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EXTRACTION OF SOME INORGANIC POLLUTANTS USING FLEXIBLE POLYMER FOAMS

by

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ABSTRACT:

Porous polyurethane and silicone rubber foams were shown to be effective in adsorbing various metal ions from aqueous solutions. The amounts of metal adsorbed varied with the acid and base strengths, foam treatment, length of foams, volume of metal ion solution, and concentration of metal ion. Foams treated with such complexing agents as sym-diphenylcarbazide, diphenylcarbazone, dithizone, dimethyl-aminoazobenzene or S-H radicals extracted in some cases as much as 99% of the mercury from aqueous solutions. Various equilibrium studies collaborated the results obtained from the flow-through method which was used for every metallic ion studied. Desorption from the foams may be achieved in a variety of ways depending on the chemical nature of the foam treatment and the metal involved.

Atomic absorption spectrophotometry was well suited to the analysis of all the elements studied.

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INTRODUCTION

There is presently a great interest amongst researchers and the public in general about pollution. Various forms of pollution exist, some are not aesthetically pleasing to the eye, while others are subtle in their nature.

Mercury was one of the first inorganic pollutants to have come to the attention of the general public. In Japan (1) several people have died and many have suffered serious physiological effects which have been directly related to mercury pollution. This incident has motivated many reports on the dispersion and effects of mercury in the environment (2-5). Since the discovery of mercury as a dangerous metallic pollutant, many other elements have come under the close scrutiny of environmental agencies, and as a result many reports (6-8) have appeared on trace elements in water, their origin, distribution and effect.

Requirements of the human body for trace metals and their specific functions within the body are not well defined, but some recent reports (9,10) have appeared in this area. A report on the relationship of trace metals to certain chronic diseases (11) has appeared which stressed the extreme importance of trace elements and trace element concentrations to the proper functioning of the human body.

Recently improved analytical methods such as spark source mass spectrometry (12) have made possible the analysis of trace elements in water down to one part in 10^{11} parts of water. There are, however, problems with accuracy and the necessity of matching the standard matrix to the sample matrix. A flameless method for atomic absorption spectrophotometers makesit possible to measure down to 10^{-10}g. for certain elements but there are many matrix interferences (13) associated with this method. Some continuous pollution monitoring has been done using flame emission spectroscopy (14), but again matrix interferences are prominent. Activation analysis has also been applied to studies of trace elements (15) but cannot be used as a routine analytical method due to equipment costs. Some ion selective electrodes are being used for elemental analysis because no separations are necessary and instantaneous and continuous results are possible, however, concentration limitations and lack of suitable electrodes for all elements have hindered its universal acceptance (16-18). Various other methods exist for the analysis of trace metals, (19,20) but they are not suitable for general use.

The previously mentioned methods for trace metals all have certain limitations on accuracy and precision at low concentrations, so that methods are required to separate and concentrate certain trace elements from others and also from organic materials.

Co-precipitation methods (21,22) are suitable for the removal of trace elements but they are rather unspecific and thus further separation methods are required before the analysis of specific trace elements is possible.

Ion exchange (anionic or cationic) is also a good method for simple separations (23-26) of ions from solutions but the resins are expensive and susceptible to fouling from suspended solids generally found in industrial wastes.

Activated carbon adsorption has been reported for a long time as a suitable method for chemical separations (27,28) as has distillation, evaporation and sublimation (29,30) although they are generally used with organic compounds rather than inorganic compounds.

Freeze concentration, either zone melting or normal freezing, has been found to be an effective method (31) for concentrating trace inorganics from aqueous and organic solutions.

Absorptive bubble separations (32) may employ foaming or non-foaming separations. These methods both work well for soluble inorganic or organic ions and concentrate as well as separate, however, the full potential of this overall method of separation has not yet been exploited.

Membrane techniques (33,34) have also been shown to be useful in the separation and concentration of soluble inorganic ions from natural, treated, and waste waters. A recent

report (35) has cited the use of cation exchange membranes for the preconcentration of trace metals before analysis.

Gas chromatography works well with volatile metal chelates for separations and quantitative analysis (36,37) but requires extensive pretreatment of samples.

A paper (38) on solvent extractions, using high-molecular-weight amines for the quantitative removal of mercury at subnanogram and macro levels from solutions of brine and other chlorides, has recently been published. Trace elements may be treated with a chelating agent, extracted with another solvent, concentrated and then analysed by spectrographic methods (39-41); however, this requires extensive pretreatment before final analyses are possible.

A recent report (42) has shown that agricultural products and by-products are capable of adsorbing methyl mercuric chloride and mercuric chloride quantitatively, but the technique has not been applied to other elements or to separations as yet.

Another very recent paper (43) has shown that carbohydrates and polyamine polymers were capable of adsorbing mercuric chloride from aqueous solutions.

By using one or more of the various separation techniques already mentioned, it is possible to separate and concentrate any desired element from any solution on a small analytical testing basis. These methods would not be suitable

for large scale operations such as industrial pollution control because of the following reasons:

(1) - high costs involved

(2) - high efficiency required

(3) - large volumes of solutions involved

(4) - necessity of quick simple analysis

In 1970, a report (44) appeared which studied distribution ratios and absorption capacities of polyurethane foams for a few selected inorganic ions, and it was this report that has been used as the basis for the research recorded in this thesis.

Previous uses of polyurethane foams for extractions have included such things as cigarette filters (45,46), oil spill cleanups (47,48), phenol adsorption (4), and the removal of polychlorinated biphenyls (PCB's) from water (50). The selective absorption of polyurethane foams has been extended to the study of specific inorganic ions as in the separation of gold (51) from aqueous solutions. Polyamine-polyurea resins which are very similar chemically to polyurethane foams have been used to extract such ions as Cu (II), Ni (II), Au (II) and Co (II) from aqueous solutions (52). From these reports it was thought that the ability of polyurethane foams, treated with various complexing agents or untreated, to absorb specific inorganic elements could make the foams a suitable

method for separating and concentrating the element prior to analysis.

The present research has been devoted to the extraction and concentration of mercury from aqueous solutions; as it was considered to be one of the most imminent and widespread pollutants; with a brief look at various other inorganic elements.

EXPERIMENTAL

Apparatus and Materials

Model 306 Perkin Elmer Atomic Absorption Spectrophotometer (54)

Graphicorder Model 8020, Dynatronic Instrument Corporation

Varian Techtron Hollow Cathode Lamps

Aeration system for Mercury Analysis (Fig. 1) (55)

Glass Columns with Teflon stop-cocks (Fig. 2)

Vacuum gas rack with high voltage discharge tube (Fig. 3)

Soxhlet Extraction Apparatus (500 ml.)

Ott Planimeter type 16, Ott, W. Germany

diSPo plugs (Canlab Winnipeg)

Silicone Rubber S5370 RTV (Dow Corning)

All the chemicals used were of reagent grade. The water used was doubly distilled and then deionized using an ion exchanger, Research Model I, Illinois Water Treatment Company.

Fig. 1 - AERATION SYSTEM FOR LOW CONCENTRATION MERCURY ANALYSIS.
(not to scale)

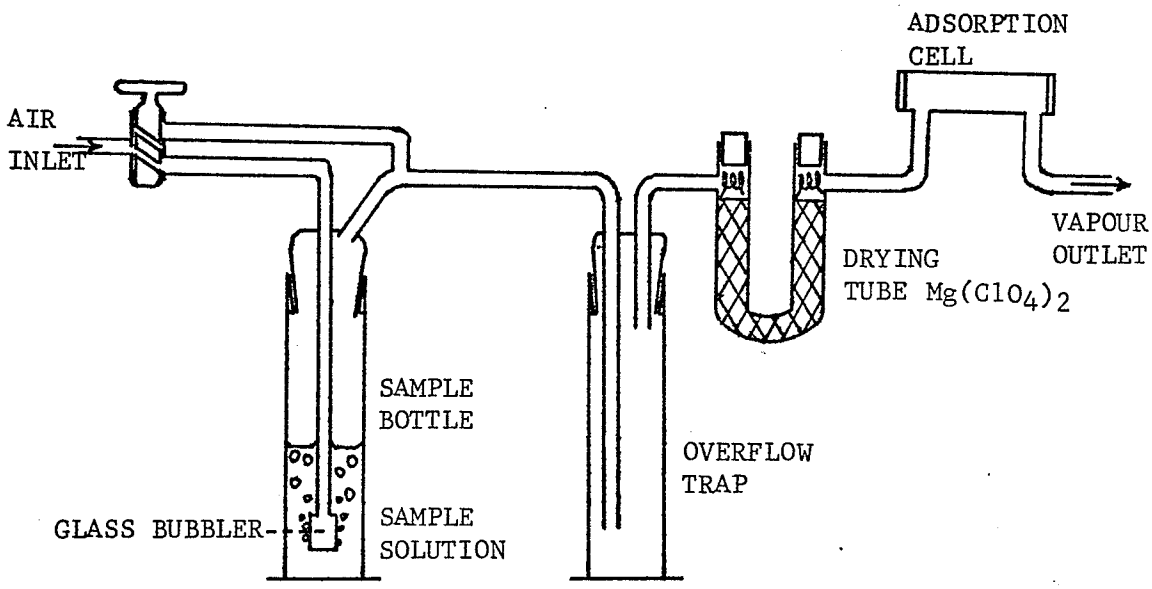
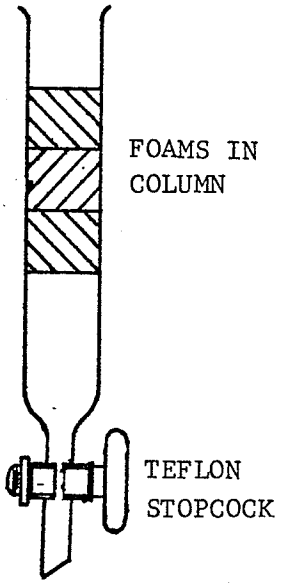


