THE SEPARATION OF RHODIUM AND IRIDIUM BY ION-EXCHANGE AND SOLVENT EXTRACTION

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy at the University of Manitoba

September 1, 1974

THE SEPARATION OF RHODIUM AND IRIDIUM BY ION-EXCHANGE AND SOLVENT EXTRACTION

by

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

DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a Ph.D. thesis entitled: .....The Separation of Rhodium and Iridium by..... Ion-Exchange and Solvent Extraction.....

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in partial fulfilment of the requirements for the Ph.D. degree.

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ABSTRACT

The chloro complexes of rhodium and iridium were separated by two methods: ion-exchange involving a strongly basic anion-exchanger, and solvent extraction employing tri-n-octylamine as a liquid anion-exchanger.

Rhodium and iridium were separated with Amberlite IRA-400 resin. Rhodium was eluted with 0.8 M hydrochloric acid prior to the removal of iridium with concentrated nitric acid heated to 74°C.

Iridium was separated from rhodium by extracting the iridium with a benzene solution of tri-n-octylamine. The extracted iridium was recovered by stripping the organic phase with ammonium hydroxide.

Both microgram and milligram quantities of rhodium and iridium were used in the two studies.

ACKNOWLEDGEMENTS

I would like to thank Dr. A. Chow for his encouragement during the course of this research, and the University of Manitoba, the National Research Council of Canada and Alcan for their financial assistance. Above all, I would like to thank my wife Anne for her patience and understanding.

G. Kanert

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I | INTRODUCTION

1. THE SEPARATION OF RHODIUM AND IRIDIUM

One of the most difficult aspects of noble metal chemistry is the separation of rhodium and iridium. This difficulty is due to the formation of a variety of hydrolyzed species under various conditions by these elements in solution. Although there are many analytical methods (such as emission spectroscopy and controlled potential coulometry) for the determination of the one noble metal in the presence of the other, separational techniques are still necessary for the production of rhodium-free iridium and iridium-free rhodium.

Since the nineteen thirties, a wide variety of separational procedures have been recorded (1,2). In general, rhodium and iridium have been separated by four methods: precipitation, chromatography, ion-exchange and solvent extraction.

1-1. Precipitation Methods

The first acceptable analytical separation of rhodium was recorded by Gilchrist (3) who converted the metals to their sulfates and then selectively reduced rhodium by using titanium (II) chloride. Two precipitations produced a quantitative separation from iridium. The titanium was separated from the iridium by precipitating the titanium with cupferron. The precipitate, being bulky, encouraged adsorption of iridium. Reprecipitation was difficult and time-consuming, although with care, acceptable results could be obtained if the amount of iridium was 100 mg or more. Pollard (4) separated very small amounts of rhodium and iridium by reducing rhodium with titanium (II) chloride in the presence of 2-mercaptobenzothiazole, giving a reddish-brown insoluble

complex of rhodium. The filtrate was treated with thiourea to give iridium sulfide.

Pshenitsyn and co-workers developed several separational procedures. One method (5) was a modification of an earlier method and involved the precipitation of rhodium from its hexanitrite solution by sodium sulfide; iridium in the filtrate could be hydrolyzed to the hydrated oxide. A second procedure (6) required the selective reduction of rhodium by chromous chloride. Neither method could be recommended where high accuracy is required or small amounts of metal are involved (1).

Various authors have used copper to selectively reduce platinum metals and cause their precipitation. Aoyama and Watanabe (7) used copper powder to separate iridium from gold, platinum and rhodium. Tertipis and Beamish (8) separated both mg and μg amounts of rhodium from iridium by precipitating the rhodium in 0.1 M hydrochloric acid with an excess of copper powder. Rhodium was separated from the admixed copper by cation-exchange after dissolution in aqua regia and then by dry chlorination. Iridium in the filtrate was also separated from the copper by cation-exchange. The method in general is quite time-consuming. For separating small amounts of rhodium and iridium, Westland and Beamish (9,10) reduced rhodium by boiling a sulfuric acid solution of the two metals with antimony dust. The antimony in the iridium-containing filtrate was removed by distillation as the trichloride. The method has not been applied to more than 200 μg of rhodium.

