

THE UNIVERSITY OF MANITOBA
THE SEPARATION OF PLATINUM AND PALLADIUM
BY FOAM CHROMATOGRAPHY

by

D. CONRAD GRÉGOIRE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

WINNIPEG, MANITOBA

May 1974

Acknowledgement

Thanks are given to Dr. A. Chow for his advice and guidance during the course of this work, and for his help with the manuscript.

I wish to thank Dr. J.A. Gibson for his assistance with the NMR work.

The Department of Chemistry deserves recognition for the teaching assistantship provided. The University of Manitoba is thanked for the use of their facilities and for providing a campus rich in wild edible fungi.

<u>Table of Contents</u>	<u>Page</u>
Abstract	1
Introduction	2
Apparatus and Reagents	6
Analysis of Silicone Rubber Foam	7
Preparation of Foam Materials	18
Characterization of Filler Material	19
Preparation of Silicone Rubber Foams	20
Column Packing Technique	23
Flow-Through Procedure	24
Cleaning of Foams	26
Adsorption of Platinum and Palladium by Dimethylglyoxime Silicone Rubber Foam	34
Adsorption of Platinum and Palladium Chlorides by α -Benzoin Oxime Silicone Rubber Foam	38
Adsorption of Platinum and Palladium by Srafion Treated Silicone Rubber Foam	41
Recovery of Palladium From Dimethylglyoxime Silicone Rubber Foam	44
Recovery of Platinum From Dimethylglyoxime Silicone Rubber Foam	51
pH Study of Adsorption of Platinum and Palladium by Dimethylglyoxime Silicone Rubber Foam	54
Flow Rate Study of Adsorption of Palladium by Dimethylglyoxime Silicone Rubber Foam	60
Palladium Capacity of Dimethylglyoxime Treated Silicone Rubber Foam	63

<u>Table of Contents</u> (cont'd)	<u>Page</u>
Separation of Platinum and Palladium by Dimethylglyoxime Silicone Rubber Foam	67
Effect of Diverse Ions on The Adsorption of Palladium by Dimethylglyoxime Silicone Rubber Foam	70
Adsorption of Nickel Chloride by Dimethylglyoxime Silicone Rubber Foam	75
Discussion	78
Conclusion	80
Bibliography	82

<u>List of Tables</u>	<u>Page</u>
I ^{19}F and ^1H spectrum Assignments for Cleavage Reaction Products	14
II Adsorption of Platinum and Palladium Chlorides by Various Washed Silicone Rubber Foams	30
III Adsorption of Platinum Chloride by Silicone Rubber Foams at Various Aqua Regia Soak Times	32
IV Adsorption of Platinum Chloride by Silicone Rubber Foam	33
V Adsorption of Platinum and Palladium Chlorides by Dimethylglyoxime Silicone Rubber Foam	36
VI Adsorption of Platinum and Palladium Chlorides by α -Benzoin Oxime, Srafion Resin Treated and Untreated Silicone Rubber Foam	43
VII Recovery of Palladium From Loaded Dimethylglyoxime Silicone Rubber Foams	46
VIII Recovery of Palladium From Loaded Dimethylglyoxime Silicone Rubber Foam With 8 M Nitric Acid at 25°C and 50°C	48
IX Recovery of Palladium From One and Two Loaded Dimethylglyoxime Silicone Rubber Foams With 8 M Nitric Acid at 25°C	50
X Recovery of Platinum Chloride Adsorbed Onto Dimethylglyoxime Silicone Rubber Foam	53
XI Separation of Platinum and Palladium by Dimethylglyoxime Silicone Rubber Foam	68
XII Effect of Various Metal Ions On The Adsorption of Palladium by Dimethylglyoxime Silicone Rubber Foam	72

<u>List of Figures</u>	<u>Page</u>
1. Vacuum Rack Apparatus	8
2. ^{19}F NMR Spectrum of Cleavage Reaction Products	11
3. ^1H NMR Spectrum of Cleavage Reaction Products	13
4. Infrared Spectrum of Silicone Foam Base	15
5. Infrared Spectrum of Catalyst S - 5370 and Stannous Octoate	16
6. Foaming Chamber	22
7. Columns Used in Flow-Through Experiments	22
8. Plot of Palladium Recovered (%) From Dimethylglyoxime Silicone Rubber Foam vs Volume of 16 M Nitric Acid at 25°C	47
9. Plot of Palladium Retained (%) by Dimethylglyoxime Silicone Rubber Foam vs pH of Solution	57
10. Plot of Palladium Leached (%) by Dimethylglyoxime Silicone Rubber Foam vs pH of Solution	58
11. Plot of Platinum Recovered (%) From Dimethylglyoxime Silicone Rubber Foam vs pH of Solution	59
12. Plot of Palladium Retention (%) vs Flow Rate (ml per minute)	61
13. Plot of Palladium Retained (%) by Dimethylglyoxime Silicone Rubber Foam vs Volume (ml) of Stock Palladium Solution	65
14. Plot of Nickel Retained (%) by Dimethylglyoxime Silicone Rubber Foam vs pH of Solution	76

Abstract

Open-pore silicone rubber foam was shown to be a good inert solid support for column separations. Foams treated with α -benzoin oxime, Srafion resin powder and dimethylglyoxime were studied for their retention of platinum and palladium from solution. The separation of platinum and palladium by dimethylglyoxime silicone rubber foam was studied and a quantitative separation of the two metals was achieved. The extraction of nickel from solution by dimethylglyoxime silicone rubber foams was also studied.

The Separation of Platinum and Palladium
by Foam Chromatography

Introduction

The use of porous polymeric materials as rigid supports in chromatography was first reported by Hollis¹ in 1966 who used polystyrene in gas chromatographic columns. In situ formed open pore polyurethane foam gas chromatographic columns were first prepared by Ross and Jefferson² who produced the foam by placing a mixture of the polymer precursors directly into a column and allowing the foaming process to take place. Liquid phases of up to 70% by weight were used in these columns by adding them to the precursor reagents. Complete separations of three metal complexes were obtained by placing a benzene solution of Cu^{2+} , Co^{2+} , and Co^{3+} heptafluorodimethyloctanedionates and eluting with a benzene carrier. Since then, some interest³ has been shown in the development of such techniques.

Bowen⁴ introduced the use of open pore polyurethane foams for the extraction of metals from solution as well as the removal of some organic compounds in low concentration from aqueous solution. Schiller and Cook⁵ investigated the properties of a polyurethane foam for the preconcentration of gold from tap water prior to analysis by neutron activation. It was found that microgram quantities of gold could be quantitatively absorbed from dilute acid solutions. These foams have also been used for the extraction and concentration of polychlorinated biphenyls⁶ and other pesticides⁷

from aqueous media as well as the recovery of gold⁸ from thiourea solutions.

Specially treated polyurethane foams⁹ have been developed for use in the separation of palladium and nickel by reverse phase partition chromatography. Nickel and palladium were loaded onto foams saturated with tri-n-butyl phosphate. Nickel was eluted with a perchloric acid solution containing thiourea and sodium perchlorate, and palladium with water.

A novel method for the extraction of mercury from aqueous solutions with sulfide treated polyurethane foam has been reported.¹⁰ These foams were capable, in most cases, of removing essentially 100% of mercury II from aqueous solutions in concentrations as low as 0.4 ppb.

A large number of reports^{11,12,13,14} have come from the laboratory of T. Braun regarding the application of polyurethane foams to the concentration and separation of metals by reverse phase foam chromatography. Techniques for the production of ion-exchange foams¹⁵ and redox foams¹⁶ as well as investigations into the nature¹⁷ of the chemical reactions taking place on these foams have also been reported by Braun et al.

Reports on the use of support bonded silicones¹⁸ for the extraction of organochlorines from water and the chemical properties of some aminoalkyl polysiloxanes¹⁹ used as stationery phases in gas chromatography have appeared in the recent literature.

However, as yet no reports have appeared on the use of silicone foams as an inert support for chromatographic separations.

Many techniques²⁰ have been developed for the separation of platinum and palladium in aqueous media. Anion exchange^{21,22} has been used to achieve a quantitative separation of the two metals in hydrochloric acid by the use of Dowex - 1 resin. However, some interferences are experienced from some of the other noble metals and pretreatment of samples is necessary.

Solvent extraction^{23,24} has extensive application for the separation of the noble metals. The metals are extracted from an aqueous phase to an organic phase containing complexing or chelating agents. A recent report²⁵ has shown that sub-milligram quantities of platinum and palladium can be separated from other noble metals by extraction into a chloroform phase containing 2 - mercaptobenzothiazole. After evaporation of the organic phase and treatment of the residue, platinum and palladium are separated by extraction into a second chloroform phase containing dimethylglyoxime.

Methods of separating platinum and palladium by partition chromatography on cellulose columns^{26,27} have been reported, but since only macro amounts of metal can be separated, these techniques have found only limited application in analytical chemistry. Separation schemes based on paper chromatography,^{28,29} however, have enjoyed broader application for the separation of platinum and palladium because of their ability to easily separate microgram quantities of the metals.

Much interest has been shown in the development of techniques for the separation of platinum and palladium by reverse phase partition chromatography. Separations at the microgram level have been achieved on columns packed with Poracil C³⁰ and Daiflon³¹ using tri-n-butyl phosphate as a stationary phase and hydrochloric and sulfuric acids as elutants.

Separations of the two metals have been reported by the selective precipitation of platinum and palladium as their hydrous oxides³² from hot bromate solutions. Many oxime reagents have also been used for the separation of the two metals by precipitation. The relative merits of many of these techniques are extensively discussed by Beamish.³³ Dimethylglyoxime³⁴ has been used successfully for the separation of the two metals in solutions containing concentrations of metal as low as 5 ppm. Palladium was precipitated from solution by an excess amount of a 1% dimethylglyoxime solution in 95% ethanol at room temperature.

This work was undertaken in an effort to discover some of the chemical and physical properties of silicone rubber foam and to explore their possible use in analytical chemistry. It was thought that these foams could find some application in column chromatographic techniques specifically in the separation of metal ions from solution. To demonstrate one possible application of these foams, the development of a technique for the separation of platinum and palladium by specially treated silicone rubber foam was undertaken.

Apparatus and Reagents

Model 306 Perkin Elmer Atomic Absorption Spectrophotometer

Varian Techtron Hollow Cathode Lamps

Model 337 Perkin Elmer Grating Infrared Spectrophotometer

Varian A56/60A Nuclear Magnetic Resonance Spectrometer

Fisher Accumet Model 520 Digital pH Meter

Dental Amalgam Mixer, Crescent Dental Manufacturing Company

Vacuum Rack Apparatus (fig 1)

Glass columns With Teflon Stopcocks (fig 7)

Soxhlet Extraction Apparatus (250 ml)

Stannous Octoate, K + K Laboratories Incorporated, Plainsview,
New York U.S.A.

Dow Corning S - 5370 RTV Silicone Rubber Foam

Stock 1000 ppm Pd^{2+} solution and all dilutions were prepared by dissolving $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ (Johnson Matthey Chemicals Limited) in 0.1 M hydrochloric acid.

Stock 1000 ppm Pt^{4+} solution and all dilutions were prepared by dissolving $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Baker Platinum of Canada Limited) in 0.1 M hydrochloric acid.

Srafion NMRR Resin, Ayalon Co.

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

Analysis of Silicone Rubber Foam

Organopolysiloxanes³⁵ are known to have physical properties very similar to those of the Dow Corning S- 5370 RTV foam base material used in the production of silicone rubber foam. It was therefore thought that perhaps the foam base and thus the foam itself was composed of such a polymer. If so, it would be relatively easy to cleave the polysiloxane into its component parts. Analysis of the reaction products would yield the building blocks of the silicone foam structure.

Hydrofluoric acid reacts quite readily with many compounds of silicon and was therefore chosen as reagent for the cleavage reaction. The products obtained from such a degradation process should be of low molecular weight and of high volatility which would make the separation of products and reactants quite easy.

^{19}F and ^1H nuclear magnetic resonance (NMR) were chosen as the method of analysis because of its speed and the specificity of the information obtained from the spectra. Also, a minimum of sample handling would be required which is of importance due to the high volatility of the products.

Functional groups too low in concentration for detection by NMR were elucidated by the use of infrared spectroscopy. An infrared spectrum was taken of the purified foam base for this purpose. It was thought that interpretation of these spectra could give information concerning the reaction responsible for

the foaming and curing of the silicone rubber foam.

Although the composition of the catalyst S- 5370 was given³⁶, an infrared spectrum of a sample of stannous octoate was taken and compared to an infrared spectrum of catalyst to make sure of the identity.

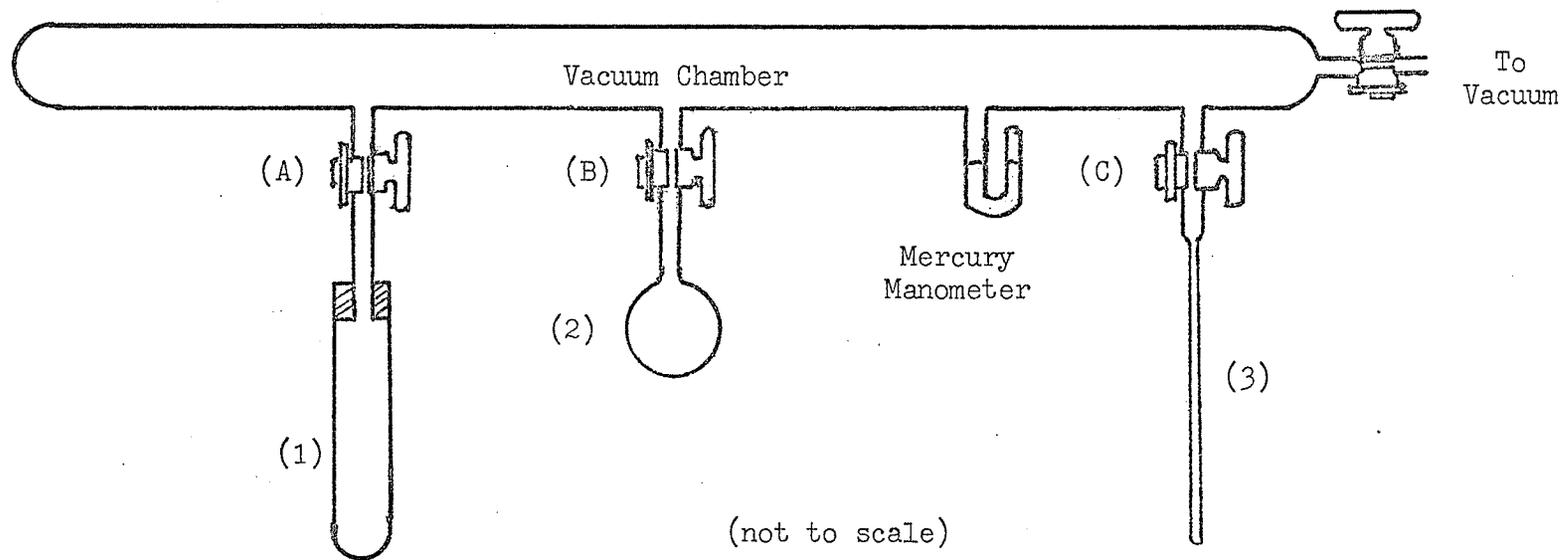
Experimental

In a polyethylene test tube (1) were placed 2.5g of cleaned silicone rubber foam and 10 ml of a one-to-one mixture of 48%hydrofluoric acid and 95% ethanol. The tube was sealed by means of a one hole rubber stopper fitted with a length of tygon tubing. The tubing was attached to a vacuum rack (figure 1) which included a mercury manometer used to monitor the progress of the reaction. The reaction was allowed to proceed for 24 hours at room temperature. The reaction was quite sluggish due to the hydrophobic nature of the silicone foam.