Fig. 2 - COLUMN USED IN ALL FLOW-THROUGH STUDIES.
(not to scale)



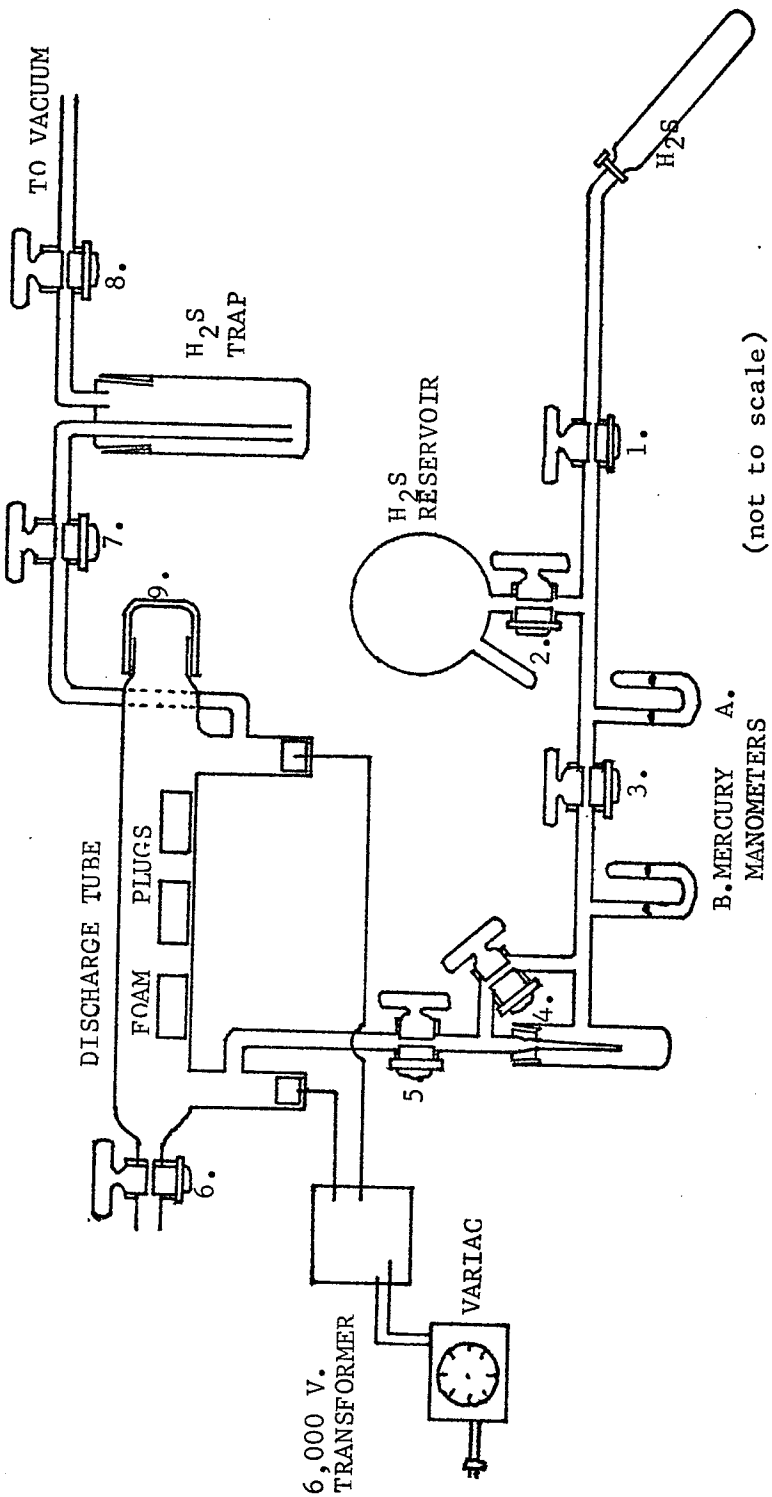


Fig. 3 - VACUUM GAS RACK WITH HIGH VOLTAGE DISCHARGE TUBE USED IN THE PRODUCTION OF S-H RADICAL diSPo PLUGS.

Production of Silicone Rubber Foam:

The silicone rubber foam was made in the laboratory from a Dow Corning mix called Silastic S5370 RTV foam. The mix consisted of a liquid base and a liquid catalyst that were mixed together in the ratio of 100 parts base to 6 parts catalyst. {There has been considerable work done on the development of new catalysts for the polymerization of siloxones as exemplified by a recent paper (56)}. Glass was too cumbersome for making foam molds in as it had to be well coated with a detergent film or a teflon spray to prevent the foam from sticking to the same. Alternatively, the foam was made to the appropriate diameter and length in polyethylene containers in order to facilitate separating the newly formed foam from its container.

After the base and catalyst were mixed together and stirred vigorously for thirty seconds, the mixture rose to seven times its initial volume and was cured well enough to handle within ten minutes. The silicone rubber foams were allowed to cure for 24 hours, soxhleted with doubly distilled deionized water for 12 hours, and then air dried before using.

The density of the silicone rubber foam, which is 0.1538 g/cc or about six times as dense as the polyurethane foam, has been reported along with other physical and chemical properties (57) of the silastic S5370 RTV foam.

Production of Diphenylthiocarbazone Silicone Rubber Foams (Dithizone)

These and other treated silicone rubber and polyurethane foams were prepared as reports (58,59) showed that their production was feasible.

Dithizone treated silicone rubber foams were produced in various fashions, but the best method devised was to dissolve 0.1 g. of dithizone, for every 7 cc. of liquid base, in as little acetone as possible. This solution was then mixed into the liquid base of the silastic foam. The liquid catalyst, in the correct proportion, was then added to the mixture and mixed vigorously for thirty seconds. After the mixture rose, it was allowed to cure for 24 hours finally producing a foam that was slightly softer, and had a smaller and more regular pore size than the plain silicone rubber foam. The foam was soxhleted with doubly distilled, deionized water for 8 hours and air dried prior to use.

Mixing 0.1 g. of dithizone, for every 7 cc. of liquid base, directly into the liquid base was also tried. This mixture had the liquid catalyst added in the correct proportion; stirred for thirty seconds; then it was allowed to cure for 24 hours after rising. The cured foam was then soxhleted with distilled and deionized water for 8 hours prior to being air dried. The foam was similar to plain silicone rubber except that small black centres of dithizone were visible throughout the foam.

Dissolving the 0.1 g. of dithizone, per 7 cc. of liquid base, in as little 2M sodium hydroxide as possible and then mixing this solution into the liquid base was tried. The catalyst was added in the prescribed fashion and stirred, but the foam refused to rise or cure; so this method was discarded.

Dissolving the 0.1 g. of dithizone per 7 cc. of liquid base in as little 2M sodium hydroxide as possible and then adding 6M hydrochloric acid to neutralize the solution was also tried. The resulting solution was mixed into the liquid base and the liquid catalyst was added. The foam rose slowly and also cured slowly, producing a very rubbery-rigid foam with larger pores than the plain silicone rubber foam.

All these dithizone treated silicone rubber foams were stored in sealed polyethylene bags until required.

Production of Sym-diphenylcarbazide Silicone Rubber Foams (SDØC).

This foam was produced by adding a solution of 0.1 g. of sym-diphenylcarbazide (Analar) dissolved in 5 ml. of acetone, directly into each 7 cc. of the liquid base. This mixture was then mixed vigorously for a minute and the liquid catalyst was added in the prescribed proportion. The entire mixture was mixed thoroughly for thirty seconds then allowed to rise and to cure for 24 hours in a polyethylene mould. The resultant foam had smaller and more regular pore sizes than the plain silicone rubber foam. After soxhleting with distilled, deionized water for 6 hours, the foam was air dried and stored in a sealed glass container until required.

A variation of this method that was used to produce the first sym-diphenylcarbazide silicone rubber foam consisted of adding 0.1 g. of sym-diphenylcarbazide directly into the liquid base and then following the above described procedure from the addition of the liquid catalyst.

Production of Polyurethane Foam.

The production of porous polyurethane foam is basically an isocyanate-amine condensation (60-63) having many diverse modifications. The possibility of making open-pore polyurethane foam from closed-pore may be accomplished by an electrical discharge treatment (64), although there may be problems with highly toxic gases that are released by the polyurethane foam (65) if sufficiently high temperatures are reached.

The open-pore polyurethane foam (diSPo brand) that was used in this research was not made in the laboratory, but was obtained from a local source (Canlab, Winnipeg). The diSPo plugs were cylindrical in shape with diameters of 16, 22, 28, 35, and 48 mm. and all had a length of 40 mm. The diSPo plugs were originally designed as test tube stoppers for biological samples. The density of these foams, calculated from average weights and volumes, was 0.025 g./cc. $\pm$ 0.005. A recent report (66) has briefly examined the various chemical properties of the polyurethanes that are similar to those used in this research.

Production of Sodium Hydroxide diSPo Foams.

Three - 22 mm. diSPo foams, that were previously soxhleted with acetone for 6 hours and then air dried, were placed in a 50 ml. solution of 2M sodium hydroxide. The foams were squeezed several times while sitting in the solution over a period of one-half hour. When the foams were removed from the sodium hydroxide solution, they were squeezed to near dryness and allowed to air dry. There was no colour change associated with this treatment of the diSPo foams. The foams were stored in a glass container until required.

Production of S-H Radical diSPo Foams (S-H)

The vacuum rack (Fig. 3) with a high voltage discharge tube, was specifically designed for the production of S-H radical diSPo foams.