McKay and Cordell (11) separated rhodium from iridium by reducing rhodium to the metal with aqueous sodium borohydride. The separation was best achieved in perchlorate medium in the presence of acetoxime. The

separation was dependent on the concentration ratio of iridium to rhodium; if this was high, some iridium was coprecipitated; if low, the rhodium obtained was free from even spectrographic traces of iridium.

Jackson (12) recorded a method for the precipitation of an organic rhodium complex in the presence of iridium. The procedure required the evaporation to fumes of a sulfuric acid-lithium sulfate solution of the two metals and additional heating with perchloric acid. Rhodium was then selectively precipitated by thioacetanilide after using fresh chromium (II) chloride solution to reduce both species to the bivalent state. Iridium in the filtrate was precipitated as its sulfide by thiourea in the presence of chromium (II). The method was applied successfully to 0.5 - 100 mg of metal. The method however is quite time-consuming.

Formamidinesulfinic acid (thiourea dioxide) was used by Prokof'eva and Bukanova (13) to precipitate rhodium in the presence of iridium. The filtrate was treated to determine iridium gravimetrically, potentiometrically or polarographically. The method was applied to amounts of 50 - 200 μg of rhodium and 50 μg to 23 mg of iridium in the ratios from 1:10 to 1:100. The accuracy of recovery was about ±4% for rhodium and about ±5% for iridium. Coprecipitation of iridium with rhodium increased with increasing iridium concentration.

1-2. Chromatographic Separations

One of the first chromatographic methods for the separation of the platinum metals involved the use of a column of alumina. Schwab and Gosh (14) were able to separate the complex chlorides of iridium, platinum, palladium and rhodium in that order. No quantitative results were given

however.

An interesting and potentially useful continuous separation of the platinum metals by paper electro-chromatography was described by MacNevin and Dunton (15). The success of the method depended upon the fact that the rate of diffusion of the four metals in descending chromatography and in horizontal electro-chromatography varied appreciably with each metal. Amounts up to 100 mg of mixtures of two or three metals could thus be separated, but the fact that conditions for rhodium required a slightly acid medium, under which conditions platinum was diffusely distributed, prevented the application to mixtures containing platinum, palladium, rhodium and iridium. However, rhodium and iridium could be separated. The procedure involved the use of ethylenedinitrilotetraacetic acid in a medium of pH 4 to complex iridium. The equipment included suitable paper, held vertically, notched at top and bottom, with platinum electrodes interwoven at the two sides. The purity of the metal obtained after the separation was studied by X-ray fluorescence.

Kember and Wells (16) described the separation of microgram amounts of platinum, palladium, rhodium and iridium by paper chromatography. Two solvent solutions and two chromatograms were necessary to separate all of the platinum metals. A solvent containing isobutyl methyl ketone (hexone), n-pentanol and hydrochloric acid in the ratios of 60:10:30 was used to separate rhodium, palladium and platinum. Iridium in low concentrations was reduced to the tervalent state, and in this condition remained with rhodium as a partially separated band. A solution of n-butanol saturated with 3 M hydrochloric acid and containing hydrogen peroxide was used for the separation of rhodium from iridium previously isolated by the hexone solvent. The

peroxide effectively moved the iridium away from the rhodium because the iridium was selectively oxidized to the more mobile iridium (IV). The separations on the paper were completed in about 14-18 hours. The platinum metals were removed from the paper for analysis by aqueous extraction with various solutions. The method in general is quite time consuming and applicable only to small amounts of the metals.

Rees-Evans, Ryan and Wells (17) separated 100 mg amounts of platinum, palladium, rhodium and iridium as their chloro complexes by cellulose column chromatography. The solvent mixtures used were hexone with 3% concentrated hydrochloric acid and an oxidizing solvent similar to the first but containing sodium chlorate. Both oxidizing and reducing conditions were applied; under oxidizing conditions platinum and iridium moved together. A separation required a second column and reducing conditions. The reduction was accomplished with tin (II) chloride, which allowed the collection of platinum as a first fraction, and subsequently the reduced iridium was eluted with a dilute acid solution. The palladium fraction follows the platinum-iridium fraction, moving away from the immobile rhodium which was eluted with water.

