurethane foams in the extraction and recovery of chlorinated insecticides and PCB from water. One litre of tap water was doped with the insecticide of interest at the ppb level and passed through the column. The extracted species were found to be quantitatively recovered. Uthe and co-workers[27] again used a 5% solution of DC 200 silicone oil in ethyl acetate to coat polyurethane foam plugs. Coated foam plugs were attached to the bottom of a wooden float and were kept under the surface of water near industrial and agricultural areas. Periodically, foam plugs were removed from the water and organic material in the foam was extracted with hexane. Recoveries of chlorinated pesticides and biphenyls were found to be successful. Gough and Gesser[20] studied the removal of phthalate esters from water with uncoated and DC 200 silicone oil-coated polyurethane foam. The results differed little from those with

uncoated foam which were described earlier. Di-n-octyl phthalate which was not extracted by untreated foam showed a 9% extraction with treated foam.

Braun et al.[28] used flexible polyurethane foam as an inert, solid support for chloranil. The reduction of Ce (IV), V (V) and Fe (III) on foam-filled column was carried out quantitatively and rapidly. Subsequently, Braun et al.[29] placed chloranil-loaded polyurethane foam in a syringe column. The reduction of micro and semimicro amounts of cerium (V), vanadium (V), and iron (III) to their lower valency states was successful.

The use of tri-n-octylamine in hydrochloric acid to load open-cell polyether type polyurethane foam column was described[30]. Trace amounts of cobalt (II) and nickel (II) were separated using 11.4 and 17.7% tri-n-octylamine-hydrochloric acid-polyurethane loadings. For the 11.4% tri-n-octylamine columns, nickel passed through the column without any retention and cobalt was later eluted with 1 M hydrochloric acid. Both metals could be adsorbed on the 17.7% tri-n-octylamine columns from which nickel could be eluted with 8 M hydrochloric acid and cobalt with 1 M hydrochloric acid.

Sukiman[16] prepared polyurethane foams treated with methyl isobutyl ketone, diethyl ether, isopropyl ether and ethyl acetate. These loaded foams were compared with untreated foams in the taking up of gold (III) from acid aqueous solution. They were shown to behave similarly. Gold chloride at a concentration of

20 ppm or 25 ppm in 1 M hydrochloric acid containing $^{198}AuCl_3$ as a tracer was passed through the column of 20 mm internal diameter at 30-40 ml min^{-1}.

Braun et al.[31] prepared plasticized foams by dissolving hydrophobic organic reagents such as dithizone, zinc dithizonate and 1-nitroso-2-naphthol in a plasticizer solution such as TBP, α-di-n-nonylphthalate, di-n-octylphthalate or dibutyladipate and then immobilizing the solution on open cell polyurethane foam. Polyurethane foam loaded with 3.9×10^{-4} M zinc dithizonate in TBP solution retained 99% of 0.01 μg. Separation of silver from lead and copper was also done. Dithizonate foams were prepared for the preconcentration of traces of mercury (II)[32]. The capacity for mercury (II) of a TBP-plasticizer zinc dithizonate foam at pH 6 was 23.4 μ eq g^{-1}. Chromogenic organic reagents dissolved in α-di-n-nonylphthalate was mixed with polyurethane foams[33]. The "chromofoams" thus formed were used in the quantitative determination of zinc (II) and lead (II) with dithizonate foams, copper (II) with rubeanic acid foams and cobalt with Amberlite LA-1 foams at ppb level. Braun[34] prepared TBP plasticized 1-nitroso-2-naphthol and diethylammonium diethyldithiocarbamate foams for the preconcentration of metal ions from aqueous solutions. Cobalt (II) was quantitatively recovered for concentrations ranging between 1 and 1,000 μg at pH values ranging between 6.6 and 9.9 at a flow rate of 5-6 ml cm^{-2} min^{-1}. TBP plasticized polyurethane

foam containing iodine or silver dithizone was also prepared[35]. Radioactive isotopes ^{131}I and ^{111}Ag were used with or without non-radioactive carrier. The isotopes of iodine and silver were found to be quantitatively exchanged with the isotope loaded on the I or Ag-treated foam.

Lypka et al.[36] described the extraction and separation of a copper-cadmium system by benzoylacetone-treated polyurethane foam and untreated foam. The benzoylacetone-treated foam gave a quantitative recovery of copper and cadmium from aqueous solution. Separation of copper from cadmium was found to be more effective by absorbing copper selectively from the solution at pH 4.86 rather than by first loading both metals on the treated foam and then sequentially eluting them.

Chow and Buksak[37] reported the use of dithizone-treated polyurethane foams in the extraction of mercury (II) and methylmercury (II) chloride from aqueous solution over a wide pH range and at various flow rates. Mercury (II) and methylmercury (II) chloride were quantitatively extracted up to 10 ppm. The mercury was then totally recovered from the foam by elution with acetone.

Lee et al.[38] used flexible open-pore urethane foam impregnated with dimethylglyoxime for the extraction of nickel (II) from aqueous solution. About 2 mg of nickel was extracted per gram of treated foam from aqueous solution in the pH range of 8-10. Quantitative extraction was obtained for nickel (II) at