The entire rack was pumped down by a vacuum pump with all stopcocks except 6 and 1 open. Stopcock 3 was then closed and with the H_2S inlet attached to the gas cylinder, stopcock 1 was opened to a slow hydrogen sulphide gas stream. The hydrogen sulphide reservoir was allowed to fill to atmospheric pressure as registered on manometer A. Stopcock 1 was closed at the same time as the hydrogen sulphide cylinder. Liquid nitrogen was used to condense the hydrogen sulphide into the trap at the bottom of the reservoir. Once the gas condensed into the trap, stopcock 2 was closed and the liquid nitrogen was taken off. Stopcocks 5 and 7 were closed and 6 opened in order to allow the discharge chamber to come to atmospheric equilibrium. Cap 9 was taken off to allow three - 22 mm. diameter diSPo foams; that were previously acetone soxhleted for 6 hours and air dried; to be placed 1 cm. apart in the discharge chamber between the two electrode entrances. Cap 9 was replaced, stopcock 6 was closed and 7 was opened in order to pump the chamber down again. Liquid nitrogen was then placed around the hydrogen sulphide trap between stopcocks 7 and 8; stopcock 4 was closed; 5 was opened; 2 was opened; and

3 was partially opened to give a 5 mm. manometer difference in B. The variac was turned on and up to 40 V., on a scale of 120 V., producing a blue discharge in the discharge tube; reddish-pink if the air was not entirely pumped out of the system. The blue discharge, controlled by the variac, was allowed to continue for two and one-half minutes. Stopcocks 5, 8, 3 and 2 were closed and 6 opened to allow the discharge tube to come to atmospheric equilibrium so that cap 9 could be removed in order to obtain the three fresh S-H diSPo foams. Once stopcock 7 was opened to release the vacuum in the H_2S trap, the liquid nitrogen was taken off and the trap was removed to the fume-hood. The old trap was immediately replaced by another one to prevent hydrogen sulphide from escaping into the air.

The newly produced S-H diSPo foams were then soxhleted with doubly distilled, deionized water for 8 hours and vacuum dried prior to use. These foams were stored in closed polyethylene bottles until required.

Production of Sym-diphenylcarbazide diSPo Foams. (SDØC)

Three - 22 mm. diSPo foams, which were previously soxhleted with acetone for 6 hours and then air dried, were placed in a 150 ml. beaker containing 50 ml. of 2.0 M. sodium hydroxide.(1M, 0.5M, 0.2M and 0.1M sodium hydroxide solutions were also used in place of the 2M solution). 0.1 g. of sym-diphenylcarbazide (Analar reagent) was placed in a 25 ml. beaker and dissolved with 10 ml. of acetone. This solution was then poured into the 2.0M sodium hydroxide solution, containing the three diSPo foams, producing a dark reddish-orange colour. The diSPo foams were squeezed several times while remaining in the solution for one-half hour. The treated foams were then taken from the solution, rinsed several times with distilled water and allowed to air dry, producing light pinkish-orange foams. Some of these foams were then soxhleted with distilled deionized water, whereupon the colour of the foams faded in the soxhlet apparatus back to the original diSPo foam colour. All of these treated foams were stored in a sealed glass beaker.

Production of Diphenylthiocarbazone diSPo Foams (Dithizone)

Three - 22 mm. diSpo foams, previously soxhleted with acetone for 6 hours and then air dried, were placed in 50 ml. of a 1M sodium hydroxide solution in a 150 ml. beaker. 0.1 g. of dithizone (Analar reagent) was mixed directly into the solution until all the dithizone was dissolved, which produced a dark orange solution. The diSPo foams were squeezed several times while remaining in the solution for one-half hour. The dark brown dithizone treated diSPo foams were then taken out of the solution, rinsed several times in distilled deionized water and then soxhleted for 8 hours in distilled deionized water, finally producing pale yellow foams. These foams once air dried, were stored in a large covered beaker until required.

Production of Diphenylcarbazone diSPo Foams (DØC)

Three - 22 mm. diSPo foams, previously soxhleted with acetone for 6 hours and air dried, were placed in 50 ml. of a 0.2M sodium hydroxide solution in a 150 ml. beaker. 0.1 g. of diphenylcarbazone (Analar reagent) was placed in a 25 ml. beaker and dissolved with 10 ml. of acetone. This solution was then added to the three diSPo foams in the 0.2M sodium hydroxide solution producing a reddish coloured solution. The diSPo foams were squeezed several times while in the solution for one-half hour. The diphenylcarbazone treated diSPo foams were then rinsed several times in distilled water and air dried finally producing light pink coloured foams. These diSPo foams faded with water in the soxhlet apparatus, back to the original diSPo foam colour. A large beaker was used for storage of these foams until they were required.

A variation in the production method for these foams was also used. It consisted of neutralizing the 0.2M sodium hydroxide with a 6M hydrochloric acid solution after the diphenylcarbazone had been added to the sodium hydroxide solution. The procedure for squeezing the foams while in this solution for one-half hour remained the same as in the above described method of treatment.

Production of Dimethylaminoazobenzene diSPo Foams (DMAAB)

Three - 22 mm. diSPo foams, previously acetone soxhleted for 6 hours and air dried, were placed in 50 ml. of 0.2M sodium hydroxide solution in a 150 ml. beaker. 0.1 g. of dimethylaminoazobenzene (Fisher reagent) was placed in a 25 ml. beaker and 15 ml. of acetone were added. A brown solution with a yellow precipitate, which formed on mixing, was then completely transferred from the 25 ml. beaker to the 150 ml. beaker with the three diSPo foams in the sodium hydroxide solution. The diSPo foams were squeezed several times while in the mixture for one-half hour. The dimethylamino-azobenzene treated diSPo foams were then removed from the mixture and rinsed several times with distilled water. These foams were then soxhleted with distilled deionized water for 24 hours producing dark yellow coloured foams when air dried. These foams were stored in a large covered beaker until required.

Procedure:

The procedure for all the flow-through studies was basically the same in every case unless otherwise specified. 100 ml. of a specific metal ion standard solution were poured through the foam, which was in a column, at a flow rate of 40 ml/min.

Standard stock solutions were made up for the elements to be studied using the reagents specified (67). These stock solutions were diluted with the required aqueous solution to the appropriate concentrations that were in the optimum analytical range of the atomic absorption spectrophotometer.

An 18 mm. O.D. glass column (Fig. 2) was used to hold the variously treated 22 mm. diameter polyurethane foams at their normal length of 40 mm. It must be noted that for the other diameter foams, the column diameter must be such that the foam inside the column is close fitting, but not too tight, in order to allow the solution to flow through the foam uniformly and not between the foam and the wall of the column.

The flow rate was controlled by the teflon stopcock at the bottom of the column.

The foams were wet with small volumes of distilled deionized water passed through them to eliminate any possible air bubbles prior to passing through the desired elemental solution.

A slight air pressure was used to force any residual solution left in the foam into the sample bottle.

125 ml. polyethylene sample bottles were used for all the elements in the flow-through and equilibrium studies, except in the case of gold and mercury, where 4 Fl. Oz. glass sample bottles were used.

For the study of chromium solutions, a special polyethylene column along with the polyethylene sample bottles, was used as chromium was known to adhere to glass surfaces.

If more than one pass of a standard solution through the foam was required, them another 100 ml. aliquot of the same metal ion standard solution would be poured through the same foam in the column at the same flow rate.

The solutions were all aspirated directly into the air-acetylene flame, except the solutions of aluminum and zirconium which required the nitrous oxide-acetylene flame. Each unknown concentration was determined by comparison to several known standards of that specific element.

The concentration difference between the standards and the sample solutions that were run through the foam was attributed entirely to the adsorption of that element by the foam.

The absorbance values for the various solutions, including standards, were recorded from the spectrophotometer 10 second integrated absorbance readout. A standard deviation was calculated from the four recorded absorbance readings that

were taken for each solution. This standard deviation was expressed as a plus and minus percentage of the mean absorbance of the standards run through the foam. It was this percentage that was reported as the experimental error for the results in Tables I and II.

Various equilibrium studies were done to confirm the results obtained in the flow-through studies. For the equilibrium tests 100 ml. aliquots of the elemental standard solution had the variously treated foams placed in them to equilibriate for certain periods of time. While in the solution, the foams were squeezed several times and the entire solution was agitated with a magnetic stirrer over the equilibrium period.

RESULTS

Initial Survey

Untreated polyurethane and silicone rubber foams were tested for their effective removal of some 23 metal ions from various aqueous solutions ranging from 6M acid to 2M base.

The results of this survey are summarized in tables I and II

The silicone rubber foams (35 mm. X 35 mm.) were only tested for the distilled deionized water solutions of the elements as a comparison to the plain polyurethane foams.

A new acetone soxhleted foam was used for each element and for each sample solution.

Generally, the results showed that both types of foams adsorbed elements with greater frequency when in a chloride solution than in a nitrate one, but this may also be due to the choice of salt.

In neutral solutions, the silicone rubber foam was more effective in removing nickel, magnesium, bismuth, palladium, silver, gold, molybdenum, mercury and chromium than the polyurethane foam. Some of this effect may be attributed to the greater volume of silicone rubber foam used, but this could not account for the total effect.

Three of the noble metals, gold, silver, and platinum showed significant adsorption onto the polyurethane foam from a wide range of acid and base strengths.

There was no adsorption by the polyurethane foam

Table I- ADSORPTION OF VARIOUS ELEMENTS IN SELECTED ACID AND BASE MOLARITIES BY POLYURETHANE AND SILICONE RUBBER FOAMS

		% adsorbed by untreated diSPo plug-----and by silicone rubber foam								
		Nitric				H_2O	Sodium Hydroxide			H_2O
ELEMENT	CONCENTRATION IN p.p.m.	6M	2M	0.2M	H_2O	24 HOUR EQUILIBRIUM	0.02M	0.2M	2M	SILICONE RUBBER
Cu (II)	20	0	0	0	0	0	0	18±2	1±1	0
Ni (II)	20.32	0	0	0	0	8+1	0	29±1	70±1	7±1
Pb (II)	40	0	0	0	0	0	3±1	1±1	0	0
Mg (II)	2.03	0	0	0	0	0	19±1	20±1	10±1	5±1
Bi (III)	100	0	0	0	0	0.3±.3	0	0	0	6.5±1
Pt (IV)	100	4±1	2±1	2±1	9±1	33±1	3±1	2±1	0	9±1
Pd (IV)	100	0	0	0	0	42±1	0	0	0	3±1
Mn (IV)	22	0	0	0	0	0	0	0	ppte	1±1
Al (III)	150	0	0	0	0	0	15±3	47±3	0	1±1
Li (I) (a)	4.8	0	0	0	0	0	0	0	0	0
Ca (II) (a)	7	0	0	0	0	0	0	ppte	ppte	0
K (I) (a)	9.7	0	0	0	0	0	0	0	0	2±1
Na (I) (a)	3.47	0	0	0	0	0	-	-	-	0

(a) These elements were run using the flame emission mode of the atomic absorption spectrophotometer, as no lamps were available for them.