Payne (18) separated the chloro complexes of rhodium, iridium, platinum and palladium by a modification of the method used by Rees-Evans et al. (17). Solid hydroquinone and hydroquinone dissolved in a hexone-hydrochloric acid mixture were added to a beaker containing a solution of the platinum metals to reduce the iridium, and the resulting organic phase was added to a 35 cm cellulose column prepared from powder slurried with hexone and hydrochloric acid. The column was eluted with additional reducing solvent. Platinum was eluted first followed by palladium. The aqueous

phase remaining in the beaker contained the rhodium and iridium. Iridium was selectively extracted by an oxidizing solvent prepared from hydrochloric acid, sodium chlorate and the acid solvent containing hydrochloric acid and hexone. The extract, added to the column, produced a dark-brown band preceeding the pink band of rhodium which appeared when the aqueous rhodium phase was subsequently added to the column. The two fractions were collected in separate beakers and were analyzed. The methods of Rees-Evans et al. (17) and Payne (18) have not been applied to amounts of the platinum metals in the microgram range.

Rhodium and palladium were separated from each other and from the other platinum metals on a tri-n-butyl phosphate-treated Poracil C column by stepwise elution with 4 M sulfuric acid and 5 M hydrochloric acid as described by Pohlandt and Steele (19). Platinum and iridium were eluted together with 0.1 M hydrochloric acid and were separated under reducing conditions on a second column. Widely varying ratios of platinum metals were separated in both the μg and mg range.

Pohlandt and Steele (20) also separated platinum, palladium, rhodium and iridium from one another using a tri-n-butyl phosphate-treated cellulose column. The platinum metals in 5 M hydrochloric acid were fed onto the column and the column eluted with a 1:1 mixture of tri-n-butyl phosphate-toluene solution. Platinum was eluted first followed by palladium. Rhodium and iridium were retained together on the cellulose column. After the elution of platinum and palladium an oxidizing solution consisting of chlorine dissolved in tri-n-butyl phosphate-toluene was allowed to penetrate the column bed. After five minutes, elution was continued with a chlorine-

free mixture of tri-n-butyl phosphate-toluene. Under these conditions iridium was eluted while rhodium remained unaffected in the upper part of the column. Rhodium was then eluted with water. Only milligram quantities of the metals were separated.

1-3. Ion-Exchange Separations

One of the first attempts to use ion-exchange methods for the separation of platinum metals was recorded by Stevenson et al. (21). Platinum, palladium, rhodium and iridium in solution were converted to their respective perchlorates and were passed through a Dowex-50 cation-exchange column. Palladium, rhodium and iridium were retained, while platinum passed through. Palladium was stripped with 0.05 to 0.5 M hydrochloric acid, then rhodium was eluted slowly with 2 M hydrochloric acid, and finally iridium with 4-6 M hydrochloric acid. No detailed results were provided however.

In an ion-exchange study of the separation of rhodium from platinum, palladium and iridium MacNevin and McKay (22) were able to obtain partial success in the separation of rhodium and iridium. The cationic hydrolyzed rhodium (III) chloride species and the anionic iridium (IV) chloride species were produced by first treating a mixture of rhodium (III) and iridium (IV) chlorides with a reducing agent until all the iridium was in the tervalent state. Strong sodium hydroxide solution was then added until precipitation of rhodium hydroxide was complete. The tervalent iridium hydroxide did not precipitate. The rhodium hydroxide was then dissolved in hydrochloric acid and the iridium reconverted to the quadrivalent chloride by bubbling chlorine through the solution. The solution was then adjusted to pH 2.8 and fed onto a Dowex-50 cation-exchange resin and the column washed with 10% chlorine

water. The iridium was washed through quantitatively while most of the rhodium was retained on the resin bed. The retained rhodium was then removed by elution with 6 M hydrochloric acid. Due to incomplete retention on the resin, the iridium was contaminated with rhodium. By a similar method Berman and McBryde (23) succeeded in separating rhodium from iridium by anion-exchange. The aged chloride solution of rhodium and iridium was treated with ammonium hydroxide to produce a yellow precipitate of rhodium, which was then just redissolved in 2 M hydrochloric acid. Passage of this solution through the anion-exchanger Amberlite IRA-400 resulted in the absorption of iridium and weakly retained rhodium which could be eluted with water. The iridium was stripped with 6 M hydrochloric acid. When fresh rhodium and iridium solutions were thus treated, the recovery of the two metals was a time-consuming process and the authors rejected the method.