When the reaction was complete, the volatile reaction products were condensed into a flask containing a quantity of molecular sieve used as a drying agent. This was accomplished by completely immersing the flask (2) in a bath of liquid nitrogen, while at the same time heating the reaction tube with warm water. Valve B was then closed and the products allowed to dry for 5 hours before once again being volatilized into the vacuum chamber. By immersing the attached NMR tube (3) in liquid nitrogen, the anhydrous reaction products were condensed into the tube. Valve C was closed

Figure 1

Vacuum Rack Apparatus



and the tube sealed with an air-acetylene flame. ^{19}F and ^1H NMR spectra were taken of the products.

Results

Figure 2 is the ^{19}F NMR spectrum obtained from the reaction products. Assignments for the resonance lines are given in table I with chemical shifts measured from the fluorine resonance line of Cl_3CF .

Figure 3 is the ^1H NMR spectrum obtained from the same reaction products. Chemical shifts are reported in table I relative to the proton resonance line of tetramethylsilane.

In both the ^{19}F and ^1H spectra, the chemical shifts agree well with those reported in the literature^{37,38} for the compounds cited.

The proton resonance lines for $(\text{CH}_3)\text{SiF}_3$ and $(\text{CH}_3)_3\text{SiF}$ do not appear on the spectrum as their concentrations are too low to contribute significant intensity to the $(\text{CH}_3)_2\text{SiF}_2$ lines which appear in the same region. Overlapping of these lines prevents the clear identification of those products on the proton spectrum.

The infrared spectrum (fig 4) of the foam base indicates the presence of Si-H groups by the appearance of a strong band at 2175 cm^{-1} .³⁹ The absence of any bands above 3000 cm^{-1} precludes the presence of aromatic groups. In short, only absorption bands characteristic of alkyl silanes and siloxanes were found on the spectrum.

The infrared spectrum of the catalyst (fig 5) and that of a commercially obtained sample of stannous octoate were identical showing these two substances to be the same.

Figure 2

^{19}F NMR Spectrum of Cleavage Reaction Products

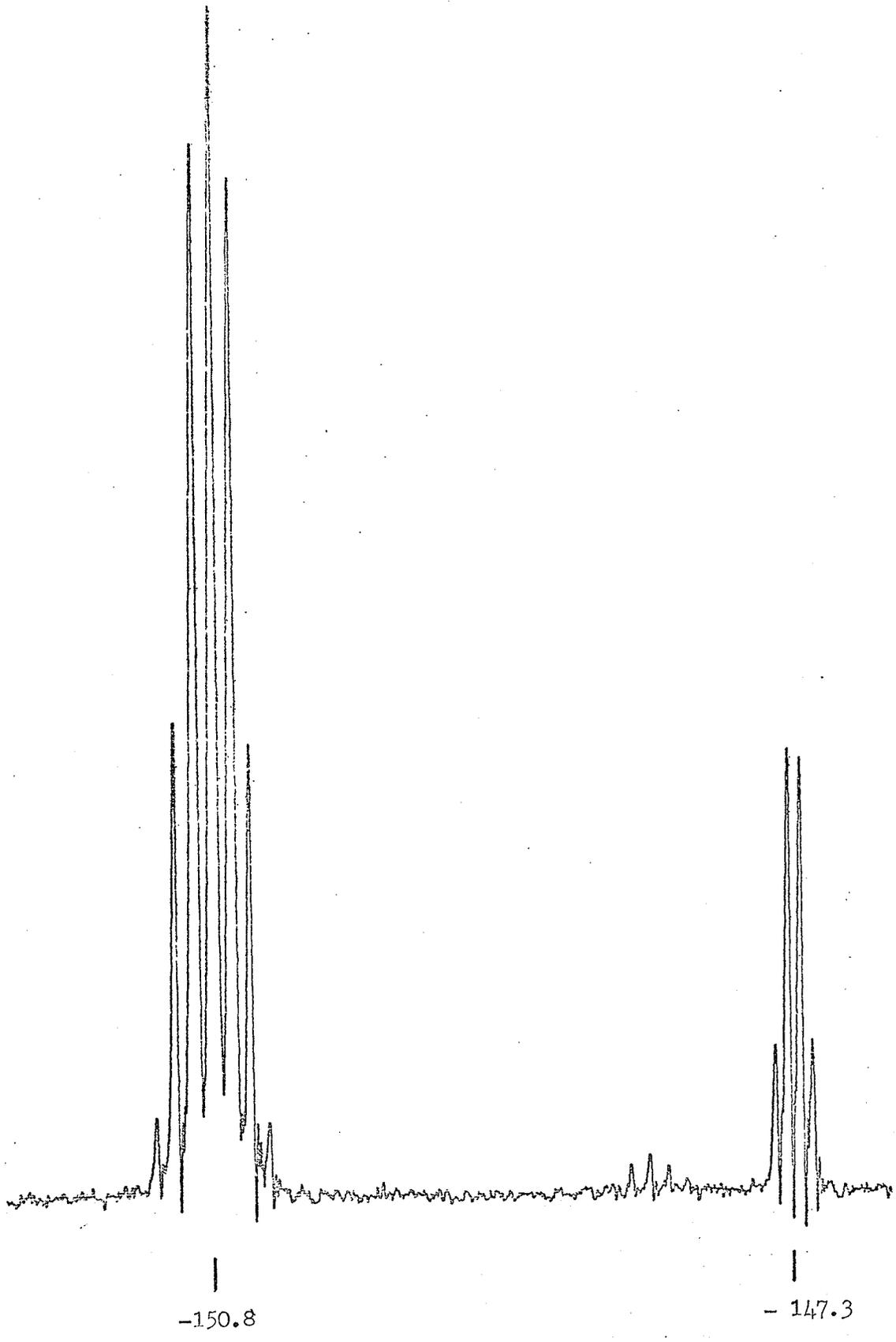


Figure 2 (cont'd)

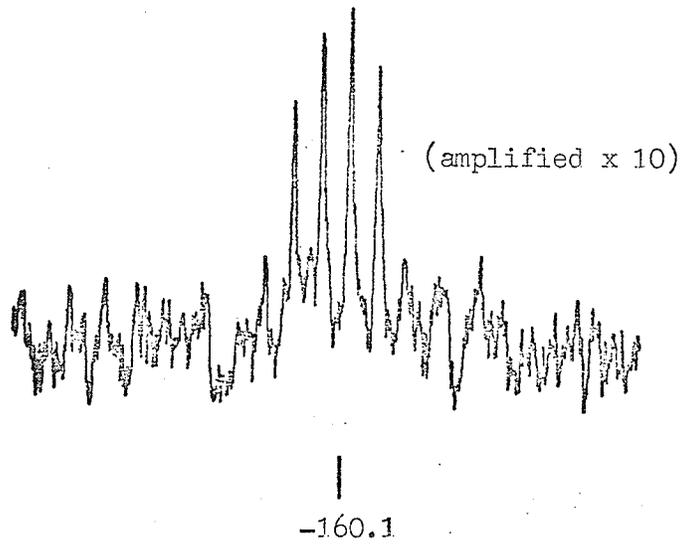


Figure 3

^1H NMR Spectrum of Cleavage Reaction Products

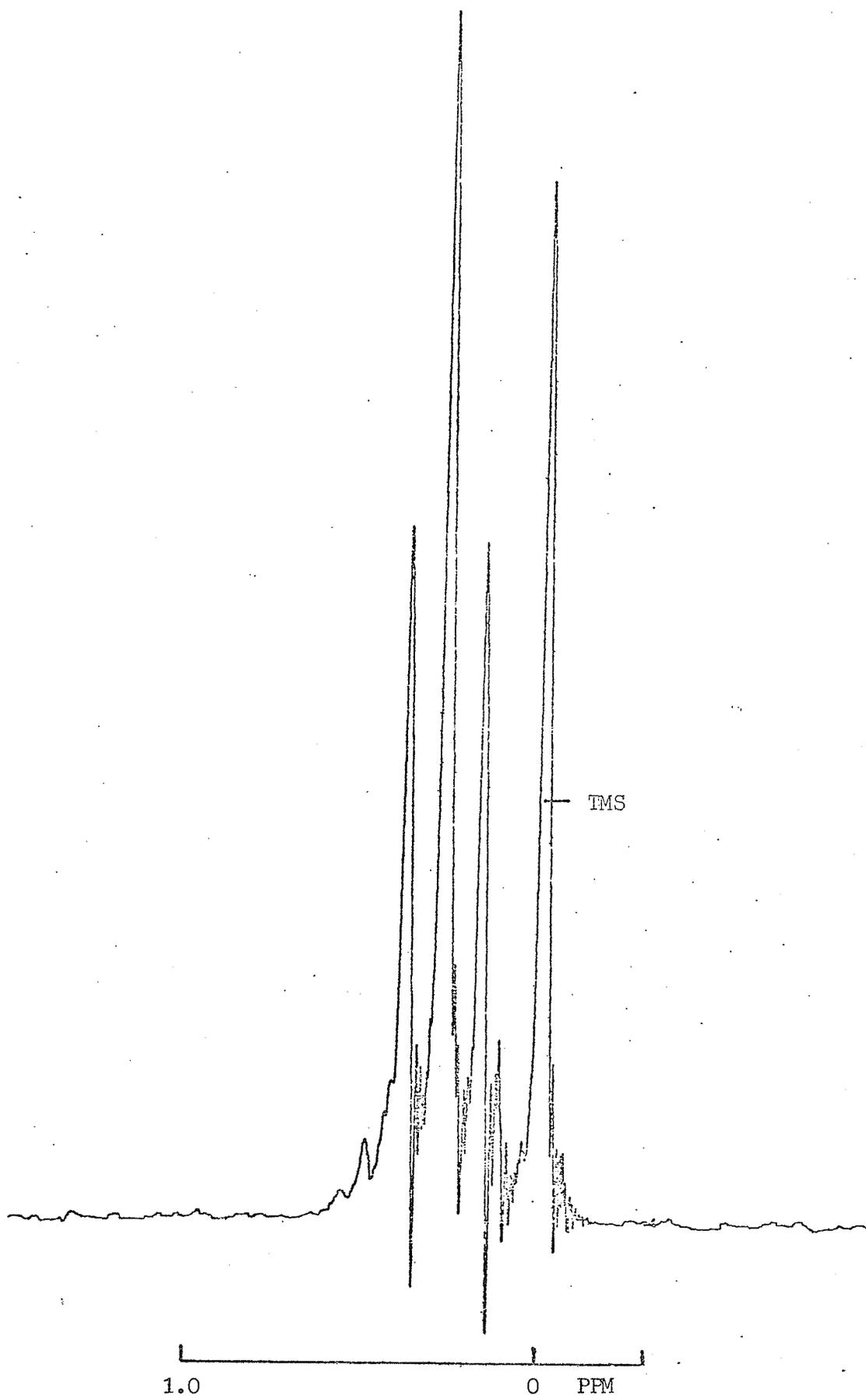


Table I - ^{19}F AND ^1H SPECTRUM ASSIGNMENTS FOR CLEAVAGE REACTION
PRODUCTS

<u>MODE</u>	<u>ASSIGNMENT</u>	<u>CHEMICAL SHIFT (PPM)</u>	<u>COUPLING CONSTANT (CPS)</u>
^{19}F	$(\text{CH}_3)\text{SiF}_3$	-147.3	4
^{19}F	$(\text{CH}_3)_2\text{SiF}_2$	-150.8	6
^{19}F	$(\text{CH}_3)_3\text{SiF}$	-160.1	8
^1H	$(\text{CH}_3)_2\text{SiF}_2$	- 0.4	6