Table II- ADSORPTION OF VARIOUS ELEMENTS IN SELECTED ACID AND BASE MOLARITIES BY POLYURETHANE AND SILICONE RUBBER FOAMS

ELEMENT	CONCENTRATION IN p.p.m.	% adsorbed by untreated diSPo plug-----and by silicone rubber foam: Hydrochloric 6M	Hydrochloric 2M	Hydrochloric 0.2M	H_2O	H_2O 24 HOUR EQUILIBRIUM	Sodium Hydroxide 0.02M	Sodium Hydroxide 0.2M	Sodium Hydroxide 2M	H_2O SILICONE RUBBER
Fe (III)	100 (a)	8±1	0	0	0	0	3±1	10±1	27±1	0
Zn (II)	10	0	0	0	0	0	0	0	0	0
Cd (II)	8.94	0	0	0	0	2±2	2±2	15±2	9±2	0
Ag (I)	7.45	0	0	3±1	8±1	10±1	18±1	18±1	7±1	54±1
Au (I)	19.6	32±1	43±1	39±1	18±1	95±1	3±1	0	0	24±1
Mo (VI)	78.14	7±1	0	0	0	0	0	0	0	18±1
Hg (II)	88	0	0	0	0	0	1±1	0	0	29±1
Cr (IV)	17.8	33±1	30±1	12±1	2±1	65±1	5±1	0	0	25±1
Sn (II)	125	2±2	13±2	0	0	3±1	0	0	1±1	0
Zr (IV)	2000	0	0	0	15±5	0	0	0	ppte	0

(a) The concentration of Fe (III) in 0.02M, 0.2M and 2M sodium hydroxide was reduced to 10 ppm.

of lithium, calcium, potassium or sodium within the acid and base molarity ranges examined.

These results suggest that the foams may be selective for one or more elements at a certain acid or base strength as many of the elemental solutions were not adsorbed.

Following the results of this initial survey, it was decided to intensively study mercury, which was considered a dangerous pollutant, using variously treated and untreated silicone rubber and polyurethane foams. These treated foams were thought to be necessary as from table II, mercury adsorption was negligible for the untreated foam over a wide range of acid and base solution strengths.

Analysis of Mercury at Low Concentrations

The analyses of both mercuric chloride and methyl mercuric chloride, at low concentrations, were difficult in that pretreatment of the samples and standards was necessary prior to analysis.

The methyl mercuric chloride was obtained from Environment Canada, Freshwater Institute at a concentration of 500 ppm methyl mercury in an ethyl acetate solution. This solution was diluted down in doubly distilled, deionized water to a concentration range from 2.0 to 0.0004 ppm methyl mercury (unless otherwise specified) for testing purposes with each type of foam.

A stock solution of 1000 ppm mercury as mercuric chloride in a 2M HCl solution was diluted down with doubly distilled, deionized water to a concentration range from 4.0 to 0.0004 ppm mercury for testing purposes with each type of foam.

The aeration system (Fig. 1) (68) was used to analyse both types of mercury over their respective concentration ranges.

For methyl mercuric chloride analysis, every 100 ml. aliquot of the standard that was passed through the foams and collected in 150 ml. beakers had 1 ml. of 1:4 sulphuric acid and 1 ml. of 4% potassium permanganate added. (69) Watch glasses were then placed over the beakers; the samples in

the beakers were heated to the boiling point; allowed to cool to room temperature and then placed in 4 fl. oz. glass sample bottles. Before analysis, 8 drops of hydroxylamine hydrochloric ($NH_2OH \cdot HCl$) were added to each 100 ml. of sample to be analyzed, shaken well, and then 4 ml. of stannous chloride solution were added just before the sample solution was to be placed into the aeration system for analysis.

Briefly, the potassium permanganate was added to the sample to oxidize the methyl mercuric chloride to the mercuric ion. The hydroxylamine hydrochloric neutralized the excess permanganate in the sample, while the stannous chloride reduced the mercuric ion to mercury metal which was vapourized by air bubbles emanating from a sintered glass bubbler in the sample bottle of the aeration system. Compressed air that had its pressure regulated to a constant flow, which produced an entire mercury standard peak in the order of 5 minutes, was used.

The volatilized mercury flowed through the overflow bottle, through the magnesium perchlorate drying tube and into the 10 cm. quartz windowed glass adsorption cell that was placed in the beam of the mercury lamp in the atomic absorption spectrophotometer. The mercury atoms in the vapour in the cell were excited by the lamp beam and gave an absorbance reading on the readout and on the recorder printout. Finally, the mercury vapour passed out of the cell and into a dithizone complexing solution.

For mercuric chloride samples only 4 ml. of stannous chloride solution per 100 ml. of sample had to be added prior to the sample being placed into the aeration system for analysis.

Blank solutions of doubly distilled, deionized water, similarly treated as their respective samples and standards, were run in all cases.

Before every use of the aeration system, the moisture laden magnesium perchlorate was replaced in the drying tube. The sample bottles and the aeration sample bottles were rinsed in aqua-regia and distilled water prior to each set of tests. The glass bubbler was soaked in aqua-regia for at least one-half hour and then thoroughly rinsed with distilled water at the start of each day of analysis.

The recorder printout was used in the analysis of the mercury solutions. The various peaks recorded for the standards, blanks and samples had the areas under them measured with the Ott Planimeter. These areas were then used to calculate the mercury concentration of the unknown samples and the percent of the mercury removed by the foam used.

Standard deviations were calculated from the areas under the peaks of several mercury standards that were run for each set of tests. These standard deviations, expressed as plus and minus percentages of the mean standard areas, were used as the

experimental errors for the percentages of mercury adsorbed by the various foams as reported in the tables to follow.

The Effects of Polyethylene Sample Bottles on Equilibrium Studies for Mercury Adsorption

When the initial equilibrium studies for mercury adsorption by the foams were performed using 125 ml. polyethylene sample bottles, irregular results were obtained. For example, when a single diSPo foam treated with SDØC, acetone and 2M sodium hydroxide (p.19) was placed in 100 ml. of a 0.04 ppm mercuric chloride solution held in a 125 ml. polyethylene sample bottle for a 20 hour test, it was found that 52 $\pm$ 3% of the total mercury was adsorbed. This equilibrium test was repeated two more times with similarly treated diSPo foams and new polyethylene bottles. These tests gave mercury adsorption values of 63 $\pm$ 3% and 75 $\pm$ 3%. These irregular results led to the testing of the polyethylene bottles themselves, for the adsorption of mercury.

The bottles were rinsed several times with tap water, then with aqua regia and distilled water prior to use.

A freshly cleaned polyethylene bottle was used for each of the results summarized in Table III. The results showed some relationship between the amount of mercury adsorbed and the equilibrium time.

A timely report (70) simultaneously verified the fact that the polyethylene bottles were adsorbing mercury.

Glass sample bottles (4 fl. oz.) were used for all the mercury studies reported in this thesis.

Table III - ADSORPTION OF MERCURIC CHLORIDE BY 125 ML. POLYETHYLENE SAMPLE BOTTLES

Mercury Concentration was 0.04 ppm.

EQUILIBRIUM TIME (HOURS)	MERCURY REMOVED (%)
4	2±1
	8±1
	12±1
24	26±2
	37±2
	15±2
48	37±2
	57±2
	77±2
72	54±2
	46±2
	48±2

Adsorption of Mercury by Silicone Rubber Foam

From table II, it was noted that an untreated silicone rubber foam adsorbed 29 $\pm$ 1% of the mercuric chloride from a 100 ml. aqueous solution of 88 ppm mercury that was poured through the foam. This result showed that a single untreated silicone rubber foam could adsorb as much as 0.0026 g. of mercury.

For the intensive study of mercury, various lengths of untreated silicone rubber foam and various repetitions of passing 100 ml. aliquots of the standard solutions through each foam were used. The results of these studies are summarized in tables IV and V.

Decreasing the concentration of mercuric chloride passed through the foams from 0.04 ppm to 0.004 ppm, decreased the percentage of mercury adsorbed. This effect was thought to be due to a shift in the equilibrium from the foam to the solvent.

For methyl mercuric chloride, very high adsorption percentages were recorded at the 0.04 ppm level, but as the concentration of mercury increased, the percentage of adsorption decreased.

Studies were also done on passing the same aliquot of standard several times through the same silicone rubber foam prior to analysis. The results of these tests are summarized in table VI. They showed the foams to be efficient for mercury removal using this method.

Table IV - ADSORPTION OF MERCURIC CHLORIDE BY SILICONE RUBBER FOAMS

NUMBER OF PASS THROUGH FOAM (a)	FOAM SIZE (mm)	CONCENTRATION OF MERCURY (ppm)	MERCURY REMOVED (%)
1	35X35	0.04	51±3
1	35X35	0.04	51±3
1	58X35	0.04	80±2
2			78±2
3			68±2
4			72±2
5			77±2
1	58X35	0.004	61±2
2			44±2
3			38±2
1	58X35	0.004	60±2
2			44±2
3			38±2

(a) each number represents a fresh solution passing through the foam.