Berg and Senn (24) used Dowex-50W exchanger to retain rhodium selectively in the presence of iridium. The solution of the metal chlorides was fumed to a moist residue with aqua regia; hydrochloric acid was added followed by solid thiourea. The cationic rhodium (III) - thiourea complex was retained at the top of the column as a sharp reddish-orange zone and was subsequently eluted by 6 M hydrochloric acid at 74°C. The first colorless fraction of the effluent contained the anionic iridium (IV) - thiourea complex which was eluted with 3 M hydrochloric acid. Both rhodium and iridium were determined spectrophotometrically, and the results indicated very acceptable accuracy for milligram quantities of the metal.

Cluett, Berman and McBryde (25) recorded an ion-exchange separation of rhodium from iridium which was comparable in effectiveness to that of

Berg and Senn (24). Amberlite IRA-400 anion-exchange resin was used to absorb the chloride solutions of rhodium in the tervalent state and iridium in the quadrivalent state; the latter was maintained by the addition of bromine water to the metal solution containing 2% sodium chloride in 0.1 M hydrochloric acid. Rhodium was eluted by the above solution, followed by iridium, with a solution of 5 M ammonium hydroxide and 1 M in ammonium chloride, then with either 6 M hydrochloric acid or 8 M nitric acid. The ammonium hydroxide reduced the iridium to the tervalent state and the ammonium chloride aided in its elution. The method was applied to weights of the order of 10 mg and a very acceptable accuracy was obtained. In a later paper (23) the authors rejected the former method of removing iridium, since the exchange required the use of large quantities of salts and acids which must be destroyed prior to the iridium determination. Also, losses of iridium in the feed solution indicated that attempts to use the procedure for smaller quantities of the metals would lead to relatively appreciable quantities of iridium remaining with the rhodium. The authors also recommended against their former use of the bromine oxidant, since for small amounts of the metals any procedure which would recover the rhodium quantitatively resulted in a loss of about 1% of the iridium present; and since the loss was more or less an absolute one, it thus became significant when microgram amounts of the metals were to be separated. The new procedure involved the passage of the samples in hydrochloric acid and sodium chloride through Amberlite IRA-400 resin in the chloride form which had been previously treated with cerium (IV) solution to counteract its reducing effect. The rhodium (III) was eluted with 0.8 M hydrochloric acid containing cerium (IV) ion and the iridium could

only be eluted by Soxhlet extracting the resin with 6 M hydrochloric acid. The method was applied with accuracy to samples of microgram amounts. Marks and Beamish (26) later extended the method to milligram amounts of the metals. Pshenitsyn et al. (27) approached the problem of separating rhodium and iridium by ion-exchange with the assumption that complex ions of rhodium and iridium of opposite charges could be obtained through a difference in rates of formation of amine complexes. Although both rhodium and tervalent iridium reacted with pyridine to form $[M(C_5H_5N)_4Cl_2]Cl$, the former reacted 65 times as fast as the latter, the iridium constituent remaining largely as the anion. Separations by the cation-exchanger KU-2 in the H^+ form were approximately quantitative for rhodium to iridium ratios of 10, 5 and 2. With both metals there was a slight absorption of the aquo complexes. In a later paper (28) the authors described a second method of separation which also involved the formation of pyridine complexes. In this case the tervalent iridium complex $[Ir(C_5H_5N)_2Cl_4]^-$ was absorbed quantitatively by an anion-exchanger while rhodium passed through as a cationic complex. In contrast to the first method, high ratios of iridium to rhodium could be used, ranging from 22 to 98. The amounts of each element were 0.1 - 10 mg.