Figure 4

Infrared Spectrum of Silicone Foam Base

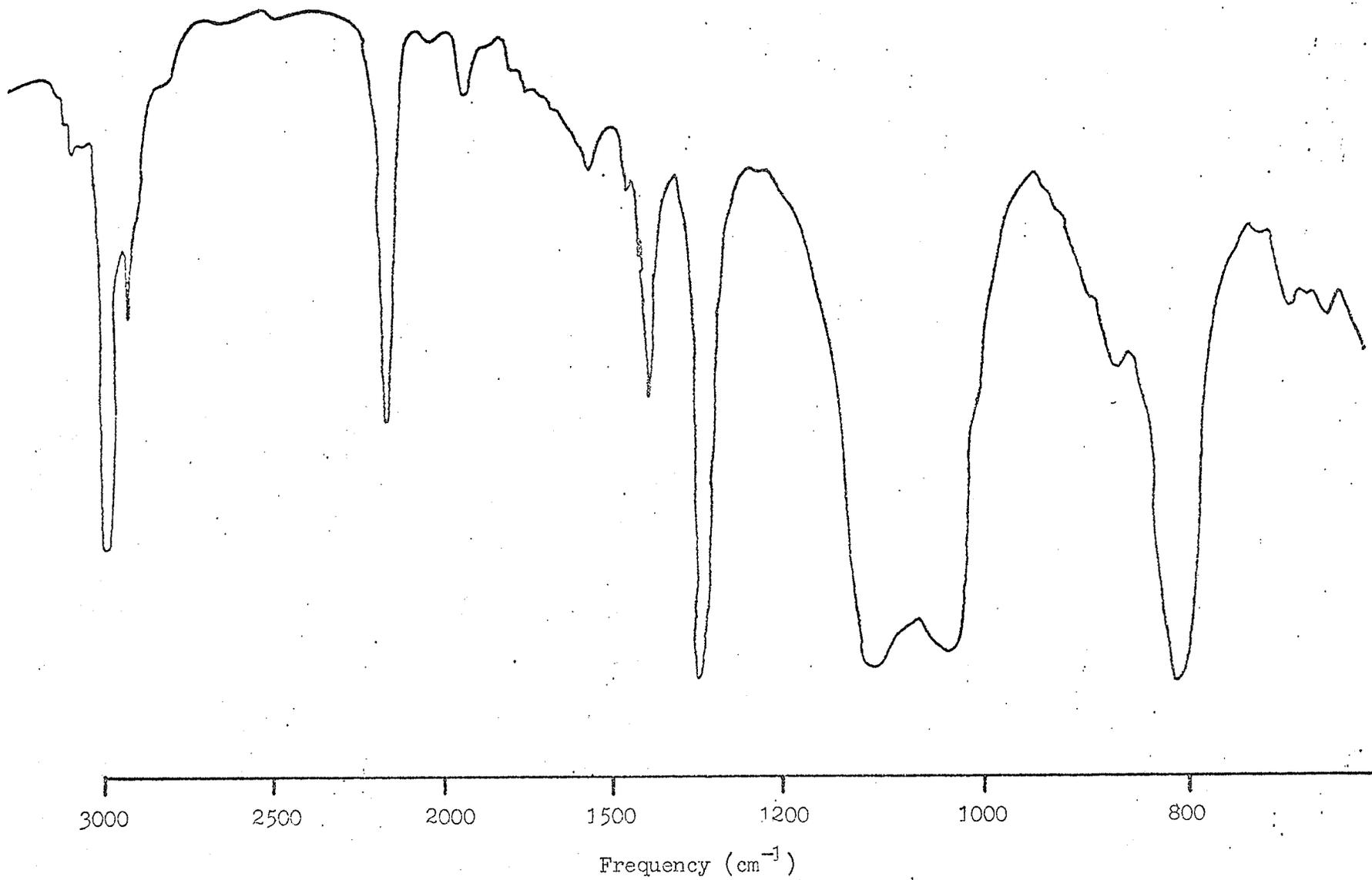
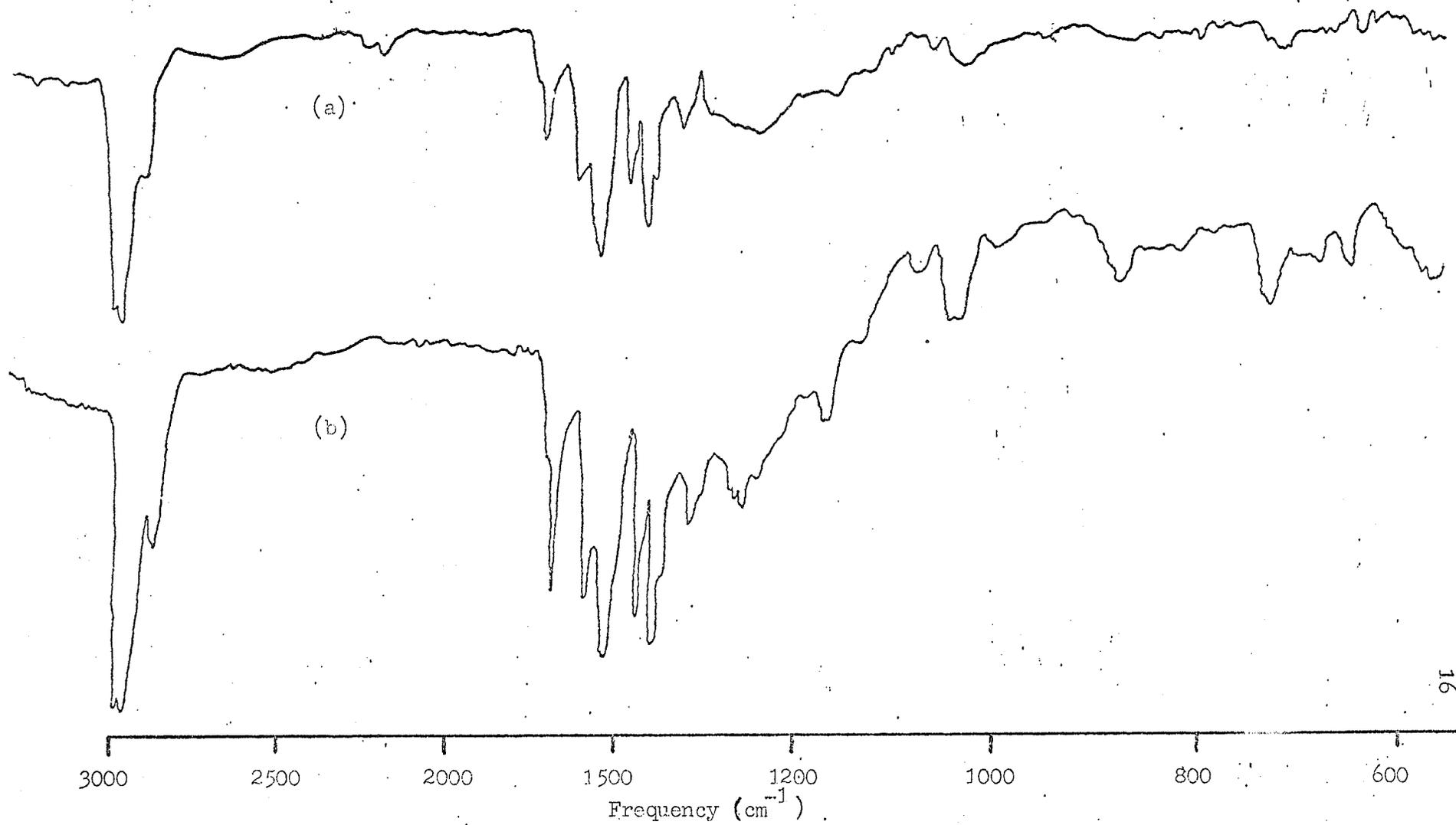


Figure 5

Infrared Spectrum of Catalyst S - 5370
and Stannous Octoate

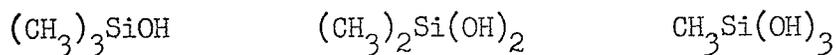
(a) Stannous Octoate

(b) Catalyst S - 5370

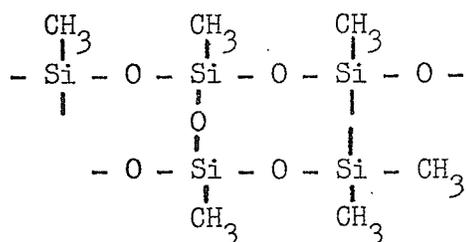


Discussion

Hydrolysis of the fluoroalkyl silanes⁴⁰ listed in Table I would produce a series of compounds as given below:

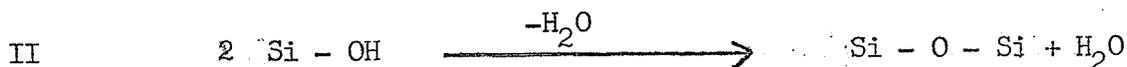
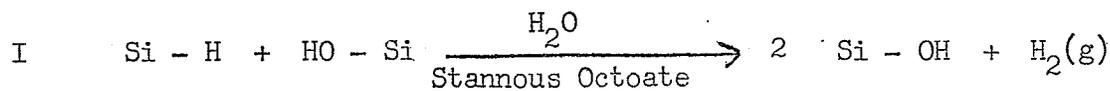


These can be condensed⁴¹ to siloxanes and finally to polysiloxanes. Reconstruction of the foam matrix is complete, and is found to be composed of a polydimethylsiloxane.



An extensive discussion on the production of silicone rubber foams has been given by Vincent.⁴²

The production of the foam involves the reaction (I,II) of an intermediate molecular weight polysiloxane containing both silanol and hydrogen functional groups.⁴³ The liberation of hydrogen gas as the polymerization process progresses produces the bubbles which are responsible for the sponge-like properties of the foam.



Preparation of Foam Materials

The silicone rubber foam was produced from a Dow Corning product called Silastic S - 5370 RTV. The kit consisted of a clear liquid catalyst (stannous octoate) and a more viscous brown foam base mixture. The foam base was found to contain polydimethylsiloxane and powdered silica used as an inert filler.

If allowed to stand undisturbed, the foam base mixture appeared to settle into two layers; A bottom layer of high density material containing much solid matter and a top layer of a lighter translucent liquid. To separate this mixture, a solution was made of foam base and carbon tetrachloride in a one-to-one ratio. To every 500 ml of this solution was added 5.0 g of activated carbon, which served as a decolorizing agent. This mixture was left to stand for 5 hours after which it was passed, with suction, through a bed of finely divided silica gel. The clear solution that resulted was then rotary evaporated at steam temperature until the now opaque solution contained about 5% by volume of carbon tetrachloride. The purified foam base solution was now ready to be used in the production of silicone rubber foams.

Characterization of Filler Material

A small quantity (2.0 g) of filler material was separated from the foam base mixture by centrifugation. The sample was then washed several times with carbon tetrachloride, dried, and then treated with 48% hydrofluoric acid. With the exception of a small quantity of a brown rubber-like substance, the entire sample volatilized when placed on a steam bath for 3 hours. This indicated that the filler material was composed of silica. No effort was made to further investigate the nature of the brown residue.

Preparation of Silicone Rubber Foams

The silicone rubber foam was produced by mixing 6 parts of catalyst S - 5370 to every 100 parts of prepared foam base, by weight. The foaming chamber (fig 6) consisted of a glass cylinder whose inner surface was coated with a film of polyvinylchloride. One end of the cylinder was stoppered by means of a rubber plug also coated with polyvinylchloride. The plastic film prevented the foam from sticking to the walls of the glass cylinder while it itself was easily separable from the finished foam.

Into the foaming chamber was placed 5.0 g of foam base with the appropriate amount of stannous octoate catalyst. After thoroughly mixing the two components with a stirring rod for 15 seconds, the foam was allowed to cure for one hour before being removed from the mold. After 24 hours of additional curing at room temperature, the foam was cut into 4.6 cm lengths and stored in a covered glass beaker.

The white foam produced had a density of 0.109 g/cc and a pore size of between 0.5 and 1.0 mm as approximated with a millimeter rule. Other physical and chemical properties, such as thermal stability and cell structure, of silastic S - 5370 RTV silicone rubber foam have been reported.⁴⁴

It was found that the density and hence the pore size of the foam could be varied by as much as an order of magnitude by either including larger amounts of carbon tetrachloride or other volatile solvents in the foam base or by reducing the pressure inside the

foaming chamber as foaming was taking place. The presence of 5% by volume of carbon tetrachloride in the foam base was found to yield a foam with good elastic properties and of uniform pore size.

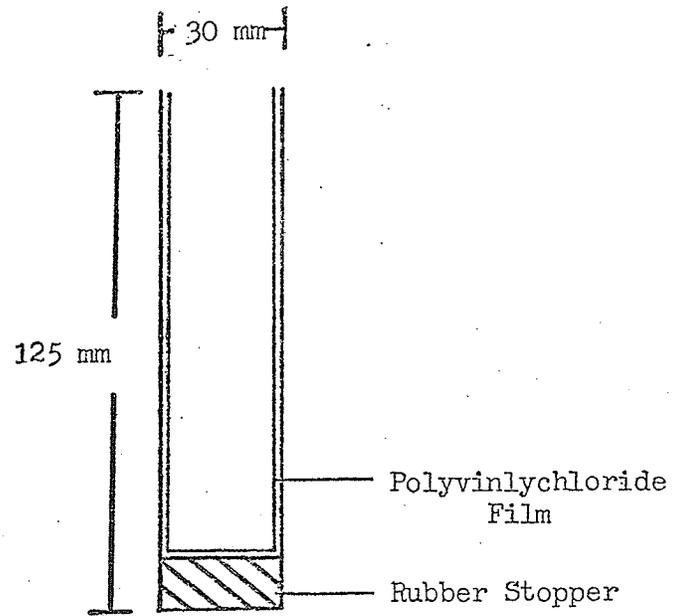
Figure 6

Foaming Chamber

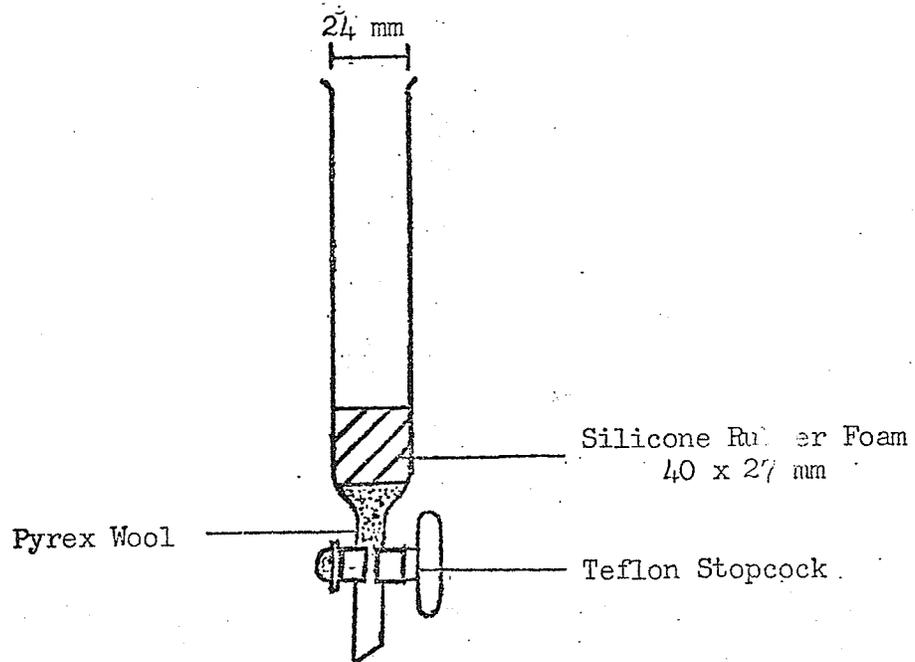
Figure 7

Columns Used In Flow-Through
Experiments

Foaming Chamber



Column



Column Packing Technique

Figure 6 illustrated the columns used in all flow-through experiments.

Column packing was achieved by first placing a small wad of pyrex glass wool at the bottom of the column. This served to trap any particles of palladium dimethylglyoxime, should any become loose. To place the foam into position, a vacuum line was attached to the open stopcock and the vacuum was turned on. By placing the foam into the mouth of the column and by repeatedly interrupting the flow of air into the column with the palm of the hand, the tight fitting foam slid into position at the base of the column.

Flow-Through Procedure

The procedure for all flow-through experiments is as follows except where specified otherwise. All volumes were measured with class A volumetric glassware.

To the packed column was pipetted 10.0 ml of hydrochloric acid solution of the appropriate concentration. A vacuum was applied to the mouth of the column and released when no more air bubbles could be seen rising to the surface. This enabled the foam to become completely saturated with acid solution, assuring good flow characteristics with a minimum of channelling as the test solution passed through the foam.

In order to minimize the dilution of the test solution when being added to the column, enough of the 10.0 ml of hydrochloric acid solution initially added was allowed to drain out of the column and into the collection flask, such that the level of the remaining acid solution was even with the top of the foam.

50.0 ml of the test solution was then pipetted into the column and allowed to flow through the foam at the desired flow rate. The flow rate was regulated by means of the teflon stopcock at the base of the column. Once the level of the test solution reached the top of the foam, an additional 10.0 ml of hydrochloric acid of the proper concentration was added and allowed to flow through the column at the same flow rate as the test solution. This ensured that the test solution in its entirety passed through the foam at

the controlled flow rate. A slight air pressure was then applied to the column to force any residual solution from the foam into the sample flask.

It was found that upon passing through the foam, some of the sample solution was absorbed by the foam, thus reducing its total volume. This made analysis of the test solution more difficult, since the volume of the solution had to be carefully measured each time. To avoid this effect, the foam was pre-wet with hydrochloric acid of the appropriate concentration and then forced free of residual liquid with compressed air prior to the addition of the first 10.0 ml aliquot of acid.

The sample solutions were analyzed for metal content by direct aspiration into the air acetylene flame of an atomic absorption spectrophotometer. Concentrations of unknown solutions were determined by comparison against several standard solutions of known concentration. All standard and blank solutions were matrix matched as closely as possible to the matrix of the sample solution. Absorbance values for the various solutions were recorded from the spectrophotometer 10 second integrated absorbance readout. The average of at least four such readings was taken for each sample analyzed. Unless otherwise stated, all experiments were run in triplicate and the results reported as an average of these with the average deviation.