Table V - ADSORPTION OF METHYL MERCURIC CHLORIDE BY SILICONE RUBBER FOAMS

NUMBER OF PASS THROUGH FOAM (a)	FOAM SIZE (mm)	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
1	58X35	2.0	69±2
2			67±2
3			55±2
1	58X35	0.4	62±5
2			50±5
3			45±5
1	63X35	0.04	97±1
2			97±1
3			89±1
4			85±1
5			81±1
1	63X35	0.04	88±2
2			93±2
3			84±2
4			87±2
5			87±2

Table VI - ADSORPTION OF METHYL MERCURIC CHLORIDE BY ONE SILICONE RUBBER FOAM

VOLUME OF STANDARD PASSED THROUGH FOAM (ml)	NUMBER OF PASSES	FOAM SIZE (mm)	CONCENTRATION OF MERCURY (ppm)	MERCURY REMOVED (%)(b)
100	3	63X35	0.04	95±1
200	3			88±1
200	5			91±1

(a) each number represents a fresh solution passing through the foam.

(b) % mercury removed that was initially present in the solution analysed after n number of passes.

Adsorption of Mercury by Dithizone Treated Silicone Rubber Foam.

As described in the production of dithizone treated silicone rubber foam (p.12), dithizone was incorporated into the foam using various procedures. Table VII summarizes these various procedures and the results obtained, when 100 ml. aliquots of a 0.04 ppm mercuric chloride standard solution were passed through the foams.

The results obtained generally showed a 20% increase for the adsorption of mercury by these foams over the untreated silicone rubber foam. There was a small percentage difference amongst the various dithizone incorporated silicone rubber foams for the adsorption of mercury for the first 100 ml. aliquot of mercury standard passed through them, but the foam produced by dissolving dithizone in acetone appears to produce greater or more uniform incorportion of the dithizone. These foams extract more mercury during the passage of a second 100 ml. aliquot than the foam produced by direct mixing of dithizone into the liquid base.

Table VII - ADSORPTION OF MERCURIC CHLORIDE BY DITHIZONE TREATED SILICONE RUBBER FOAMS

TREATMENT PROCEDURE (a) (b)	NUMBER OF PASS THROUGH FOAM	CONCENTRATION OF MERCURY (ppm)	MERCURY REMOVED (%)
Dithizone mixed directly into the liquid base	1	0.04	68±2
	2		53±2
Dithizone dissolved in acetone, then into foam base	1	0.04	72±2
	1	0.04	68±2
	2		68±2
Dithizone dissolved in 2M NaOH and neutralized with 6M HCl then into liquid base	1	0.04	72±2

(a) see p. 12
(b) foam size was 35 X 35 mm. in all cases.

Adsorption of Mercury By Sym-diphenylcarbazide treated Silicone Rubber Foam.

These foams were originally prepared by placing the SDØC directly into the base of the foam during the production stage, but a more homogeneous foam was produced by dissolving the SDØC in acetone prior to mixing it into the liquid base of the foam (p.14).

Table VIII shows the adsorption percentages, using the flow-through method, for the two types of treated SDØC silicone rubber foams for a 0.04 ppm mercuric chloride solution.

Dissolving the SDØC in acetone for the foam production and increasing the length of the foam used, increased the adsorption of mercury to over 90%; however, when this was compared to the adsorption of mercury by an untreated silicone rubber foam of similar size, the increase in adsorption was only 10%. This increase of 10% was attributed to the effect of the sym-diphenylcarbazide complexing agent. The addition of the sym-diphenylcarbazide resulted in a larger effect for adsorbing mercury in short silicone rubber foams than in longer ones when compared to similar untreated silicone rubber foams. The effect of having the solution in the foam for a longer period of time (ie. longer foams) increased the mercury adsorption more than the effect of adding sym-diphenylcarbazide.

Table VIII - ADSORPTION OF MERCURIC CHLORIDE BY SYM-DIPHENYLCARBAZIDE TREATED SILICONE RUBBER FOAMS

TREATMENT PROCEDURE (a)	NUMBER OF PASS THROUGH FOAM	FOAM SIZE (mm)	CONCENTRATION OF MERCURY (ppm)	MERCURY REMOVED (%)
SDØC directly mixed into the liquid base	1	35X35	0.04	68±2
SDØC dissolved in acetone then into the liquid base	1	63X35	0.04	91±2
	1	76X35	0.04	95±1
	2			95±1

(a) see p.14

Adsorption of Mercury by Untreated Polyurethane diSPo Foam

There was one set of equilibrium studies done using 100 ml. aliquots of a 0.04 ppm mercuric chloride standard solution with each diSPo foam. The percentage of mercury removed over 72 hours was 63 ± 2% for each of the two foams studied.

The flow-through method was also studied using 3 - 100 ml. aliquots of a standard mercury solution at each concentration for three untreated diSPo foams in a column.

The results of these tests are found in tables IX and X for the mercuric chloride and methyl mercuric chloride solutions respectively.

For mercuric chloride, there was a large decrease in the percent adsorption of mercury over successive passes of the 4.0 ppm mercury standard. This suggested that a saturation effect was taking place in the foam; whereas, at progressively lower concentrations the percent of mercury adsorbed increased.

From table X the adsorption pattern of the methyl mercuric chloride was seen to be similar to that of the mercuric chloride, although the pattern was not as pronounced from one concentration to another. When comparing the adsorption of mercury by the untreated foams for the two types of mercury solutions, it was found that the mercuric chloride solution was

Table IX - ADSORPTION OF MERCURIC CHLORIDE BY UNTREATED diSPo PLUGS

NUMBER OF FOAMS PER COLUMN (a)	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY (ppm)	MERCURY REMOVED (%)
3	1	4.0	9±2
	2		6±2
	3		4±2
3	1	0.4	18±2
	2		14±2
	3		15±2
3	1	0.04	42±2
	2		30±2
	3		19±2
3	1	0.004	57±2
	2		50±2
	3		47±2

(a) diSPo plug size was 22 mm. in diameter X 40 mm. in length for each plug.

Table X - ADSORPTION OF METHYL MERCURIC CHLORIDE BY UNTREATED diSPo PLUGS

NUMBER OF FOAMS PER COLUMN (a)	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY (pmm)	MERCURY REMOVED (%)
3	1	2.0	1±1
	2		1±1
	3		0
3	1	0.4	19±3
	2		18±3
	3		16±3
3	1	0.04	15±3
	2		12±3
	3		8±3
3	1	0.004	26±3
	2		30±3
	3		22±3

(a) diSPo plug size was 22 mm. in diameter X 40 mm. in length for each plug.

adsorbed at least twice as effectively as the methyl mercuric chloride over the concentration range examined.

DiSPo foams were also tested for the possibility of mercury contamination as new foams may in some manner have picked up mercury prior to being used. This test consisted of passing 100 ml. aliquots of distilled, deionized water through three foams placed in a column. A total of 200 ml. of water was passed through these foams and each 100 ml. aliquot was analysed for mercury. With a detection limit of 0.05 ppb mercury using the aeration system, no mercury above this level was washed out by either of the 100 ml. aliquots of water.

The ability of the diSPo foam to adsorb mercury after several litres of water have passed through it was also tested. A single diSPo foam was placed in a column that was directly connected to the domestic water supply. A total of 560 litres of water was allowed to pass through the foam before it was tested for mercury adsorption by the flow-through method. The results of passing three 100 ml. aliquots of a 0.04 ppm mercuric chloride standard solution through this foam are summarized in table XI.

The results showed that running the tap water through the foam enhanced the adsorption of mercury by that foam. Three untreated diSPo foams were required to adsorb 42 $\pm$ 2% of the mercury; whereas this single foam removed 67 $\pm$ 3% of the mercury from similar solutions.

Table XI - ADSORPTION OF MERCURIC CHLORIDE BY A SINGLE diSPo PLUG AFTER 560 LITRES OF TAP WATER PASSED THROUGH IT. (a)(b)

NUMBER OF PASS THROUGH FOAM	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
1	0.04	67±3
2		53±3
3		33±3

(a) The tap water was from the domestic supply.
(b) The single diSPo plug was untreated prior to the water being passed through it.

While the 560 litres of tap water were being passed through the foam, the foam changed colour from white to a pale yellow. It was thought that chlorine and other ions were being adsorbed by the foam while the tap water was passing through it and these ions in turn made the foam more conducive to mercury adsorption.

Adsorption of Mercuric Chloride by Sodium Hydroxide Treated diSPo Foam

Both equilibrium and flow-through studies were done using these foams. Initial equilibrium studies at a concentration of 0.04 ppm mercury are summarized in table XII. These results were higher than those obtained for the untreated diSPo foams.

The flow-through results are tabulated in table XIII. The amount of mercury adsorbed by the foam seemed to peak around a concentration of 0.04 ppm. At 0.4 ppm, the amount of mercury adsorbed was higher by 30% than the untreated diSPo foam and at 0.04 ppm the adsorption enhancement of the treatment was up to 40%.

These results showed that the treatment of polyurethane foam by sodium hydroxide enhanced the mercury adsorbing efficiency of the foam by as much as 40% over the range examined.

Table XII - ADSORPTION OF MERCURIC CHLORIDE IN EQUILIBRIUM STUDIES WITH 2M SODIUM HYDROXIDE diSPo PLUGS.

NUMBER OF FOAMS USED	EQUILIBRIUM TIME (HOURS)	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
1	24	0.04	67±2
1	24	0.04	69±2
3	48	0.04	82±2

Table XIII - ADSORPTION OF MERCURIC CHLORIDE BY 2M SODIUM HYDROXIDE TREATED diSPo PLUGS.

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
3	1	4.0	9±2
	2		6±2
	3		4±2
3	1	0.4	51±2
	2		34±2
	3		26±2
3	1	0.04	82±2
	2		74±2
	3		74±2
3	1	0.004	75±2
	2		64±2
	3		62±2

Adsorption of Mercury by S-H Treated diSPo Foam

The flow-through method was used to intensively study these S-H diSPo foams (p.17). The results obtained for the adsorption of mercuric chloride are summarized in table XIV. Repetitions of the various tests were shown to indicate how reproducible the results were.