For the separation of 0.1 - 1 mg of rhodium, iridium, palladium and platinum by partition chromatography on ion-exchange resins Moskvin and Preobrazhenskii (29) used the sulfostyrene cation-exchange resins KU-2X4 and KU-2X10. The chloro complexes of the metals were dissolved in an acetylacetone-hydrochloric acid solution saturated with chlorine and added to the exchanger, which was then washed successively with 0.1 M hydrochloric acid saturated with chlorine, 0.1 M hydrochloric acid, and acetylacetone saturated with 0.1 M hydrochloric

acid, thus removing the palladium. Platinum was removed by adding to the column a mixture of equal volumes of dibutyl ether saturated with gaseous hydrogen chloride and sulfur dioxide, (the latter to reduce the iridium to the tervalent state), and then by eluting with a 50% solution of n-butanol or tributyl phosphate in dibutyl ether pretreated with hydrochloric acid and sulfur dioxide. The column was then washed first with carbon tetrachloride and then with the tetrachloride saturated with chlorine to produce iridium (IV) which was then eluted with tributyl phosphate in carbon tetrachloride pretreated with hydrochloric acid and chlorine. Rhodium was then eluted with 4 M hydrochloric acid.

Blasius and Rexin (30) recorded a method for separating milligram quantities of rhodium and iridium with the chloride form of the weakly basic anion-exchange resin Amberlite IR-4B. The chloro complexes of the metals were converted to hydroxychloro complexes in 0.1 M sodium hydroxide and were fed onto the column. Rhodium was eluted with 1 M acetic acid and iridium with 1 M sodium hydroxide. The iridium fraction, however, contained traces of rhodium.

Kononov et al. (31) used a resin containing iminoacetic groups in a study of the separation of the complex chlorides of platinum (IV), palladium (II), rhodium (III), ruthenium (III), and iridium (III). The solution containing the metals was fed onto the resin and the column eluted with 0.1 M sodium hydroxide and 0.1 M sodium chloride which selectively desorbed platinum, iridium and ruthenium with palladium and rhodium being retained on the resin. When the resin was treated with thiourea, palladium and rhodium were removed. Although the method cannot be used for purifying platinum from iridium and ruthenium, it probably could be used to separate the two-component rhodium-

iridium system.

Iridium was separated from rhodium, platinum and palladium by cation-exchange in a paper reported by Sidorov and his co-workers (32). A solution containing the platinum metal chlorides was treated with perchloric acid to convert the metals to their perchlorates. The metals in a 2.5 M perchloric acid solution were fed onto a column of a strongly acidic cation-exchange resin. Platinum was eluted with 0.025 M hydrochloric acid, palladium and rhodium with 2 M hydrochloric acid and iridium with 6 M hydrochloric acid. Presumably this method could be applied to the separation of rhodium and iridium in a two-component system.

1-4. Solvent Extraction Separations

Wilson and Jacobs (33) used tributyl phosphate for the separation of iridium from rhodium. Two procedures had to be used, depending upon the rhodium concentration; one of which was used for 60-200 µg of rhodium and the other for 20 µg or less. The maximum iridium concentration for both methods was 1 mg. The procedures required adjustment to 6-7 M hydrochloric acid, treatment of the sample with hydrogen peroxide to oxidize the iridium to the quadrivalent state and addition of tributyl phosphate, previously equilibrated with hydrochloric acid. Two extractions were recommended. No determination of the iridium in the organic phase was made.

Faye and Inman (34) extended the Wilson and Jacobs separation by extracting iridium from the tributyl phosphate-hexane phase with hydrobromic acid and determining it with tin (II) bromide. Extractions from the iridium-tributyl phosphate-hexane phase could also be accomplished by hydrochloric or perchloric acids. Various ratios of the metals in the microgram and milligram range were separated.