Cleaning of Foams

It was observed that the catalyst (stannous octoate) would cause the reduction and precipitation of palladium by itself, thus before the foams could be expected to give reproducible results, the catalyst that remained trapped in the polymer matrix had to be removed. Since the stannous octoate catalyst is readily soluble in acetone and since its hydrolysis products are soluble in mineral acids and acetone, some combination of these was thought to be suitable for cleaning the foams. Several procedures of washing the foams were devised and are discussed below.

It was found that both platinum and palladium are precipitated from acid solution in the presence of stannous octoate. This effect was utilized to measure the effectiveness of each washing technique.

A volume of standard platinum and palladium chloride solution was passed through the washed foam at a standard flow rate. The percent metal removed from the solution after a single pass was taken to indicate the degree to which the catalyst had been washed free of the foam.

Experimental

For every test case, 50.0 ml of a solution containing 9.85 ppm palladium and 10.0 ppm platinum in 0.01 M hydrochloric acid was passed through the foam at a flow rate of 2.0 ml per minute. Where multiple passes are reported, the same solution was

once again passed through the same foam at the same flow rate. The amount of metal retained by the foam on successive passes is reported as the percent metal retained of the actual amount of metal remaining in the solution after the previous pass.

Washing Procedure A

Two unwashed silicone rubber foams were placed in a 250 ml soxhlet extraction apparatus and soxhleted with acetone for 12 hours. The foams were then pressed between two pieces of filter paper to remove excess acetone. The washed foams were air dried for 12 hours and stored in a covered glass beaker.

Washing Procedure B

Two silicone rubber foams were placed in a 50 ml beaker and washed with four 20 ml aliquots of a one-to-one mixture of 6 M hydrochloric acid and acetone. This was followed by washing with four 20 ml aliquots of double distilled deionized water.

Washing was accomplished by successively depressing and releasing the foam several times with the base of a small graduated cylinder. Excess liquid was removed by pressing the foam between two pieces of filter paper. After being air dried for 12 hours, the foams were stored in a covered glass beaker until needed.

Washing Procedure C

Three foams were washed as in procedure B, with four 20 ml aliquots of 6 M hydrochloric acid. This was followed with four 20 ml washings with double distilled deionized water. After

being pressed dry between two sheets of filter paper and air dried for 12 hours, the cleaned foams were stored in a covered glass beaker.

Washing Procedure D

In a beaker containing 100 ml of aqua regia were placed two unwashed silicone rubber foams. The foams were saturated with the solution by squeezing out the trapped air bubbles with the base of a graduated cylinder. After soaking for 20 minutes, the foams were removed from the aqua regia solution and washed several times with double distilled deionized water. The foams, which had taken on a brown color, were soxhleted in acetone for one hour. The white foam which resulted were pressed free of excess acetone and air dried for 12 hours. The foams were then stored in a covered glass beaker until required.

Washing Procedure E

A silicone rubber foam was washed, as previously described in procedure B, with four 20 ml aliquots of acetone. After drying, the foam was soaked for 20 minutes in 50 ml of aqua regia. The foam was then washed several times with double distilled deionized water. This was followed with four additional washings with 20 ml portions of acetone. After being pressed between sheets of filter paper and air dried for 12 hours, the foam was placed in a glass beaker for storage.

Results

The results for the various washing procedures are presented in table II.

In almost every case, the foam became saturated with platinum more quickly than it did with palladium. This suggests that the catalyst trapped in the foam reacts with platinum at a faster rate than does palladium. The amount of platinum adsorbed onto the foam perhaps is the more sensitive indicator of the effectiveness of each washing technique.

A perfectly catalyst-free or "clean" foam is expected to be completely inert towards solutions of platinum and palladium. Thus, the cleaning method that most closely reproduced this effect was chosen as the most suitable. Table II summarizes the results obtained for palladium and platinum retention by foams washed by each method.

Procedure D produces a foam that adsorbed only 3.1% of the palladium and 15.4% of the platinum from the original solution. This method was chosen as the one showing most promise. All other methods studied gave substantially higher adsorptions of one or both of the metals.

Table III gives the percent platinum removed by a foam treated as in method D, but with variable aqua regia soaking periods. Results indicate that a minimum platinum adsorption is reached at about 0.5 hours and that any additional time spent soaking in aqua regia is of no advantage. The platinum retention values obtained

Table II - ADSORPTION OF PLATINUM AND PALLADIUM CHLORIDES BY
VARIOUS WASHED SILICONE RUBBER FOAMS

<u>WASHING</u> <u>PROCEDURE</u>	<u>NUMBER OF PASS</u> <u>THROUGH FOAM</u>	<u>PALLADIUM</u> <u>RETAINED (%)</u>	<u>PLATINUM</u> <u>RETAINED (%)</u>
A	1	5.9 ± 1.0	35.5 ± 1.7
	2	7.5 ± 2.0	25.9 ± 0.0
	3	2.8 ± 1.5	0.0 ± 0.0
B	1	21.1 ± 9.0	58.3 ± 8.3
	2	16.8 ± 1.2	36.5 ± 1.7
	3	16.4 ± 0.9	0.0 ± 0.0
C	1	55.5 ± 3.0	40.5 ± 6.0
D	1	2.0 ± 0.0	15.4 ± 0.7
	2	1.1 ± 0.0	0.0 ± 0.0
	3	0.0 ± 0.0	0.0 ± 0.0
E	1	3.0	23.1
	2	0.1	10.0
	3	0.0	0.0

in table III were higher than those obtained for the experiments summarized in table II, because a flow rate of 1.0 ml per minute was used.

The adsorption of platinum by foams soaked in aqua regia for 30 minutes is given in table IV. Values were obtained comparable to those of foams soaked in aqua regia for only 20 minutes which again showed that a 30 minute aqua regia soaking period was sufficient.

The foams produced by this method were pure white in color. The average density of the foam changed from 0.109 g/cc before cleaning to 0.163 g/cc after the cleaning process was completed. The washing procedure caused a 13% shrinkage to occur, thus reducing the length from 4.6 cm to 4.0 cm and the width from 3.1 cm to 2.7 cm.

Table III - ADSORPTION OF PLATINUM CHLORIDE BY SILICONE RUBBER
FOAMS AT VARIOUS AQUA REGIA SOAK TIMES ^a

<u>TIME (HRS)</u>	<u>PLATINUM</u> <u>RETAINED (%)</u>
0.2	45.4 ± 6.1
0.5	31.1 ± 2.9
4.0	30.0 ± 0.0
18.5	30.7 ± 0.6

(a) flow rate: 1.0 ml per minute

Table IV - ADSORPTION OF PLATINUM CHLORIDE BY SILICONE RUBBER FOAM

<u>NUMBER OF PASS</u> <u>THROUGH FOAM</u>	<u>PLATINUM</u> <u>RETAINED (%)</u>
1	8.1 ± 1.8
2	2.5 ± 0.6
3	0.9 ± 0.5

Adsorption of Platinum and Palladium by Dimethylglyoxime Silicone Rubber Foam

Dimethylglyoxime was chosen as a complexing agent for palladium because of its relative insolubility in water (0.63 g/l)⁴⁵ and because of its inertness toward platinum under normal conditions. Also, dimethylglyoxime is quite soluble in acetone at room temperature, thus allowing the use of such a solution to saturate foam with the complexing agent. Once accomplished, it was hoped that foams treated with dimethylglyoxime could be used to selectively complex palladium out of solutions containing platinum and other metals.

Experimental

A silicone rubber foam cleaned by washing procedure D was placed into a beaker containing 50 ml of a saturated solution of dimethylglyoxime in acetone. Trapped air bubbles were expelled from the foam by gently compressing it with the base of a graduated cylinder. After the foam was allowed to soak for 6 hours, it was removed from the solution and pressed between two sheets of filter paper. This expelled excess amounts of dimethylglyoxime solution from the foam. The foam was then air dried for 24 hours.

To remove loose particles of dimethylglyoxime, the foam was washed five times with 20 ml portions of double distilled deionized water. After being air dried for 24 hours, the foam was placed in a sealed polyethylene bag for storage.

By weighing a number of foams before and after being

treated with dimethylglyoxime, the finished foam was found to contain 16.8 mg of dimethylglyoxime per gram of foam.

To each of three columns containing a dimethylglyoxime silicone rubber foam, 50.0 ml aliquots of solutions containing 9.85 ppm palladium and 10.0 ppm platinum respectively, were passed at a flow rate of 2.0 ml per minute. The concentration of palladium and platinum remaining in each solution was determined.

Results

The results presented in table V show that palladium is easily adsorbed onto the dimethylglyoxime treated foam. Platinum, however, passes almost unhindered through the foam. The possibility that the platinum was adsorbed by the dimethylglyoxime was rejected since earlier experiments (table IV) have shown that the foam itself is most likely responsible for the retention of platinum. Thus, the possibility for a separation of the two metals by this method seemed quite feasible.

Table V also suggests that platinum and palladium in 10^{-4} M hydrochloric acid gives a better separation than platinum and palladium solutions made up with 10^{-2} M hydrochloric acid. This indicates that there exists a pH dependence upon the adsorption of the two metals by the dimethylglyoxime silicone rubber foam.

The use of two foams in a column reduces the efficiency of palladium adsorption onto the foam. This is difficult to explain since it seems reasonable that more foam would provide more active

Table V - ADSORPTION OF PLATINUM AND PALLADIUM CHLORIDES BY
DIMETHYLGLYOXIME SILICONE RUBBER FOAM

<u>NUMBER OF FOAMS</u> <u>PER COLUMN</u>	<u>pH OF TEST</u> <u>SOLUTION</u>	<u>PALLADIUM</u> <u>RETAINED (%)</u>	<u>PLATINUM</u> <u>RETAINED (%)</u>
1	2.0	97.6 ± 0.5	3.4 ± 0.6
1	4.0	98.0 ± 0.5	0.4 ± 0.1
2	2.0	96.8 ± 0.9	0.0 ± 0.1
2	4.0	97.3 ± 1.3	6.7 ± 0.2

sites thus increasing the efficiency of extraction. Similarly, two foams should increase the possibility of platinum adsorption. This effect is seen in the case where two foams per column were used for platinum and palladium solutions made up in 10^{-4} M hydrochloric acid.

As an added note, it is of interest to point out that as the test solution passes through the treated foam, the appearance of the yellow palladium dimethylglyoxime complex can be easily seen. Also, if a loaded foam is cut in half, it is evident from the irregular coloration of the foam that palladium adsorption has not taken place evenly over the entire volume of the foam. This channelling effect is due to the presence of closed pores in the foam which serve to block the even flow and distribution of the test solution as it passes through the foam.

Adsorption of Platinum and Palladium Chlorides by α -Benzoin Oxime
Silicone Rubber Foam

A series of foams were produced to find if a treated silicone rubber foam could be produced by actually mixing in the desired complexing agent directly into the foam base before the foaming process took place. It was thought that this would produce a foam where the complexing agent would be more tightly bound than in the case where the complexing agent was adsorbed onto the foam by soaking in a saturated solution of that complex.

This technique had been investigated by Mazurski⁴⁶ for the extraction of mercury by variously treated silicone rubber foams. However, he neglected to take into account the effects of the catalyst left in the foam matrix.

In an attempt to wash the foam free of this catalyst, an alternate method of washing was used. Contact of the treated foam with aqua regia would certainly denature the α -benzoin oxime and so method D of washing was not considered useful.

α -Benzoin oxime was chosen because, as in the case of dimethylglyoxime, it is reported⁴⁷ to be a selective precipitant for palladium in solutions containing noble metals. α -Benzoin oxime was then chosen as a suitable complexing agent for this preliminary experiment.

Experimental

0.1 g of α -benzoin oxime was dissolved in as little acetone (about 1 ml) as possible and thoroughly mixed with 5.0 g of purified foam base. After adding the required amount of catalyst and mixing thoroughly for 15 seconds, the foam was allowed to rise and cure for one hour. The foam was removed from the foaming chamber and cured for an additional 24 hours before being cut into 4.6 cm lengths.

Washing was accomplished by first soxhleting the foams for 6 hours in acetone. After squeezing and air drying, the foams were soxhleted for an additional 6 hours with 6 M hydrochloric acid. The foams were then washed several times with double distilled deionized water and air dried for 24 hours before use.

Results

In the case of both platinum and palladium, more metal was adsorbed by the plain foam when these were used under identical experimental conditions. The plain foams were washed in exactly the same manner as were the treated foams.

These results indicate that it is likely that the α -benzoin oxime was either washed out during the washing process or itself denatured during the foaming process. This could have occurred as a result of a reaction of α -benzoin oxime with the catalyst or some other component of the foam mixture.

The fact that the percent metal adsorbed is lower in the treated foam strongly indicates that the method of washing used was ineffectual or at least yielded inconsistent or non-reproducible results. In this case, it can be postulated that more of the catalyst was left in the untreated foams, hence the higher platinum adsorption values in these.

It was concluded that the inclusion of complexing ligands into the foam base before foaming takes place does not seem to be a viable technique for the production of chromatographic silicone rubber foams largely since this method severely restricts the type of cleaning treatment possible.

Absorption of Platinum and Palladium by Srafion Treated Silicone
Rubber Foam

A powdered sample of Srafion resin was incorporated into the foam base in an attempt to prepare an ion exchange silicone rubber foam. Previously, only organic complexing agents had been used to remove metal ions from solution. Srafion resin⁴⁸ is reported to be selective for the removal of palladium chloride from acid solutions. The extraction involves the formation of a square planar complex of palladium with the sulfa-guanidine groups present on the resin.

Experimental

Powdered Srafion resin was prepared by placing 1.0 g of the resin in a dental amalgam mixer. After five minutes of grinding, the sample was completely reduced to a fine dust.

0.1 g of the Srafion resin dust was mixed directly with 5.0 g of prepared foam base. The required amount of catalyst was added and mixed in thoroughly for 15 seconds. After one hour, the partially cured foam was removed from the foaming chamber. Washing and further treatment of the foam was done exactly as in the preparation of α -benzoin oxime treated silicone Rubber foam.

50.0 ml of 10^{-2} M hydrochloric acid solutions containing 9.85 ppm palladium and 10.0 ppm platinum respectively, were passed through the foams at a flow rate of 2.0 ml per minute. This was also done for the α -benzil oxime and plain silicone rubber foams.

Results

The results are summarized in table VI. Three factors contribute to the apparently low results obtained. First, as the washing process took place, much of the powdered resin could be seen falling free of the foam. This was especially noticeable during the 6 hour acetone soxhlet extraction where the foam expanded considerably when saturated with acetone. Secondly, the possibility exists that the sulfa-guanidine groups were rendered inactive by the foaming or washing processes. Thirdly, the resin contains sulfa-guanidine groups only on the surface of the spherical beads. The grinding process greatly increased the surface area of the resin, but did not affect the number of active groups in the resin sample. Once incorporated into the foam, particles of resin with active as well as inactive surfaces were left exposed to the sample solution. This effect served to lower the possibility of interaction with the palladium solution.