The S-H foams saturated quickly with successive passes of the 4.0 ppm mercuric chloride standard, although they adsorbed 8 times the amount of mercury that the untreated foam adsorbed. At 0.4 ppm, the adsorption is very close to 100%, but the value decreases after the third standard has been passed through the foam indicating the start of saturation.

At 0.04 ppm the results showed that the foam was quite capable of adsorbing over 99% of the mercury from the first three passes of 100 ml. aliquots of the mercury standard and these results were very reproducible.

The adsorption of mercuric chloride by these treated foams was in every case much more efficient than the untreated foams.

The effectiveness of the S-H foam does not appear to be dependent on the length of storage time before the foam was used, as freshly prepared and one month old foams gave similar adsorption values at a concentration of 0.04 ppm.

The S-H foam was also tested for methyl mercuric

Table XIV - ADSORPTION OF MERCURIC CHLORIDE BY S-H RADICAL TREATED diSPo PLUGS

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
3	1	4.0	69±2
	2		46±2
	3		23±2
3	1	4.0	74±2
	2		46±2
	3		20±2
3	1	0.4	99±1
	2		99±1
	3		98±1
3	1	0.04	99±1
	2		99±1
	3		99±1
3	1	0.04	99±1
	2		99±1
	3		99±1
3	1	0.04	99±1
	2		99±1
	3		99±1
3	1	0.04	99±1
	2		99±1
	3		99±1
3	1	0.04	99±1
	2		99±1
	3		99±1
6	1	0.04	99±1
	2		99±1
	3		99±1

Table XIV (cont'd)

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
3	1	0.004	96±1
	2		98±1
	3		98±1
3	1	0.0004	99±1
	2		99±1
	3		99±1
	4		99±1
	5		99±1
	6		99±1

chloride adsorption. These results are given in table XV.

There was a saturation effect at the 2.0 and 0.4 ppm levels where percentage adsorption decreases rapidly with successive passes of the mercury standards.

Overall, the S-H diSPo foam was much more efficient for adsorbing mercury than the untreated diSPo foam.

Since mercury monometers were used in the production of these foams, it was decided to test distilled, deionized water washings of the S-H foams for any traces of mercury contamination. This was done using 2 columns with 3 S-H foams in each. A 100 ml. aliquot of water was passed through one of the columns and two 100 ml. aliquots of water were passed through the other. No mercury above the aeration system detection limit of 0.05 ppb was found in these washings.

Table XV - ADSORPTION OF METHYL MERCURIC CHLORIDE BY S-H RADICAL diSPo PLUGS.

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
3	1	2.0	50±2
	2		34±2
	3		29±2
3	1	0.4	75±2
	2		47±2
	3		33±2
3	1	0.04	80±2
	2		75±2
	3		66±2
3	1	0.004	94±2
	2		91±2
	3		83±2
3	1	0.0004	80±2
	2		80±2
	3		72±2

Adsorption of Mercury by Sym-diphenylcarbazide Treated diSPo Foam

Various extensive equilibrium studies were done on these foams using mercuric chloride solutions. These results are tabulated in table XVI.

For a single SDØC treated foam, every twenty hours of equilibrium time between the 4 and 48 hour periods, doubled the amount of mercuric chloride adsorbed.

Increasing the number of foams used for the same equilibrium time does not greatly enhance the adsorption of mercury.

It was thought that there was a competition between the foams when more than one was placed in a solution to equilibrate It was also thought that the equilibrium process was not fast enough to show a large adsorption difference in the allotted time for different numbers of foams used.

For SDØC diSPo foams equilibriated for 72 hours in mercury concentrations greater than 0.04 ppm, the adsorption increased with increasing mercury concentration, which showed that the foams were not saturated completely at the 0.04 ppm level after 48 hours.

Tabulated in table XVII are the results obtained in the flow-through studies of the SDØC foam for the adsorption of mercuric chloride. These results showed that the most efficient adsorption was around the 0.4 and 0.04 ppm mercury levels.

Table XVI - ADSORPTION OF MERCURIC CHLORIDE IN EQUILIBRIUM STUDIES BY SYM-DIPHENYLCARBAZIDE TREATED diSPo PLUGS.

NUMBER OF FOAMS USED	EQUILIBRIUM TIME (HOURS)	CONCENTRATION OF MERCURY(ppm)	MERURY REMOVED (%)
1	4	0.04	18±1
1	4	0.04	18±1
1	4	0.04	18±1
1	24	0.04	30±1
1	24	0.04	33±1
1	24	0.04	33±1
1	24	0.04	32±1
1	24	0.04	32±1
1	48	0.04	70±1
2	48	0.04	77±1
3	48	0.04	84±1
1	48	0.04	72±2
3	48	0.04	80±1
3	72	0.1	88±1
3	72	1.0	92±1

Table XVII - ADSORPTION OF MERCURIC CHLORIDE BY 2M SODIUM HYDROXIDE SYM-DIPHENYLCARBAZIDE TREATED diSPo PLUGS.

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
3	1	4.0	56±2
	2		33±2
	3		21±2
3	1	0.4	95±1
	2		94±1
	3		94±1
3	1	0.04	90±1
	2		85±1
	3		83±1
	4		83±1
3	1	0.04	90±2
	2		92±2
	3		87±2
3	1	0.004	76±2
	2		64±2
3	1	0.0004	68±3
	2		70±3
	3		70±3

The SDØC foams were not as efficient as the S-H foams over the concentration range examined, but they were nevertheless much more efficient than the untreated diSPo foams. The addition of SDØC to the untreated foams increased the adsorption efficiency by as much as 70%

Studies were also done using various sodium hydroxide concentrations in the preparation of the SDØC diSPo foams (p. 19). The adsorption of mercuric chloride by these foams was tabulated in table XVIII. The results showed little variation in mercury adsorption except for the 1M sodium hydroxide SDØC diSPo foams, where the adsorption was as much as 20% lower than the other values. The 2M foams demonstrated the least saturation effect and the 0.2M foams gave the highest adsorption value for the first pass of the mercury standard. From these tests, it was decided to study the saturation of three, 0.2M sodium hydroxide SDØC diSPo foams by passing 15-100 ml. aliquots of a 0.04 ppm mercuric chloride solution through them. These results, summarized in table XIX, showed a steady decline in the percentage of mercury adsorbed until a levelling off occurred. After the fifteenth pass, the foam was still quite capable of adsorbing mercury efficiently if the solution were to be recycled through the foam several times.

As mentioned in the experimental section (p.23), the diSPo foams were held in the columns at their normal length of 40 mm. each. This was done to keep the surface areas of the

Table XVIII - ADSORPTION OF MERCURIC CHLORIDE BY VARIOUS SODIUM HYDROXIDE CONCENTRATIONS OF THE SDØC diSPo PLUGS.

NUMBER OF FOAMS PER COLUMN	SODIUM HYDROXIDE CONCENTRATION	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED(%)
3	2M	1	0.04	90±2
		2		92±2
		3		87±2
3	1M	1	0.04	71±2
		2		65±2
		3		67±2
3	0.5M	1	0.04	88±2
		2		76±2
		3		74±2
3	0.2M	1	0.04	95±2
		2		90±2
		3		84±2
3	0.1M	1	0.04	92±2
		2		87±2
		3		85±2

Table XIX - SATURATION EFFECT OF MERCURIC CHLORIDE ADSORPTION BY 3-0.2M SODIUM HYDROXIDE SDØC diSPo PLUGS.

NUMBER OF PASS THROUGH FOAMS	MERCURY REMOVED (%)
1	97±2
2	94±2
3	86±2
4	83±2
5	73±2
6	64±2
7	59±2
8	53±2
9	50±2
10	48±2
11	45±2
12	50±2
13	38±2
14	47±2
15	45±2

foams as constant as possible from test to test. Having the foams squashed in the column would decrease the surface area and the mercury adsorbed, if the adsorption was dependent on surface area. This was exemplified by the results obtained when 3-2M sodium hydroxide SDØC diSPo foams were squashed in a column to a total length of 20 mm. The amount of mercury adsorbed by these squashed foams was 13 ± 3%, 8 ± 3%, and 8 ± 3% respectively for the first three 100 ml. aliquots of a 0.04 ppm mercuric chloride solution passed through them. These results are in comparison to those of table XVIII where similarly treated foams adsorbed 90 ± 2% of the mercury in the first pass of a similar solution.

The possibility of reusing the diSPo foams that were treated and had adsorbed mercury was studied. Two of three SDØC foams that had had 0.04 ppm mercuric chloride solutions passed through them, adsorbing 68, 73, and 68 ± 1% of the mercury from each pass respectively, were soxhleted with acetone for 6 hours and then air dried. The two foams were treated using the general SDØC treatment (p.19) as if they were new diSPo foams.

Once treated the foams were equilibriated with 100 ml. aliquots of a 0.04 ppm mercuric chloride solution for 20 hours. The results gave a mercury adsorption of 79 ± 1% for each of the retreated foams. These results demonstrated that retreatment enhanced mercury adsorption when compared to the originally treated foams.

It was thought that washing the SDØC foams in acetone did not entirely remove all the complex and then with retreatment, the amount of complex on the foam was more than the original treatment had put on. This increase in SDØC content was thought to be responsible for the increase in mercury adsorption by the retreated foams.

The effect of passing domestic tap water through the foam prior to testing with a mercury standard was also examined. These results are tabulated in table XX. The results showed that the foams were not affected for mercury adsorption by large amounts of water that had previously passed through them.

The adsorption of methyl mercuric chloride by the SDØC foams was also examined, with the results summarized in table XXI. These SDØC foams, although very effective for mercuric chloride adsorption, were not very efficient for the removal of methyl mercuric chloride, except at the 2.0 ppm level where they came within 8% of the efficiency of the S-H foams.