A method for separating 37-185 μg of rhodium from 1-33 mg of iridium was described by Ryan (35). In 3 to 9 M hydrochloric acid solutions the amber-to-red complex of bivalent rhodium with 5,5-dimethyl-2-mercapto-thiazole was formed after reduction of tervalent rhodium with stannous chloride. Rhodium was quantitatively separated from iridium by chloroform extraction of this product. The complex, after removal of the chloroform, was dissolved in dilute hydrochloric acid and the rhodium determined spectrophotometrically. A similar separation was achieved using chromous chloride as a reducing agent for solutions that had been fumed with sulfuric acid.

Beamish and Tertipis (36) developed a simple and rapid extraction method for the separation of 10-100 μg of rhodium from 7.5-73.8 μg of iridium which involved the formation of the tin (II) bromide complex in a perchloric-hydrobromic acid medium and its extraction with isopentyl alcohol. Single extractions were sufficient except for larger amounts of rhodium. The use of 200 μg of rhodium resulted in 5 μg or more remaining in the aqueous phase, in which case a second extraction was necessary. The aqueous phase containing the iridum was heated to 99°C and the absorbance of tin (II) bromide complex measured at 403 mμ. The absorbance of the rhodium complex in the organic phase was measured directly.

For the isolation of 0.1 mg of rhodium in the presence of up to 100 mg of iridium, Fedorenko and Filimonova (37) used piperidine dithiocarbamate to precipitate rhodium selectively from nitrite solutions of rhodium and iridium. The yellow flakes were then extracted repeatedly with dichloroethane. A fifteen to sixtyfold excess of the carbamate, based on the rhodium content, increased the coextraction of iridium from 0.02 to 0.10 mg. The extract was evaporated, and the residue was treated with a

solution of hydrogen peroxide and nitric acid to decompose organic matter. Rhodium was then converted to the chloride. The proposed procedure can be considered a method of separation only insofar as the final determination of rhodium is not affected adversely by the presence of small amounts of iridium. The authors used tin (II) chloride and polarographic methods for determination.

In a separation study of iridium from rhodium (as well as other two-component platinum metal systems) Busev and Akimov (38) used diantipyrylpropylmethane in dichloroethane to extract iridium in the form of its chloro complex from a 1 M hydrochloric acid solution containing milligram amounts of both metals. It was found that 5-6% of the rhodium present was also extracted. In order to achieve complete separation, the iridium and the small amount of rhodium in the organic phase were stripped with 25% nitric acid, the metals reconverted to their chloro complexes and the extraction procedure repeated. The entire procedure was repeated a large number of times before rhodium-free iridium was obtained.

Fedorenko and Ivanova (39) studied separately the extraction of iridium (III), (IV) and rhodium (III) with tri-n-octylamine from hydrochloric acid solutions in which they were present in the form of their complex chlorides. The extraction study was performed over a hydrochloric acid concentration range from 1 to 12 M. The tervalent ions extracted only to a slight extent and iridium (IV) was extracted with a high distribution coefficient. However, the iridium (IV) was partially reduced on contact with the organic phase and had to be maintained in the quadrivalent state by bubbling chlorine through the solution. Although calculations of the separation factor for the pair, rhodium (III)-iridium (IV), indicated the possibility of a separation in 6 M hydrochloric acid, no experimental results were given.

For the separation of platinum, palladium and iridium from rhodium, Borbat et al. (40) treated the chloride solutions of the metals with triisobutylamine hydrochloride and extracted with chloroform. The extractions were made from 0.3 M hydrochloric acid. Platinum, palladium and iridium could be removed from the organic phase by washing with 0.1 M hydrochloric acid. Presumably this method could be applied to separations of rhodium from iridium in a two-component system.

2. PURPOSE OF STUDY

From the discussion presented above it can be seen that a variety of procedures has been used to separate rhodium and iridium either when present together as a simple two-component system or as part of a multi-component system of the platinum group metals. Many of the procedures, however, have limitations or disadvantages.