Considering the above factors, the net effect of the resin in the foam could have been so small as to have been undetectable. As was concluded in the case of α -benzoin oxime treated foams, the presence of small amounts of catalyst in the foam due to insufficient washing could also yield uninterpretable results.

Table VI - ADSORPTION OF PLATINUM AND PALLADIUM CHLORIDES BY α -BENZOIN OXIME, SRAFION RESIN TREATED AND UNTREATED SILICONE RUBBER FOAM

<u>TYPE OF</u> <u>FOAM</u>	<u>PALLADIUM</u> <u>RETAINED (%)</u>	<u>PLATINUM</u> <u>RETAINED (%)</u>
α -benzoin oxime	32.5 ± 3.1	33.3 ± 3.2
plain	49.5 ± 0.7	55.5 ± 3.0
Srafion resin	45.0 ± 4.5	45.2 ± 3.2

Recovery of Palladium From Dimethylglyoxime Silicone Rubber Foam

Once palladium was adsorbed onto the foam, a method had to be devised by which to recover the metal.

Mineral acids were thought to be quite suitable for this purpose since palladium dimethylglyoxime is quite soluble in strongly acidic solutions.

Experimental

Three dimethylglyoxime silicone rubber foams were placed in separate columns and loaded with palladium metal. Loading of the treated foams with palladium was done by passing through each foam 50.0 ml of a solution containing 9.85 ppm palladium in 10^{-2} M hydrochloric acid. After removing the residual amounts of solution left in the foam with compressed air, the amount of palladium adsorbed by each foam was measured by determining the concentration of palladium remaining in the solution.

To recover the palladium from the foam, various concentrations and volumes of hydrochloric and nitric acids were used at a standard flow rate of 10.0 ml per minute. This was accomplished by first placing 10.0 ml of the solvent solution into the column and applying a vacuum to free trapped air bubbles from the foam. The remaining portion of the acid solution was added and left to run through the foam. After residual amounts of solution were blown free from the foam with compressed air, the amount of palladium extracted from the foam was determined and the efficiency of the method calculated.

Once a solvent was chosen, a study was made of the volume required for the total extraction of the palladium from the foam. This was done by collecting successive 25.0 ml aliquots and by measuring the amount of palladium extracted with each volume of wash solution.

To study the effect of temperature on the extraction of palladium, this study was repeated using the acid solution at a temperature of 50°C. In addition to this, the above experiments were run on columns containing two loaded dimethylglyoxime silicone rubber foams. A comparison of palladium recovery from columns containing one and two foams was made.

Results

The results in table VII show that a 200.0 ml solution of 8 M to 12 M nitric acid is quite suitable for complete palladium recovery. Figure 8 indicates that about 125 ml of 16 M nitric acid would be needed for the complete recovery of palladium from a single foam.

A study of the palladium recovered from a single foam by 8 M nitric acid at different temperatures is summarized in table VIII.

The results obtained show that the use of 50°C solutions is of no real advantage when volumes under 100 ml are used. However, when the concentration of palladium on the foam is greatly diminished, the use of 8 M nitric acid at 50°C becomes important. The hot acid extracts a full 3% more palladium than the 25°C solutions, yielding a quantitative recovery.

Table VII - RECOVERY OF PALLADIUM FROM LOADED DIMETHYLGLYOXIME
SILICONE RUBBER FOAMS

<u>VOLUME OF RECOVERY</u> <u>SOLUTION (ML)</u>	<u>NATURE OF</u> <u>SOLUTION</u>	<u>PALLADIUM</u> <u>RECOVERED (%)</u>
50.0	6 M HCl	69.6 ± 5.6
50.0	12 M HCl	90.0 ± 1.6
50.0	8 M HNO ₃	85.5 ± 0.6
50.0	16 M HNO ₃	84.0 ± 0.7
200.0	8 M HNO ₃	99.7 ± 1.9
200.0	16 M HNO ₃	101.0 ± 0.3

temperature of recovery solutions was 25°C

Figure 8

Plot of Palladium Recovered (%) From
Dimethylglyoxime Silicone Rubber Foam
vs Volume of 16 M Nitric Acid at 25°C

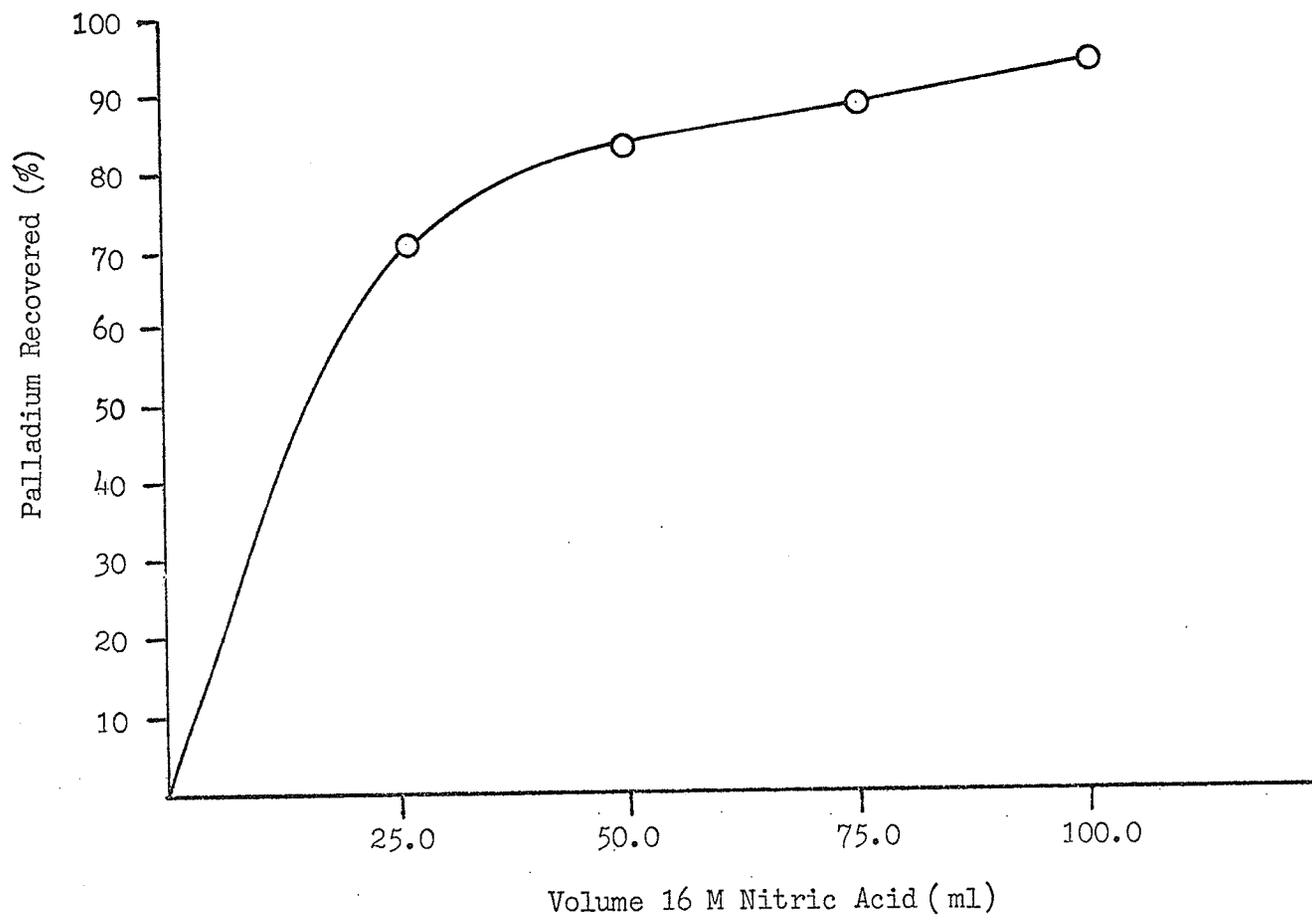


Table VIII - RECOVERY OF PALLADIUM FROM LOADED DIMETHYLGLYOXIME
SILICONE RUBBER FOAM WITH 8 M NITRIC ACID AT 25°C
AND 50°C

<u>VOLUME OF 8 M</u> <u>NITRIC ACID (ML)</u>	<u>TEMPERATURE (°C)</u>	<u>PALLADIUM</u> <u>RECOVERED (%)</u>
50.0	25	88.5 ± 2.5
50.0	50	88.0 ± 0.1
100.0	25	94.9 ± 1.8
100.0	50	94.6 ± 0.2
150.0	25	97.7 ± 1.4
150.0	50	98.2 ± 0.2
200.0	25	97.9 ± 1.5
200.0	50	100.9 ± 0.4

Table IX compares the results obtained for palladium extraction from columns containing one and two foams. As expected, for each volume studied, the palladium was extracted more easily from one foam than from two. After passing 200.0 ml of nitric acid through the two foam column, over 12% of the palladium was still present on the foam. Extraction from the single foam was quantitative.

The above data suggests that extraction can be most easily done from a single foam column. Also, for these columns, quantitative recovery can be obtained by passing 200.0 ml of 8 M nitric acid at 50°C through the foam at a flow rate of 10.0 ml per minute.

Table IX - RECOVERY OF PALLADIUM FROM ONE AND TWO LOADED
DIMETHYLGLYOXIME SILICONE RUBBER FOAMS WITH
8 M NITRIC ACID AT 25°C

<u>VOLUME OF 8 M</u> <u>NITRIC ACID (ML)</u>	<u>NUMBER OF FOAMS</u> <u>PER COLUMN</u>	<u>PALLADIUM</u> <u>RECOVERED (%)</u>
50.0	1	88.0 ± 0.1
50.0	2	79.1 ± 0.6
100.0	1	94.6 ± 0.2
100.0	2	85.1 ± 0.8
150.0	1	98.2 ± 0.2
150.0	2	86.9 ± 0.6
200.0	1	100.9 ± 0.7
200.0	2	87.9 ± 0.5

Recovery of Platinum from Dimethylglyoxime Silicone Rubber Foam

When 50.0 ml of a solution of 10.0 ppm platinum in 10^{-2} M hydrochloric acid is passed through a dimethylglyoxime silicone rubber foam, a small amount (3% to 7%) of the metal is adsorbed onto the foam. The experiments that follow were performed in an effort to discover a method of stripping this platinum from the foam.

Experimental

Three columns were each packed with a dimethylglyoxime silicone rubber foam. A 50.0 ml solution containing 10.0 ppm platinum in 10^{-2} M hydrochloric acid was passed through each column at a flow rate of 1.0 ml per minute. The procedure followed was the same as that used in the palladium recovery study.

The wash solutions studied consisted of 50.0 ml of hydrochloric and nitric acids of concentrations ranging from 6 M to 10^{-4} M. These solutions were also passed through the foam at a flow rate of 1.0 ml per minute. These experiments were repeated for columns containing two foams using 50.0 ml of a 10^{-4} M hydrochloric acid solution.

The amount of platinum recovered was taken as the sum of the platinum found in the test solution and that found in the wash solution.

Results

The results presented in table X indicate that strong mineral acids could recover up to 95% of the platinum from the foam. However, acids of such concentrations would cause much of the palladium already held onto the foam to be stripped away (p58). For this reason, very dilute acid solutions were found to be more useful in that while recovering the platinum from the foam, little of the palladium dimethylglyoxime complex was dissolved (p58).

Of all the acid solutions tested, the best results were obtained for wash solutions consisting of 10^{-4} M hydrochloric acid. However, when two foams were placed in the columns, the efficiency of recovery dropped from nearly quantitative recovery (99.6%) for one foam columns to 93.3% recovery for two foam columns. Therefore, a column containing one foam lends itself better to platinum recovery than a column containing two foams. Also, the data in table X suggests that the efficiency of platinum recovery is a function of the pH of the wash solution.

Although 50.0 ml of wash solution seemed sufficient for quantitative platinum recovery, 100.0 ml of solution were used under experimental conditions to ensure complete recovery of the platinum. Other experiments (p58) have shown that 100.0 ml of 10^{-4} M hydrochloric acid would remove only 0.2% of the palladium already adsorbed onto the foam.

Table X - RECOVERY OF PLATINUM CHLORIDE ADSORBED ONTO DIMETHYLGLYOXIME
SILICONE RUBBER FOAM

<u>WASH SOLUTION</u>	<u>NUMBER OF FOAMS</u> <u>PER COLUMN</u>	<u>PLATINUM</u> <u>RECOVERED (%)</u>
6 M HCl	1	91.2 ± 2.3
6 M HNO ₃	1	95.5 ± 0.5
10 ⁻² M HCl	1	98.1 ± 2.0
10 ⁻² M HNO ₃	1	98.7 ± 1.4
10 ⁻⁴ M HCl	1	99.6 ± 1.2
10 ⁻⁴ M HCl	2	93.3 ± 1.6

pH Study of Adsorption of Platinum and Palladium by Dimethylglyoxime
Silicone Rubber Foam

This study was undertaken to determine the optimum pH at which a separation of platinum and palladium could be accomplished. The parameters of interest were the percent palladium adsorbed onto the foam from the test solution, the percent palladium leached from the foam by the 100.0 ml wash solution and the percent recovery of platinum metal.

Experimental

For each pH studied, the sample and rinse solutions were brought to the same pH. Solutions of sodium hydroxide or hydrochloric acid were used to adjust the pH of the solutions. The experimental procedure was as described in the section entitled "Flow-Through Procedure". All test solutions consisted of 50.0 ml of 9.85 ppm palladium and 10.0 ppm platinum made up in hydrochloric acid of the appropriate concentration. The flow rate in all cases was kept at 2.0 ml per minute.

The percent palladium adsorbed onto the foam was determined in each case by measuring the concentration of palladium remaining in the test solution. The percent platinum recovered was taken to be the sum of the percent platinum retained in the test solution and the percent platinum recovered from the foam by the wash solution. Wash solutions consisted of 100.0 ml of hydrochloric acid of the appropriate concentration.

Also studied was the percent of palladium leached from the loaded foam. This was done by measuring the amount of palladium in the 100.0 ml of wash solution, and comparing this to the amount of palladium adsorbed onto the foam.

Results

The percent palladium retained (fig 9) reached a maximum plateau very quickly at pH = 1.0, and was maintained until about pH = 5.0. This broad range of high extraction efficiency peaked slightly at pH = 4.0 and so this pH was chosen as the most desirable for the adsorption of palladium by the treated foam.

The curve describing the pH relationship of the percent palladium leached by the 100.0 ml of wash solution (fig 10) from the loaded foam dips down to a minimum near pH = 4.0. As can be seen, at this pH the percent palladium leached is 0.2% or essentially nil.

The dependance of platinum recovery on pH (fig 11), however, shows two definite maxima; One at pH = 4.0 and the other at pH = 10.0. The possibility of choosing pH = 10.0 as a usable pH for wash solutions was not considered wise because at this pH, a considerable amount of palladium is leached off of the loaded foam. The curve showing this (fig 10) indicates that 7.7% of the palladium would be leached off of the foam.

In all three cases, for palladium extraction, palladium leached by the wash solution and for platinum recovery, a pH of 4.0

stands out as the best choice for achieving a complete separation of platinum and palladium. A pH of 4.0 is then the acidity at which the palladium dimethylglyoxime is least soluble and most easily formed under these experimental conditions. The mechanism by which platinum is adsorbed onto the foam is least functional at this pH.