Table XX - ADSORPTION OF MERCURIC CHLORIDE BY SDØC diSPo PLUGS AFTER DOMESTIC TAP WATER WAS PASSED THROUGH THEM

NUMBER OF FOAMS USED	NUMBER OF PASS THROUGH FOAMS	AMOUNT OF WATER THROUGH FOAMS (1)	SODIUM HYDROXIDE CONCENTRATION	MERCURY REMOVED(%)
1	1	400	2M	78±2
1	1	400	0.2M	85±2
3	1	1,484	0.2M	93±2
	2			93±2
	3			90±2

Mercury concentration was 0.04 ppm in all cases.

Table XXI - ADSORPTION OF METHYL MERCURIC CHLORIDE BY 2M SODIUM HYDROXIDE SDØC diSPo PLUGS.

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY (ppm)	MERCURY REMOVED (%)
3	1	2.0	42±2
	2		10±2
	3		5±2
3	1	0.4	25±2
	2		13±2
	3		16±2
3	1	0.04	25±2
	2		19±2
	3		18±2
3	1	0.004	39±2
	2		19±2
	3		25±2

Adsorption of Mercury by Dithizone Treated diSPo Foam

These dithizone treated diSPo foams were studied by the usual flow-through method, with the results of the mercuric chloride adsorption tabulated in table XXII. The table showed that the efficiency of the dithizone foams reached a peak around 0.04 ppm. and at higher concentrations these foams saturated rapidly.

The dithizone foams were also tested for their adsorption of methyl mercuric chloride, with the results for these tests summarized in table XXIII.

No pattern relating concentration to percentage of mercury adsorption was found, but the high adsorption of methyl mercuric chloride at the 0.04 ppm level was the best obtained for any of the treated diSPo foams.

Table XXII - ADSORPTION OF MERCURIC CHLORIDE BY DITHIZONE TREATED diSPo PLUGS

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY (ppm)	MERCURY REMOVED (%)
3	1	4.0	25±2
	2		15±2
	3		5±2
3	1	0.4	79±2
	2		60±2
	3		49±2
	4		49±2
3	1	0.04	95±2
	2		92±2
	3		86±2
3	1	0.004	70±2
	2		72±2
	3		80±2

Table XXIII - ADSORPTION OF METHYL MERCURIC CHLORIDE BY DITHIZONE TREATED diSPo PLUGS.

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
3	1	2.0	60±2
	2		33±2
	3		35±2
3	1	0.4	24±3
	2		26±3
	3		16±3
3	1	0.04	86±2
	2		80±2
3	1	0.004	26±2
	2		23±2

Adsorption of Mercuric Chloride by Diphenylcarbazone Treated diSPo Foam

The results of the flow-through studies for mercuric chloride adsorption by these foams are shown in table XXIV. The table showed that the 4.0 ppm mercury solution saturated the dithizone foam, but at a rate that was slower than the saturation effect on the untreated diSPo foams. At the 0.04 ppm level, these treated foams were not as efficient or as reproducible in adsorbing mercury, as the S-H foams.

A variation of these DØC foams was made and studied for mercuric chloride adsorption. The variation consisted of neutalizing the 0.2M sodium hydroxide solution with 6M hydrochloric acid while the foams were soaking in the treatment solution (p.21).

These neutalized foams, once soxhleted and air dried, were tested by the flow-through method for the adsorption of mercuric chloride at a concentration of 0.04 ppm.

The percentages of mercury adsorbed were 91, 85, and 80 ± 2% respectively, for each of the first three - 100 ml. aliquots of the mercury standard passed through them.

These foams saturated faster than the 0.2 M sodium hydroxide DØC foams as exemplified in table XXIV where the adsorption averaged 90%.

Table XXIV - ADSORPTION OF MERCURIC CHLORIDE BY DIPHENYLCARBAZONE TREATED diSPo PLUGS.

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
3	1	4.0	44±2
	2		33±2
	3		22±2
3	1	0.04	96±2
	2		91±2
	3		88±2
3	1	0.04	94±2
	2		88±2
	3		91±2

Adsorption of Mercuric Chloride by Dimethylaminoazobenzene Treated diSPo Foam

The results from a flow-through study of these foams at a concentration of 0.04 ppm mercury were tabulated in table XXV.

The adsorption of mercuric chloride by these foams was not as efficient as that by the S-H, SDØC or DØC treated foams, but the DMAAB foams still adsorbed a significant amount of mercury from a 100 ml. aliquot of the standard.

Recycling and increasing the foam length would improve the results obtained for the adsorption of mercury by these treated foams.

Table XXV - ADSORPTION OF MERCURIC CHLORIDE BY DIMETHYLAMINOAZOBENZENE TREATED diSPo PLUGS.

NUMBER OF FOAMS PER COLUMN	NUMBER OF PASS THROUGH FOAMS	CONCENTRATION OF MERCURY(ppm)	MERCURY REMOVED (%)
3	1	0.04	87±1
	2		68±1
	3		61±1
3	1	0.04	90±2
	2		75±2
	3		63±2

Matrix Effect of Sewage Water on Mercury Analysis

Metro Winnipeg sewage water was used as the medium for testing matrix effects on mercuric chloride analysis.

The mercury content of the sewage water, the spike to be added, and the spiked sewage water were analysed using the methyl mercuric chloride analysis treatment for the aeration system.

The areas under the peaks recorded for the spike and the sewage water should equal the total area under the peak obtained for the spiked sewage water if no matrix effect was observed. The results of this study are given in table XXVI.

The study showed that the matrix effect is small in sewage water indicating that negligible matrix interferences occurred when analysing for mercury in distilled deionized water solutions.

Table XXVI - MATRIX EFFECT OF SEWAGE WATER ON MERCURY ANALYSIS

SEWAGE AREA	SPIKED AREA	SPIKED SEWAGE AREA	$\frac{(\text{SPIKED SEWAGE})}{(\text{SEWAGE + SPIKE})}$ (%)
0.0070	0.0443	0.0507	98.9
0.0216	0.0227	0.0421	95.0

Extraction of Mercury from Foam

Extracting the mercury from the various foams was not studied in detail as the main objective of the research was to obtain efficient adsorption of mercury by the use of foams.

However, a test, using ten - 2M sodium hydroxide SDØC diSPo foams placed in 100 ml. of a 1000 ppm mercuric chloride solution for one hour, was run to study a possible method for the re-extraction of mercury from this type of treated foam.

The foams were squeezed to near dryness as they were taken from the mercury solution which, when later analysed by the flame atomic absorption method, had 34.6 ± 1% of the mercury removed from it.

The foams were then squeezed in an acetone solution for several minutes and then squeezed to near dryness before they were set aside to dry. The acetone solution was then flash evaporated, and as much as possible of the residue remaining was dissolved in 100 ml. of 2M HCl. The 2M HCl solution was then analysed for mercury, with the result being that 55 ± 1% of the mercury adsorbed by the foam was re-extracted.

It was thought that soxhleting with hydrochloric or nitric acid may extract the mercury from the foam without extracting the complexing agent.

The use of organic solvents to dissolve the complexing agent and mercury from the foam was also thought feasible.

Adsorption of Other Elements by the Variously Treated diSPo Foams

Chromium, cadmium, molybdenum and copper distilled, deionized water solutions, were each tested by the flow-through method for adsorption onto the S-H, SDØC, DØC and dithizone diSPo foams. The tests were conducted at concentrations of 8.94 ppm for cadmium, 17.8 for chromium, 78 for molybdenum, and 20 for copper. No adsorption of these elements was detected for any of the foams used.

Nickel, at 20 ppm was tested for adsorption by SDØC and dithizone treated foams and again no adsorption was observed.

These results indicate that mercury can be separated from chromium, cadmium, molybdenum, copper and nickel in neutral aqueous solutions by using the variously treated diSPo foams.

DISCUSSION

The data obtained from the flow-through studies for the adsorption of mercury by treated and untreated polyurethanes is summarized in Figures 4 and 5. The graphs represent the percentage adsorption of mercury by the first pass of the mercury standard through three foams. Where more than one study was done at a particular concentration for a certain type of foam, the graphed percentage was the average value.