The precipitation methods of separation are generally time-consuming and are usually limited to certain restricted quantities of the metals (9,10,11). The separation of rhodium and iridium by paper chromatography (16) is tedious and restricted to micro amounts. The use of column chromatography for the separation of the two metals has been successful in many cases but has been generally restricted to certain quantities (17,18,19). Ion-exchange methods have been complicated by the fact that aged solutions of rhodium and iridium behave in a different manner than fresh ones (23). Some cation-exchange procedures require the formation of noble metal organic complexes prior to the separation (24,27,28), while most anion-exchange separations require either excess amounts of salts and acids (25) or Soxhlet extraction techniques (23) to remove the iridium from the resin. Most of the successful solvent extraction separations of rhodium and iridium have been

applied to restricted amounts of the metals (35,36,38).

The purpose of the present study was to develop more simplified procedures for separating microgram and milligram amounts of rhodium and iridium in a two-component system. The procedures developed involved the separation of the chloro complexes of rhodium (III) and iridium (IV) by anion-exchange and by solvent extraction with a high molecular weight amine.

3. REACTIONS OF RHODIUM AND IRIDIUM CHLORO COMPLEXES IN DILUTE ACID SOLUTION

Rhodium and iridium form the following stable chloro complexes: $RhCl_6^{3-}$, $IrCl_6^{3-}$ and $IrCl_6^{2-}$. Anion-exchange separation studies have shown that aged dilute hydrochloric acid solutions of these complexes behaved differently than freshly prepared solutions (23). This behaviour was attributed by Berman and McBryde to partial hydrolysis of the rhodium and iridium chloro complexes on ageing.

Studies of the reactions of the chloro complexes of rhodium and iridium in dilute acid have indicated that these reactions are complex and that a large number of products are possible.

Robb and Harris (53) investigated the kinetics of the equilibration

$$RhCl_6^{3-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh(OH_2)Cl_5^{2-} + Cl^-$$

using spectrophotometric techniques. The reaction was studied in perchloric acid-hydrochloric acid media of a constant ionic strength ($\mu = 4$). The aquation of $RhCl_6^{3+}$ and the anation of $Rh(OH_2)Cl_5^{2-}$ were examined independently and it was shown that either process is described by the rate law

$$-d(RhCl_6^{3-})/dt = k_1(RhCl_6^{3-}) - k_{-1}(Rh(OH_2)Cl_5^{2-})(Cl^-)$$

Values of k_1 and k_{-1} were obtained at several temperatures by both the aquation and anation procedures, and good agreement was obtained between the two sets of data. At 25°C, $k_1 = 0.11\ min^{-1}$ and $k_{-1} = 0.013\ M^{-1}min^{-1}$. The reaction was essentially independent of H^+ concentration up to 4 M but appeared to be quite sensitive to the size of cations present in the solution. The substitution of NaCl for hydrochloric acid greatly decelerated the reaction, whereas LiCl had little or no effect. No explanation for this phenomenon was given. From the obtained values of the rate constants for aquation and anation, it was shown that on a equimolar basis, chloride-for-water substitution in $Rh(OH_2)Cl_5^{2-}$ was considerably more facile than water-for-chloride in $RhCl_6^{3-}$. The comparable second-order rate constants at 25°C (allowing for the statistical advantage of 6 in the latter reaction) were $k_{-1} = 0.013\ M^{-1}min^{-1}$ and $k_1(cor.) = k_1/6 \times 50 = 0.0004\ M^{-1}min^{-1}$.

Similar studies were also made on the equilibrium

$$Rh(OH_2)Cl_5^{2-} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Rh(OH_2)_2Cl_4^- + Cl^-$$

by Robb and de V. Steyn (54) and values for k_2 and k_{-2} were obtained at several temperatures in perchloric-hydrochloric acid media of ionic strength $\mu = 4.00$. At 30°C, $k_2 = 8.0 \times 10^{-5}\ sec^{-1}$ and $k_{-2} = 6.4 \times 10^{-4}\ M^{-1}sec^{-1}$.

Bridges and Chang (55) also produced the second aquation product, $Rh(OH_2)_2Cl_4^-$, by heating $Na_3RhCl_6 \cdot 12H_2O$ in dilute perchloric acid at 100°C. The diaquotetrachlororhodium anion was present in the form of cis and trans isomers. Along with anionic species, neutral and cationic species were also isolated (presumably the third and fourth aquation products of $RhCl_6^{3-}$, $Rh(OH_2)_3Cl_3$ and $Rh(OH_2)_4Cl_2^+$ (56)).