Figure 9

Plot of Palladium Retained (%) by
Dimethylglyoxime Silicone Rubber
Foam vs pH of Solution

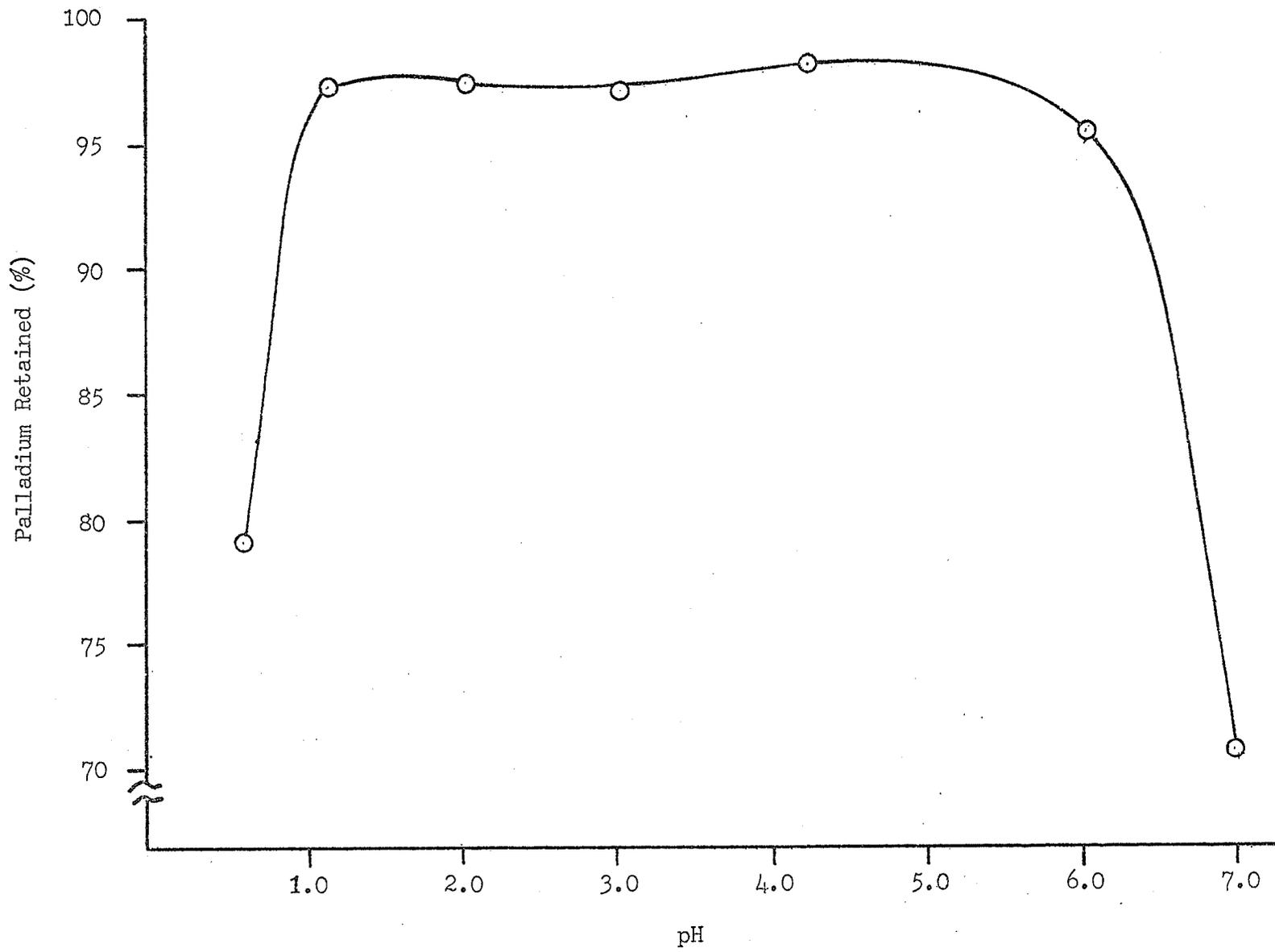


Figure 10

Plot of Palladium Leached (%) by
Dimethylglyoxime Silicone Rubber
Foam vs pH of Solution

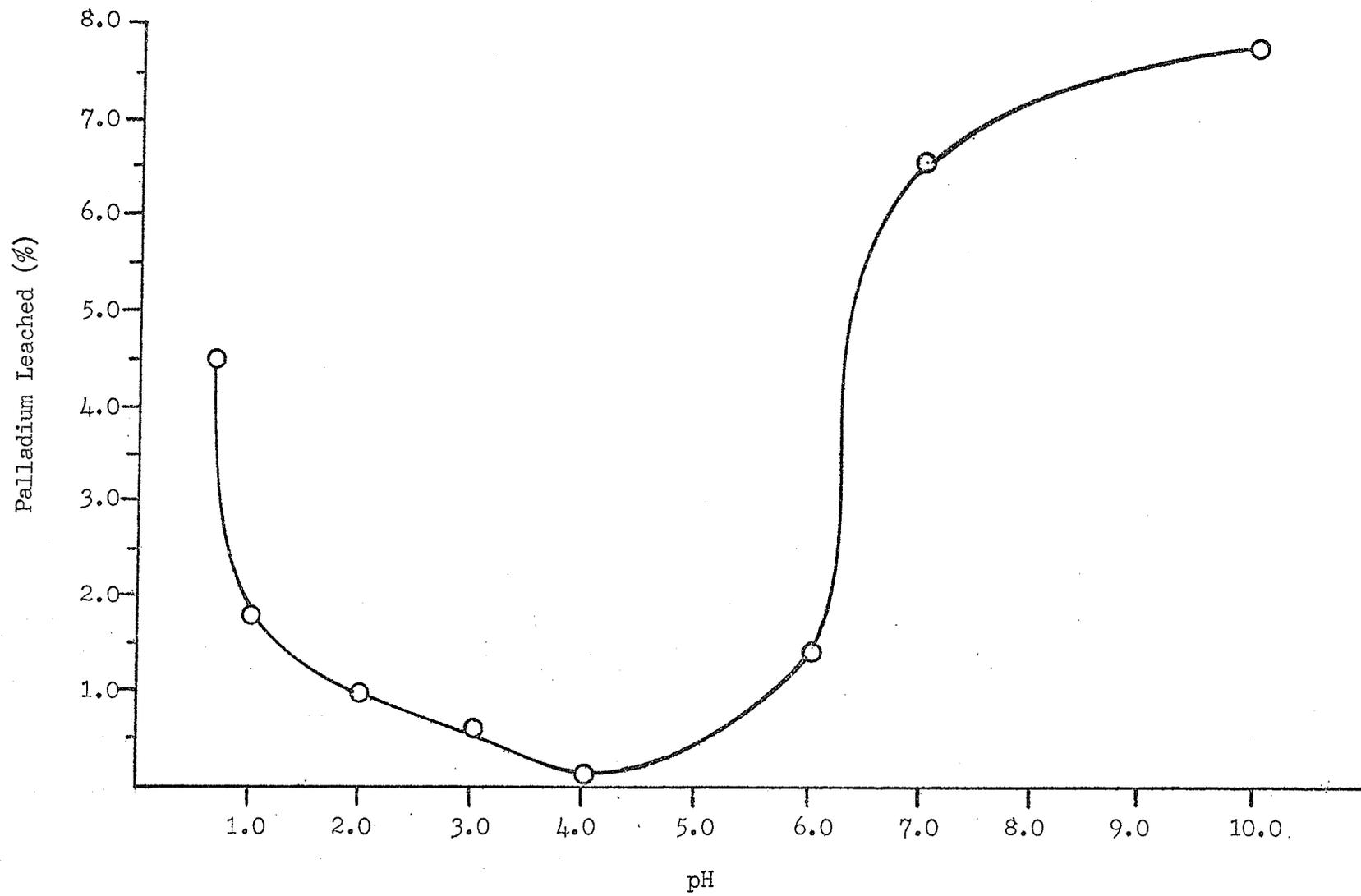
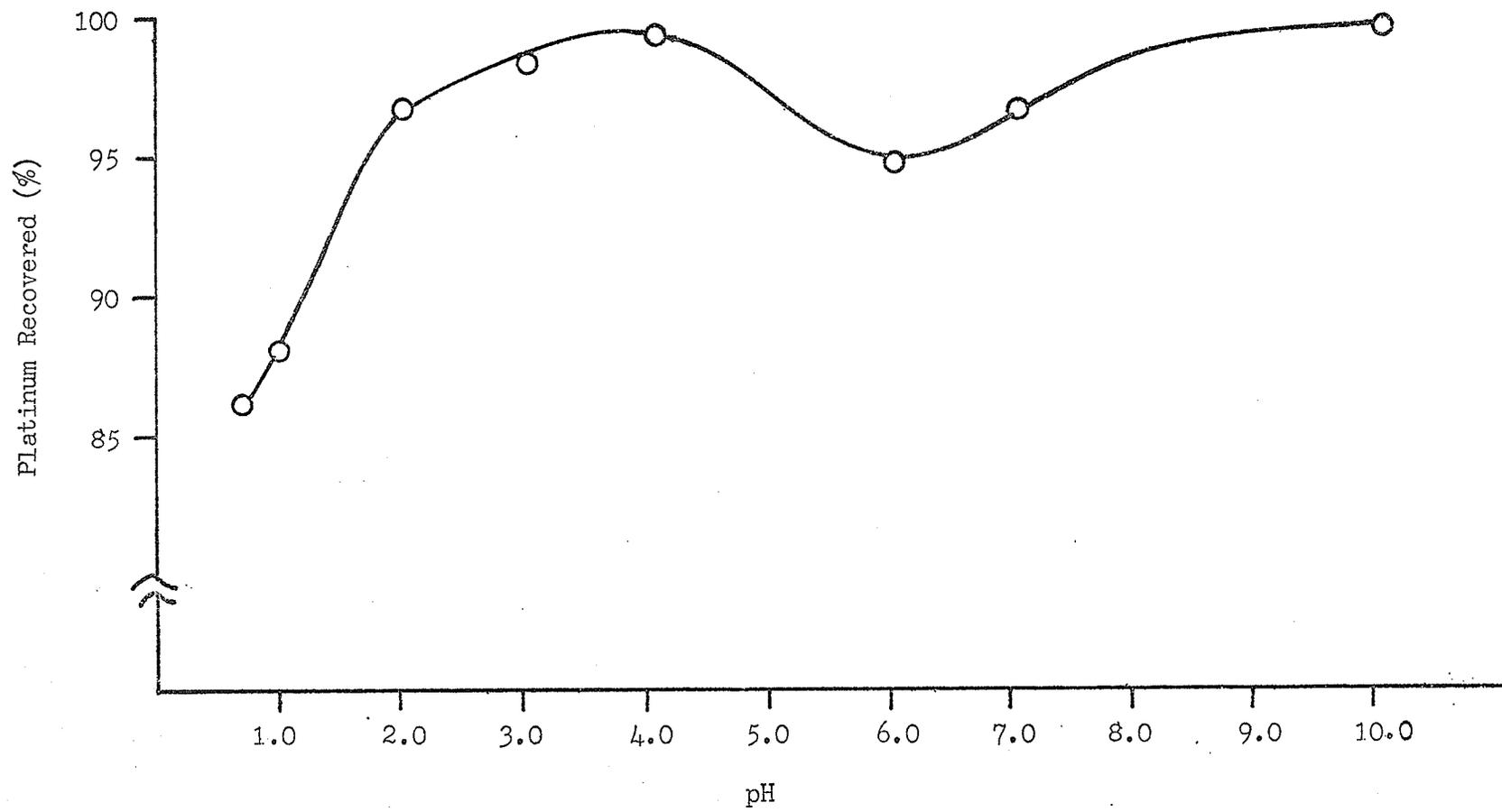


Figure 11

Plot of Platinum Recovered (%) From
Dimethylglyoxime Silicone Rubber Foam
vs pH of Solution



Flow Rate Study of Adsorption of Palladium by Dimethylglyoxime
Silicone Rubber Foam

In all previous experiments, flow rates were arbitrarily chosen since in every case, it was only of importance that flow rates be kept consistent throughout a given series of experiments. This group of experiments were carried out in an effort to discover at which flow rate the maximum amount of palladium would be retained from the test solution by the dimethylglyoxime treated foam.

Experimental

For each flow rate studied, three columns were each packed with a dimethylglyoxime silicone rubber foam. The flow rate was regulated by means of a teflon stopcock attached to the base of the column. The actual flow rate was obtained by recording the number of minutes required for the entire volume of test solution to pass through the foam. The test solution consisted of 50.0 ml of 9.85 ppm palladium metal in 10^{-4} M hydrochloric acid.

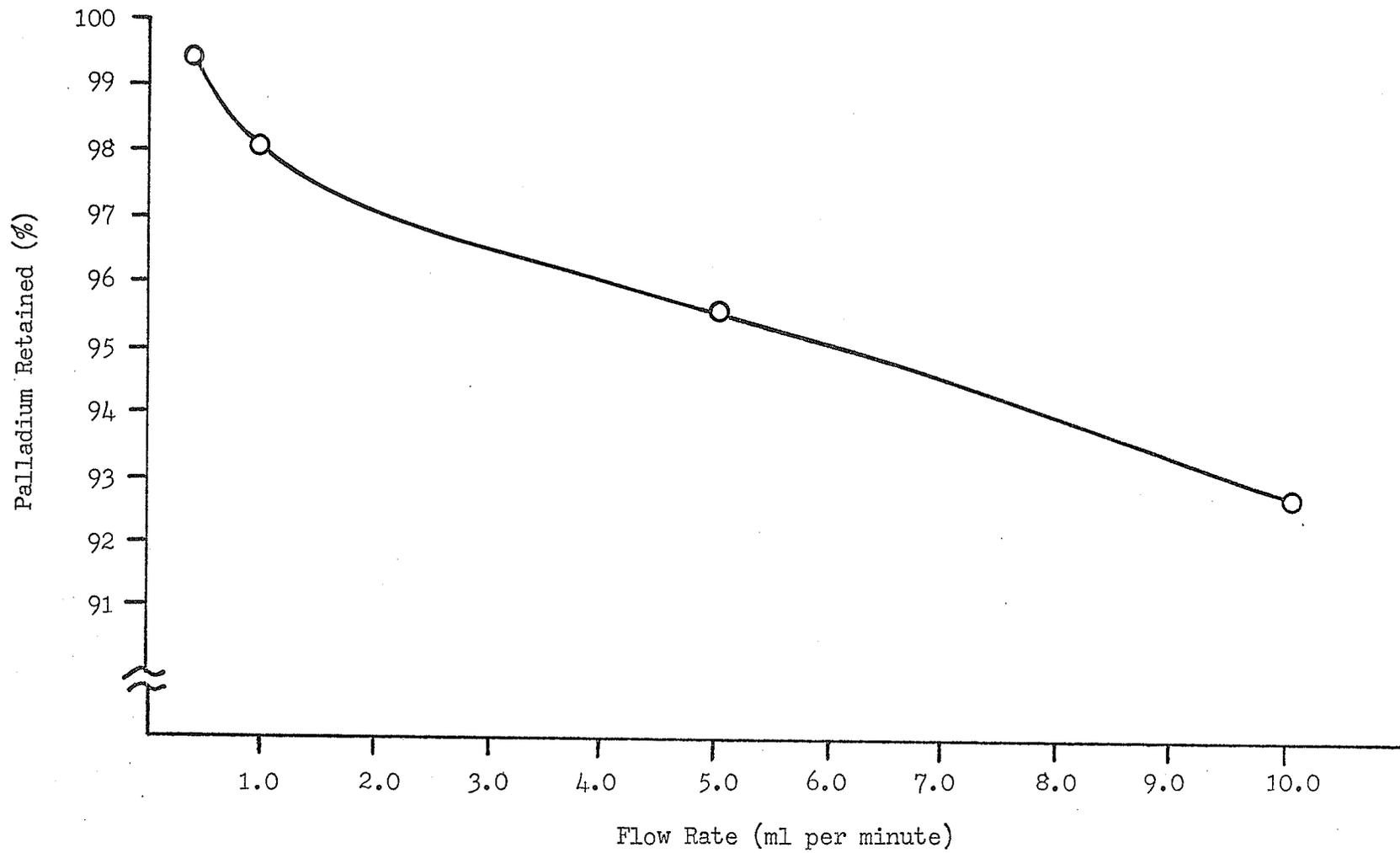
Results

Figure 12 summarizes graphically the results obtained from this study.