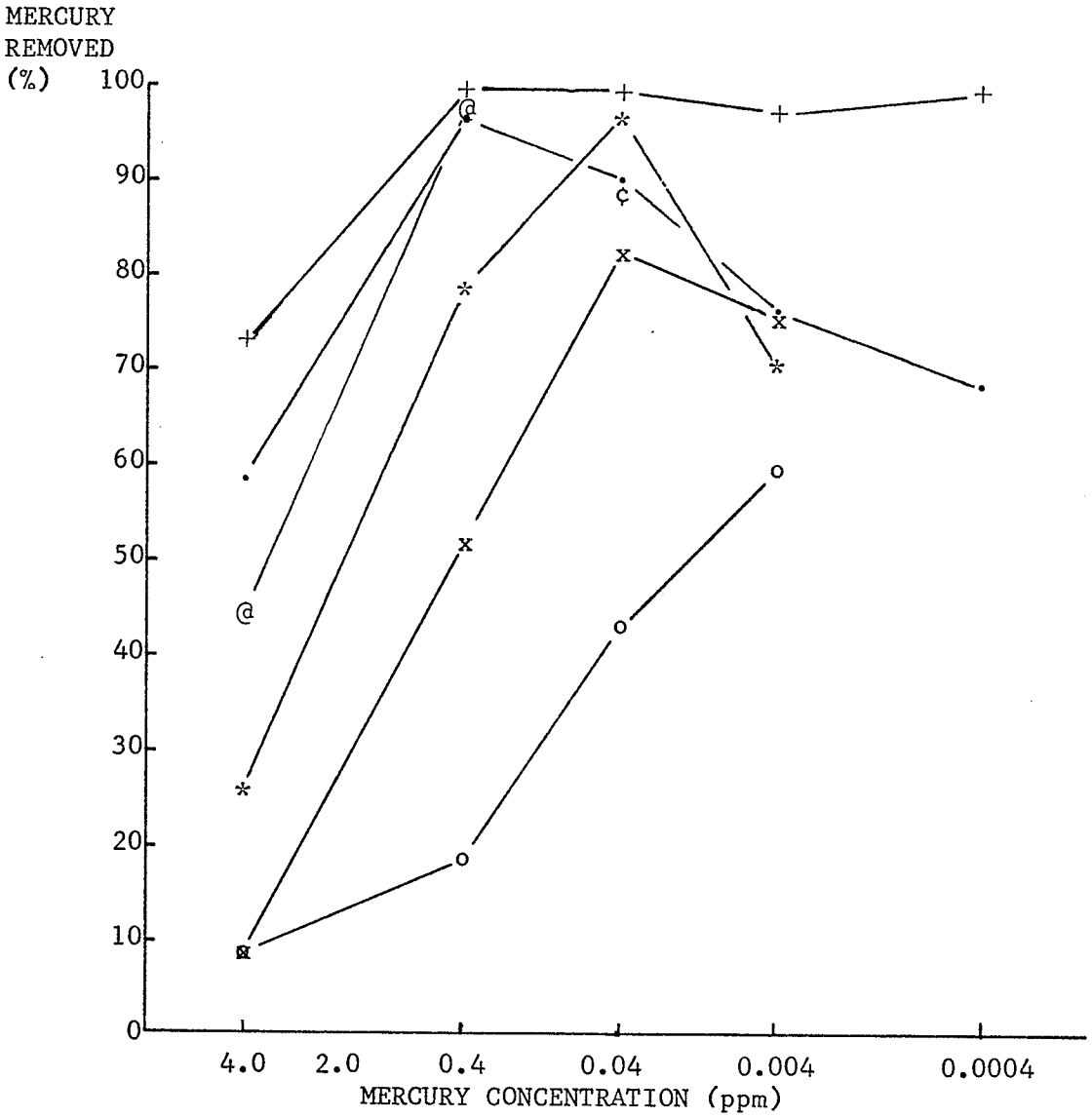
From the graph in Figure 4, it was seen that the S-H foams were the most effective mercury adsorbers over the concentration range studied. They were followed in efficiency by the SDØC diSPo foams; the DØC diSPo foams; the dithizone diSPo foams; the sodium hydroxide diSPo foams and finally by the untreated diSPo foams.

Although DMAAB diSPo foams adsorbed mercury efficiently at the 0.04 ppm level, no tests were run at other concentrations to determine its overall effectiveness.

The general results, as displayed in Figure 4, are those of one type of treated foam being more adsorbant than another throughout the entire concentration range examined. Treatment of the diSPo foams by the various complexing agents increased the amount of mercury adsorbed in every case.

From the graph in Figure 5, the S-H diSPo foams

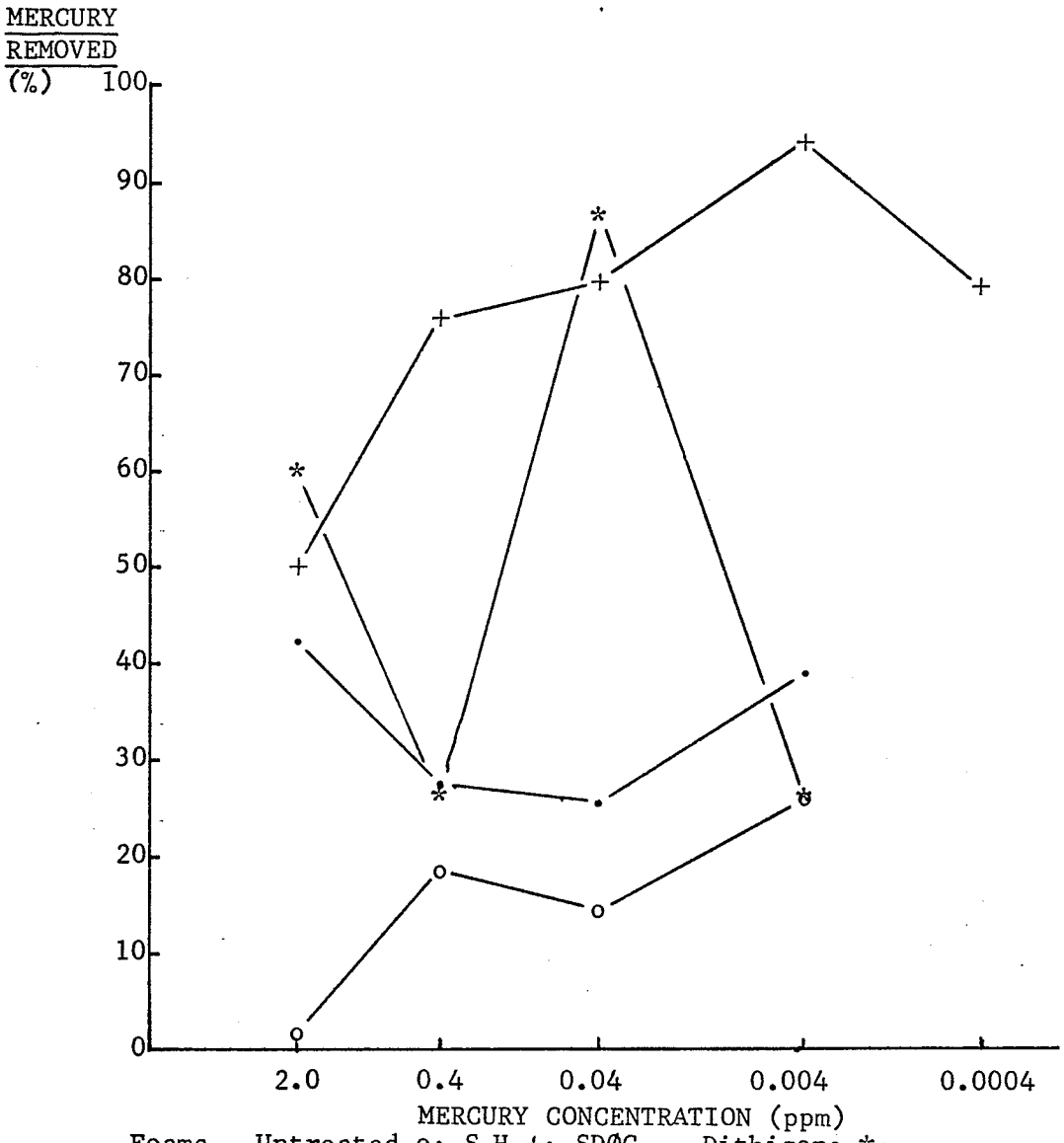
Fig. 4 - SUMMARY OF MERCURIC CHLORIDE REMOVED (%) BY THE VARIOUS FOAMS OVER THE CONCENTRATION RANGE EXAMINED.



Foams- Untreated-o; NaOH-x; S-H-+; SDØC-·; Dithizone-*; DØC-@; DMAAB-ç;

Values graphed portray the first pass of the mercury standard through the various foams.

Fig. 5 - SUMMARY OF METHYL MERCURIC CHLORIDE (%) REMOVED FOR THE VARIOUS FOAMS OVER THE CONCENTRATION RANGE EXAMINED.



Foams- Untreated-o; S-H-+; SDØC-·; Dithizone-*;

Values graphed portray the first pass of the mercury standard through the various foams.

were again the best means for adsorbing mercury over the entire concentration range studied. The dithizone foams, although irregular for methyl mercuric chloride adsorption over the concentration range examined, generally adsorbed efficiently. The SDØC diSPo foams were not much more efficient than the untreated diSPo foams for the adsorption of methyl mercuric chloride.

Untreated silicone rubber foams were shown to be very effective for the removal of methyl mercuric chloride at a concentration of 0.04 ppm. The volume of silicone rubber used was comparable to the volume of three diSPo foams. Generally, the silicone rubber foams were as effective or more effective than the S-H diSPo foams for removal of methyl mercuric chloride, while their removal of mercuric chloride was comparable to that of the SDØC diSPo foams.

For all the types of foams, increasing the amount of time that the mercury solution is in contact with the foam, increases the percentage adsorption of mercury by the foam. This may be accomplished by using longer foams in the columns, increasing the equilibrium times, recycling the mercury solutions through the foam several times or decreasing the flow rate.

The overall results showed that by placing enough silicone rubber and variously treated diSPo foams in the same column, the system would then be able to efficiently adsorb all the mercury from water solutions, over the concentration range

examined.

The mercury adsorption percentages of the various foams were reproducible making the foams useful as monitoring devices. By knowing the amount of mercury in a foam after a specific volume of solution has passed through it, the original concentration of the solution could be determined. This would be very useful at extremely low concentrations of mercury as the foams could concentrate the mercury from the sample to a level that could be determined by conventional analytical methods. Besides concentrating, the foams could separate the mercury from elements that may interfere with the type of analysis to be used.

CONCLUSION

As demonstrated in this work, it is possible to produce silicone rubber foams and treat polyurethane foams to provide a means of selectively and efficiently extracting mercury from mercuric chloride and methyl mercuric chloride solutions.

The preparation and treatment of the foams is simple, fast and relatively inexpensive. The foams are also sufficiently durable to be retreated and reused several times.

Re-extraction of the mercury may be attained by acetone soxhleting or possibly by soxhleting with dilute nitric acid.

In the laboratory, the foams may be used for eliminating mercury from aqueous solutions and for monitoring trace mercury levels in sample solutions.

In addition, the foams may be useful in removing mercury from industrial wastes, or for cleaning up existing contaminated waters.

The foams may also be useful to environmental agencies as monitoring devices for mercury levels.

The simplicity of the technique for separating and concentrating mercury from aqueous solutions will be an important factor in the future uses of these foams.

The possibility of silicone rubber and polyurethane

foams being combined with other complexing agents for the selective and efficient removal of other elements from aqueous solutions provides a vast field for future study.

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