On going from 0.35 to about 2.0 ml per minute, the efficiency of adsorption of palladium onto the foam drops off quite rapidly, but is still at about 97% at 2.0 ml per minute. From that point on, the drop is less pronounced and extraction efficiency

Figure 12

Plot of Palladium Retention (%) vs
Flow Rate (ml per minute)



is reduced at a rate of about 0.6% for each increase of 1.0 ml per minute in flow rate.

For quantitative results, the flow rate must be kept below 0.5 ml per minute. A slow flow rate is required because palladium chloride reacts slowly with dimethylglyoxime in the solid phase. Longer interaction times are thus needed to ensure that the reaction has gone to equilibrium. This becomes especially important when low metal concentrations are used as shown on p68 .

Palladium Capacity of Dimethylglyoxime Treated Silicone Rubber Foam

The capacity of the dimethylglyoxime silicone rubber foam for adsorption of palladium chloride was determined under the normal experimental conditions. The capacity of the foam is of importance since its value determines the maximum volume of solution, of a given palladium concentration, that can be passed through a treated foam at an efficient rate of palladium retention.

Experimental

Three columns each containing a single dimethylglyoxime silicone rubber foam of known weight were used to ascertain the capacity of the foam for palladium. A solution containing 9.85 ppm palladium in 10^{-4} M hydrochloric acid was passed through each column in the usual manner. The flow rate was maintained at 0.35 ml per minute to ensure maximum efficiency. By means of small volumetric flasks (25.0 ml), aliquots were collected of each 25.0 ml of solution that passed through the foam. The concentration of palladium remaining in each aliquot was determined and the percent palladium adsorbed onto each foam was calculated.

An average value of the percent palladium adsorbed from each of the three columns at each 25.0 ml volume was taken and plotted against the total volume of solution passed through the foam. The area under the curve was obtained by counting the squares enclosed by the resulting curve. The curve was plotted on ten

divisions to the centimeter graph paper. From the area, the amount of palladium adsorbed per foam was calculated. Dividing this result through by the average masses of the foams, the capacity of the foam was calculated. The capacity was reported in milligrams of palladium metal adsorbed per gram of treated foam. A graphical representation of the results is given in figure 13.

Results

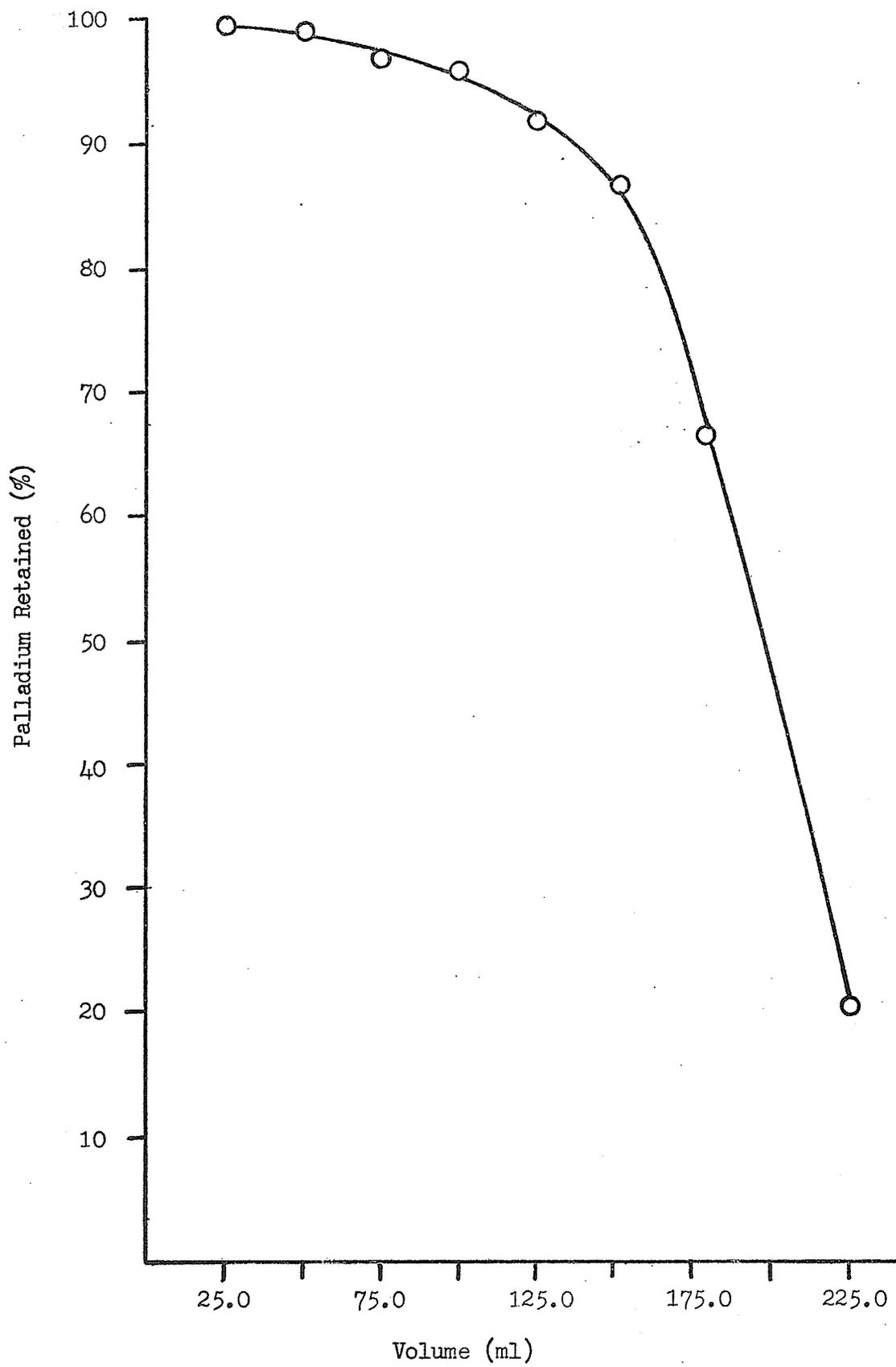
For the first 125.0 ml of solution that passed through the foam, over 90% of the palladium was adsorbed onto the foam. The next 125.0 ml, however, saw the adsorption of palladium dramatically drop to zero. This indicates that the extraction is efficient nearly up to the saturation point of the foam. Also, the effectiveness of the foam in removing palladium from solution does not drop off at a regular rate as the number of unused dimethylglyoxime sites are diminished. This is probably so, because the flow rate used (0.35 ml per minute) is greater than what is actually required thus giving adequate time for all palladium ions to find their way to dimethylglyoxime sites.

Using the method outlined above, the capacity of the foam was calculated to be 0.53 mg of palladium metal per gram of dimethylglyoxime treated silicone rubber foam.

A further calculation was made of the amount of dimethylglyoxime complexed, at capacity, comparing this to the actual amount of ligand originally present in the foam. The result showed that

Figure 13

Plot of Palladium Retained (%) by
Dimethylglyoxime Silicone Rubber Foam vs
Volume (ml) of Stock Palladium Solution



only 6.5% of the original amount of dimethylglyoxime was present in the complexed form at capacity.

Severe channelling effects coupled with the moderate solubility of dimethylglyoxime in 10^{-4} M hydrochloric acid could be used to explain this extremely low result. As the test solution passed through the foam, much of the dimethylglyoxime was dissolved, thus reducing the number of available sites for complexation. Channelling would simply divert the sample solution away from available dimethylglyoxime sites. Both would serve to give a low efficiency of complexation.

Separation of Platinum and Palladium by Dimethylglyoxime Silicone
Rubber Foam

The experimental parameters of importance relating to the separation of platinum and palladium were all maximized. In all previous experiments, however, the volume of the test solution has been kept at 50.0 ml and the concentration of both metals at 9.85 ppm and 10.0 ppm for palladium and platinum, respectively. The experiments discussed here examine the effectiveness of the technique at various metal concentrations and in one case, at a larger volume of test solution.

Experimental

Solutions containing various concentrations of platinum and palladium and dilutions of these solutions were passed through dimethylglyoxime silicone rubber foams. Each experiment was done in triplicate and all runs consisted of a single pass through the foam at a flow rate of 0.35 ml per minute. All solutions were made up in 10^{-4} M hydrochloric acid, including the 100.0 ml used to recover the platinum metal bound to the foam. In all cases, the normal flow-through procedure was used. (see p 24,51) Table XI summarizes the results obtained in this series of experiments.

Results

Good results for palladium retention were obtained in every case where 50.0 ml of test solution were used. Although low

Table XI - SEPARATION OF PLATINUM AND PALLADIUM BY DIMETHYLGLYOXIME SILICONE RUBBER FOAM

<u>TOTAL VOLUME OF TEST SOLUTION (ML)</u>	<u>PALLADIUM CONCENTRATION (PPM)</u>	<u>PLATINUM CONCENTRATION (PPM)</u>	<u>PALLADIUM RETAINED (%)</u>	<u>PLATINUM RECOVERED (%)</u>
50.0	9.85	100.0	97.6 ± 0.8	98.1 ± 1.5
50.0	9.85	30.0	98.0 ± 0.7	99.6 ± 1.2
50.0	9.85	10.0	99.7 ± 0.2	99.6 ± 1.1
50.0	1.0	100.0	100.0 ± 0.0	97.1 ± 1.1
1000.0	0.1	1.0	13.7 ± 1.0	102.6 ± 1.6

results appeared for the case in which the platinum-palladium concentration ratio was ten to one, quantitative retention resulted in the sample where this same ratio was one hundred to one. The concentration of platinum in the solution does not seem to effect the adsorption of palladium onto the foam.

Where 1.0 l of 0.1 ppm palladium solution was passed through a foam, an exceedingly low extraction of 13.7% resulted. As previously mentioned, this is probably due to two factors. The much lower concentration of palladium decreased the chance of interaction between the palladium ions and the dimethylglyoxime. Also, the large volume of solution used surely dissolved much of the dimethylglyoxime out of the foam. This essentially made the foam inert towards palladium after some volume of the solution had eluted.

Recovery of platinum was quantitative (99%+) in every case with the exception of those solutions containing 100.0 ppm platinum. At these concentration levels, perhaps more wash solution is required to recover the remaining platinum from the foam.

Effect of Diverse Ions on The Adsorption of Palladium by Dimethylglyoxime
Silicone Rubber Foam

To this point, the effect of foreign ions on the adsorption of palladium onto the foam had not been studied. The metal ions chosen for this investigation were those thought to occur most commonly with palladium, notably other noble metals and some base metals.

Experimental

Solutions already containing 9.85 ppm palladium and 10.0 ppm platinum were made up to also contain 100 and 1000 ppm concentrations of the foreign metal ion under study. All foreign metal solutions were made up from 10,000 ppm stock solutions of the chloride salt of the metal, with the exception of silver which was made from the nitrate salt.

50.0 ml of each of these solutions were passed through a dimethylglyoxime silicone rubber foam in the usual manner. All solutions were made up in 10^{-4} M hydrochloric acid with the exceptions of iron and silver which were made up in 10^{-2} M acid to avoid precipitation of metal hydroxides. For solutions containing silver, 10^{-2} M nitric acid was used to avoid precipitation by chloride ion. Platinum could not be included in a solution of nitric acid since the nitrate of platinum does not exist under normal conditions and precipitation would occur. Palladium nitrate was produced by evaporating to dryness several times a solution of palladium chloride in 8 M nitric acid.

From the amount of palladium remaining in each solution after

a single pass through the foam, the percent palladium adsorbed onto the foam was calculated and the effect of each metal on that process was evaluated. The results are listed in table XII.

Results

At the 1000 ppm level, iron, chromium, lead and silver substantially reduced the adsorption of palladium by the treated foam. None of these ions form a complex with dimethylglyoxime thus the lower adsorption of palladium metal could be attributed to a "blocking effect" caused by the high concentration of foreign metal ion in solution. Iron, however, forms a complex with palladium and almost completely hinders the complexation of palladium with dimethylglyoxime, even at a concentration of 100 ppm. A releasing agent was used (sodium potassium tartrate) and at 100 ppm of iron, a good palladium extraction was achieved. No other ions interfered extensively with palladium extraction at the 100 ppm level. In cases where significant concentrations of nickel were present, both nickel and platinum dimethylglyoxime⁴⁹ were formed. The nickel complex appeared as a pink-colored solid, whereas the platinum complex was blue-bronze in color. These observations were confirmed by dissolution of the complexes in 8 M nitric acid and analysis by atomic absorption. At the concentration studied, rhodium and iridium did not hinder palladium adsorption.

The nitrate form of palladium also lent itself well to adsorption by the treated foam. This is illustrated in the case where silver was the foreign ion under study.

Table XII - EFFECT OF VARIOUS METAL IONS ON THE ADSORPTION OF PALLADIUM BY DIMETHYLGLYOXIME SILICONE RUBBER FOAM

<u>METAL ION</u>	<u>CONCENTRATION (PPM)</u>	<u>pH OF SYSTEM</u>	<u>PALLADIUM RETAINED (%)</u>
-	-	4.0	99.7 ± 0.2
Ni ²⁺	1000	4.0	99.6 ± 0.5
Ni ²⁺	100	4.0	99.6 ± 0.5
Fe ²⁺	1000	2.0	0.9 ± 0.1
Fe ²⁺	100	2.0	0.7 ± 0.1
Fe ^{2+(a)}	100	5.0	98.3 ± 0.5
Cu ²⁺	1000	4.0	100.0 ± 0.0
Cu ²⁺	100	4.0	99.1 ± 1.2
Cr ³⁺	1000	4.0	92.3 ± 2.2
Cr ³⁺	100	4.0	99.2 ± 0.0
Pb ²⁺	1000	4.0	91.8 ± 1.3
Pb ²⁺	100	4.0	99.0 ± 0.4

^a contained 2.5 g of sodium potassium tartrate per 50.0 ml of solution

Table XII (cont'd)

<u>METAL ION</u>	<u>CONCENTRATION (PPM)</u>	<u>pH OF SYSTEM</u>	<u>PALLADIUM RETAINED (%)</u>
Ag ^{+(b)}	1000	2.0	93.3 ± 0.7
Ag ⁺	100	2.0	97.2 ± 0.6
Pt ⁴⁺	100	4.0	97.6 ± 0.8
Pt ⁴⁺	10	4.0	99.7 ± 0.2
Rh ³⁺	10	4.0	99.0 ± 0.1
Ir ⁴⁺	10	4.0	99.0 ± 0.1

^b silver nitrate salt used; nitric acid substituted for hydrochloric acid

From the above data it is evident that solutions containing iron, chromium, lead and silver in appreciable concentrations (i.e. greater than 100 ppm) must first be freed of these metal ions. Several techniques^{50,51} for the separation of base metals from the noble metals in solution are reported in the literature.

Adsorption of Nickel Chloride by Dimethylglyoxime Silicone Rubber Foam

As nickel also forms a complex with dimethylglyoxime, a study was made of the pH dependence of the extraction of nickel by dimethylglyoxime treated silicone rubber foam. This was done in the hope that a method could be devised for the separation of nickel and palladium by use of treated foams.

Experimental

Aqueous solutions of nickel chloride containing 10.0 ppm nickel were made up and adjusted to the desired pH with sodium hydroxide or hydrochloric acid, as required. The nickel solutions were made up from a 10,000 ppm nickel stock solution prepared by dissolving nickel chloride in a solution of 1 M hydrochloric acid.

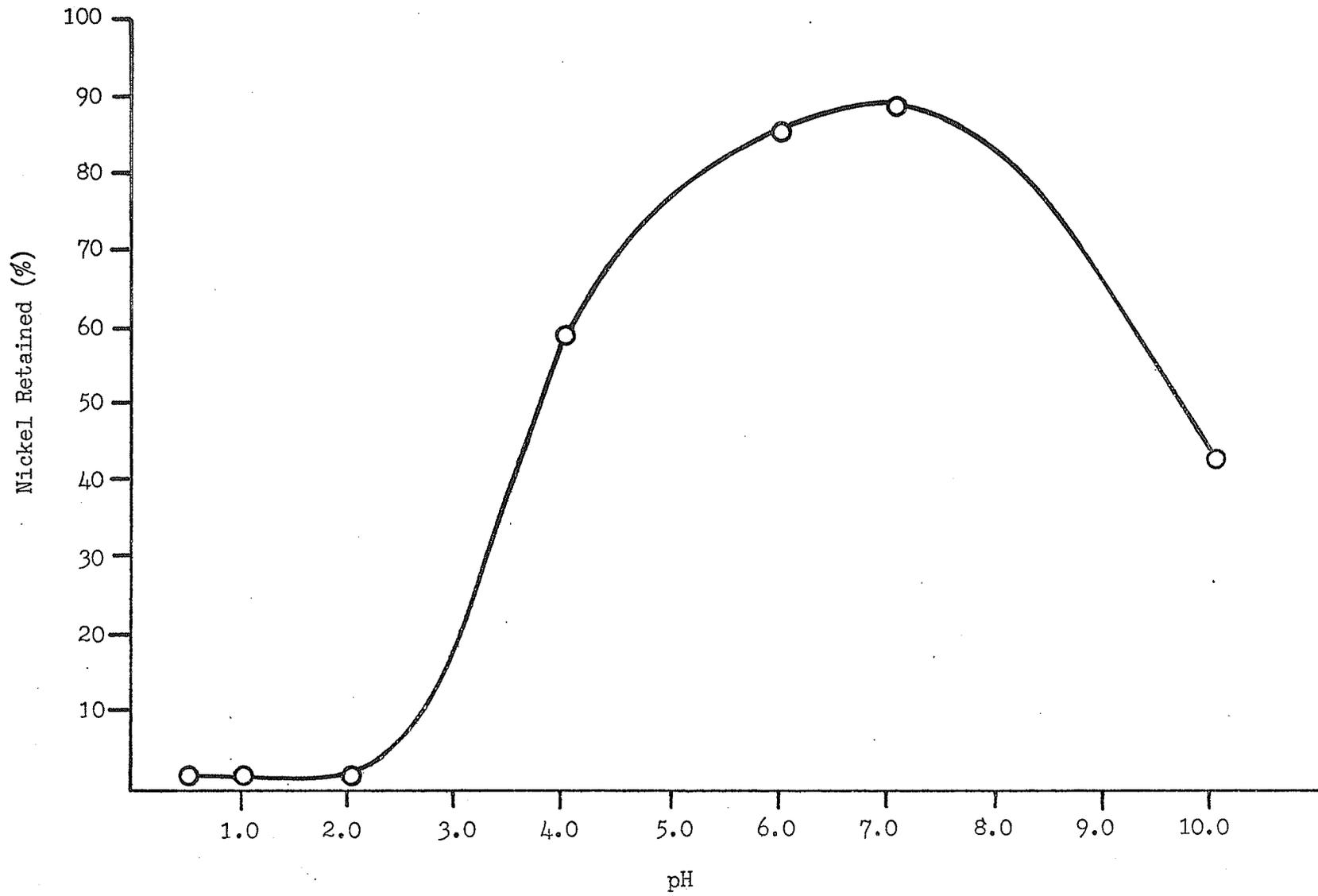
50.0 ml of each of the 10.0 ppm nickel solutions were passed a single time through three columns each containing one dimethylglyoxime silicone rubber foam, at a flow rate of 0.35 ml per minute. The amount of nickel remaining in the test solution was determined by atomic absorption and the percent nickel adsorbed onto the foam was calculated. Figure 14 is a graphic representation of the results obtained in this study.

Results

The extraction of nickel by the treated foam peaks at a pH of 7.0. A relatively low 88.3% adsorption is achieved at neutrality. Throughout this series of experiments, nickel could be seen complexing

Figure 14

Plot of Nickel Retained (%) by
Dimethylglyoxime Silicone Rubber
Foam vs pH of Solution



in the collection flask with the dimethylglyoxime dissolved by the sample solution. This indicates that the reaction between dimethylglyoxime and nickel is considerably slower than the analogous reaction with palladium. To achieve quantitative extraction, slower flow rates or more foams in each column would be required.

The curve (fig 14) strikes a minimum at a pH of 1.0 to 2.0. As the extraction of palladium is rather high at these pH levels, the possibility for a separation technique for palladium and nickel is strongly suggested. However, no further work was done to explore the feasibility of such a separation.

Discussion

This work shows that silicone rubber foam can be used as a solid support for chromatographic separations. An attractive feature of these foams is their chemical stability in strong mineral acids. Foams soaked in aqua regia for 24 hours showed no signs of disintegration or deformation. Concentrated sulfuric acid, however, completely dissolves the foam on contact.

The foams were reused as many as ten times without showing any noticeable changes in the flexibility or in the dimensions of the foam. Foams were recycled by subjecting them to the normal wash procedure.

Dimethylglyoxime silicone rubber foams provide an easy means of separating platinum and palladium. Quantitative results are obtained for samples containing a moderate concentration of palladium (i.e. greater than 0.1 ppm). Prior separation of other noble metals accompanying platinum and palladium is unnecessary.

Once the separation has been completed, the complexed palladium metal can be quantitatively recovered with little effort.

The production of these foams, including treatment with dimethylglyoxime is time consuming. A group of 30 foams would require a single person in excess of two days to produce. However, a production scheme could be devised whereby production time could be greatly diminished.

For a quantitative separation to be done on 50.0 ml of solution, a minimum of about four hours are needed, however, since few actual operations are required, many samples could be run simultaneously. If base metals are present, removal of these is essential to the efficiency of the separation.

Because of the moderate solubility of dimethylglyoxime, only samples of small volumes can be handled necessitating preconcentration, by evaporation or by some other means, of solutions whose volume exceeds 100 ml. Ligands with even lower solubilities must be found if the method is to be useful for samples of larger volumes.

In conclusion, the technique resulting from this work provides an elegant method for the separation of platinum from palladium in aqueous solutions, requiring in most cases little or no pre-treatment of sample solutions. Also, palladium metal adsorbed onto the foam can be easily and quantitatively recovered from the foam thus providing a method of concentrating palladium metal from dilute solutions.

Conclusion

This work has shown that silicone rubber foam can be used as a solid support for chromatographic separations of metals in solution. Further work, however, is needed in search of better complexing agents that exhibit the essential characteristics of low solubility and high selectivity. Also, new methods of incorporating or attaching complexing ligands to the foam matrix are required to make ligand particles less vulnerable to dislocation and dissolution by the sample solution.

Ligands could perhaps be more tightly bound onto the foam by first evaporating a solution of the ligand onto the foam and then by raising the temperature so as to melt in place the particles of ligand onto the foam. This was attempted with the dimethylglyoxime silicone rubber foam, but unfortunately, the compound sublimed out of the foam before its melting point was reached.

Prepolymers containing a low concentration of phenyl or other functional groups could also be used in the production of silicone rubber foam. Reactions could be performed on the finished foam to produce active sites for the complexation or exchange of metals in solution. For example, a foam containing phenyl groups could perhaps be treated so as to place a mercaptan group on the para position of the ring, thus producing a new "thiophenol" reagent which could be very efficient for the removal of platinum from solution. Analogously, polystyrene resin beads could be incorporated into the foam and later treated to produce anion or cation exchangers. This would avoid possible

denaturation of active groups, during foaming and washing, if ready-made anion or cation exchange beads were used.

Silicone foam could also be used as a solid support for reverse phase partition chromatography. Organic compounds insoluble in water, for example tri-n-butyl phosphate, could be adsorbed onto the foam surface and used for the concentration, extraction and separation of metals or even other organic compounds from solution.

In short, there is much opportunity for further research into the possible application of the silicone rubber foams as well as other foams in analytical chemistry. Development of these techniques could see wide application of foams in the laboratory and in industry.

Bibliography

1. Hollis, O.L., Anal. Chem. 38, 309(1966)
2. Ross, W.D., and Jefferson, R.T., J. Chromatog. Sci. 8, 386(1970)
3. Hileman, F.D., Sievers, R.E., Hess, G.L., and Ross, W.D., Anal. Chem. 45, 1126(1973)
4. Bowen, H.J.M., J. Chem. Soc. 1082(1970)
5. Schiller, P., and Cook, G.B., Anal. Chim. Acta. 54, 364(1971)
6. Gesser, H.D., Chow, A., Davis, F.C., Uthe, J.F., and Reinke, J., Anal. Lett. 4, 883(1971)
7. Uthe, J.F., Reinke, J., and Gesser, H.D., Environ. Lett. 3, 117(1972)
8. Braun, T., and Farag, A.B., Anal. Chim. Acta., 66, 419(1973)
9. Braun, T., and Farag, A.B., Talanta, 19, 828(1972)
10. Mazurski, M.A.J., Chow, A., and Gesser, H.D., Anal. Chim. Acta., 65, 99(1973)
11. Braun, T., and Farag, A.B., Anal. Chim. Acta. 65, 115(1973)
12. Braun, T., and Farag, A.B., Anal. Chim. Acta. 61, 265(1972)
13. Braun, T., Bakos, L. and Szabo, Z.S., Anal. Chim. Acta. 66, 57(1973)
14. Braun, T., Huszar, E., and Bakos, L., Anal. Chim. Acta. 64, 77(1973)
15. Braun, T., Bekeffy, O., Haklits, I., Kadar, K., and Majoros, G., Anal. Chim. Acta. 64, 45(1973)
16. Braun, T., and Farag, B., Anal. Chim. Acta. 65, 139(1973)
17. Braun, T., Farag, A.B., and Klimes-Szmik, A., Anal. Chim. Acta. 64, 71(1973)
18. Aue, W.A., Kapila, S., and Hastings, C.R., J. Chromatog. 73, 99(1972)
19. Ashes, J.R., and Haken, J.K., Anal. Chem. 45, 1131(1973)

20. Modern Methods For The Separation of Rarer Metal Ions, Korkish, J. Ch. 19, Pergamon Press, Toronto, Ontario, 1969
21. MacNevin, W.M., and Crummett, W.R., Anal. Chem. 25, 1628(1953)
22. Berman, S.S., and McBryde, W.A.E., Canad. J. Chem. 36, 835(1958)
23. Anil, K., and Rahaman, S., Analyst, 89, 795(1964)
24. Diamantatos, A., Anal. Chim. Acta. 66, 147(1973)
25. Diamantatos, A., Anal. Chim. Acta. 67, 317(1973)
26. Rees-Evans, D.B., Ryan, W., and Wells, R.A., Analyst 83, 356(1958)
27. Payne, S.T., Analyst 85, 698(1960)
28. Plummer, M.E.V., Lewis, C.L., and Beamish, F.E., Anal. Chem. 31, 255(1959)
29. Nath, S.K., and Agarwal, R.P., Michrochim. J. 11, 472(1966)
30. Pohlandt, C., and Steele, T.W., Talanta 19, 839(1972)
31. Akaza, I., Kiba, T., and Kiba, T., Bull. Chem. Soc. Japan 43, 2063(1970)
32. Ayers, G.H., and Belknap, H.J., Anal. Chem. 29, 1539(1957)
33. The Analytical Chemistry of The Noble Metals, Beamish, F.E., Pergamon Press, Toronto, Ontario, 1966
34. Ayers, G., and Berg, E.W., Anal. Chem. 25, 980(1953)
35. Organosilicon Compounds, Earborn, C., Butterworths Scientific Publications, London, 1960
36. Information About Silastic Brand Silicone Rubber, Dow Corning, Bulletin Number 08-295, September 1967
37. Schnell, E., and Rochow, E.G., J. Inorg. and Nucl. Chem. 6, 303(1958)
38. Schmutzler, R., J. Chem. Soc. 4551(1964)
39. Westermark, H., Acta. Chem. Scan. 9, 947(1955)

40. Ibid. 35, p. 250
41. Ibid. 35, p. 246
42. Plastic Foams Part I, Frisch, K.C., and Saunders, J.H., Ed. Marcel Dekker Inc., New York, N.Y. U.S.A. Ch.7, 1972
43. Ibid. 42, p. 393
44. Ibid. 36
45. Quantitative Chemical Analysis, 4th ed. Kolthoff, I.M., Sandell, E.B., Meehan, E.J., and Bruchenstein, S., p. 277, Collier-Macmillan Ltd., London, 1969
46. Mazurski, M.A.J., M.Sc. Thesis, The University of Manitoba, 1972
47. Ibid. 33, p. 289
48. Feigenbaum, A.G.H., and Schmuckler, G., Anal. Chim. Acta. 59, 397(1972)
49. Ibid, 33, p. 385
50. Beamish, F.E., Coburn, H.G., and Lewis, C.L., Anal. Chem. 8, 1297(1956)
51. Recent Advances In The Analytical Chemistry of The Noble Metals, Beamish, F.E., Van Loon, J.C., p, 7 Pergamon Press, Toronto, Ontario, 1972