Poulsen and Garner (57) have shown that the iridium (III) chloro complex is not as labile as the rhodium (III) species in the reversible

reaction

$$IrCl_6^{3-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ir(OH_2)Cl_5^{2-} + Cl^-$$

The rate constants obtained for the reaction at 50°C (1.2 M Cl^-, 2.5 M H^+ and μ = 3.7, NaCl + $NaClO_4$) were $k_1 = 2.53 \times 10^{-4} sec^{-1}$ and $k_{-1} = 11.7 \times 10^{-5}$ $M^{-1}sec^{-1}$. Studies were similarly made on the equilibrium

$$Ir(OH_2)Cl_5^{2-} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ir(OH_2)_2Cl_4^- + Cl^-$$

by Chang and Garner (58) and values of $k_2 = 1.26 \times 10^{-5} sec^{-1}$ (2.5 M H^+ and μ = 3.7, $NaClO_4$) and $k_{-2} = 6.7 \times 10^{-5} M^{-1} sec^{-1}$ (0.3-0.9M Cl^-, 2.5 M H^+ and μ = 3.7 NaCl + $NaClO_4$) were obtained at 50°C. Preliminary measurements were also made of the aquation

$$Ir(OH_2)_2Cl_4^- + H_2O \xrightarrow{k_3} Ir(OH_2)_3Cl_3 + Cl^-$$

and an estimated value of $k_3 = 2.9 \times 10^{-6} sec^{-1}$ at 50°C in 2.5 M $HClO_4$ - 1.2 M $NaClO_4$ was obtained.

A study of the equilibrium

$$IrCl_6^{2-} + H_2O \rightleftharpoons Ir(OH_2)Cl_5^- + Cl^-$$

by Martinez (59) has shown that the iridium (IV) chloro complex is not as labile as the iridium (III) species. The aquation rate constant for $IrCl_6^{2-}$ at 50°C in 0.5 - 2.8 M $HClO_4$ (μ = 1.32 - 4.91, $NaClO_4$) was $1.01 \times 10^{-6} sec^{-1}$ as compared to $1.85 \times 10^{-4} sec^{-1}$ for the $IrCl_6^{3-}$ aquation rate constant at 50°C in 2.5 M $HClO_4$ (μ = 3.7, $NaClO_4$) as found by Poulson and Garner (57). Poulson and Garner have suggested that the aquation rate constant obtained by Martinez may only be an upper limit due to the possible catalysis of the

aquation of $IrCl_6^{2-}$ by the formation of an $IrCl_6^{3-}$ intermediate in Cl_2-free solutions through the reaction sequence

$$IrCl_6^{2-} + Cl^- \rightleftarrows IrCl_6^{3-} + \tfrac{1}{2}Cl_2$$

$$IrCl_6^{3-} + H_2O \rightleftarrows Ir(OH_2)Cl_5^{2-} + Cl^-$$

$$Ir(OH_2)Cl_5^{2-} + \tfrac{1}{2}Cl_2 \rightleftarrows Ir(OH_2)Cl_5^{-} + Cl^-$$

As can be seen from the above discussion, a large variety of aquation products are possible in aged, dilute acid solutions of the chloro complexes of rhodium and iridium. The presence of these products in solutions containing the chloro complexes of rhodium (III) and iridium (IV) could complicate the separation of these two metals. In order to ensure that the rhodium and iridium used in the separation studies presented on the following pages were initially in the form of their tervalent and quadrivalent chloro complexes respectively, the samples (which were prepared from the respective stock chloro complex solutions) were pre-treated with hot aqua regia and hot concentrated hydrochloric acid before use. The aqua regia, a strong oxidizing agent, ensured that the iridium was in the quadrivalent state. The high oxidation potential of the $IrCl_6^{2-}/IrCl_6^{3-}$ system (1.02 V (60)) necessitated the use of a strong oxidizing agent.

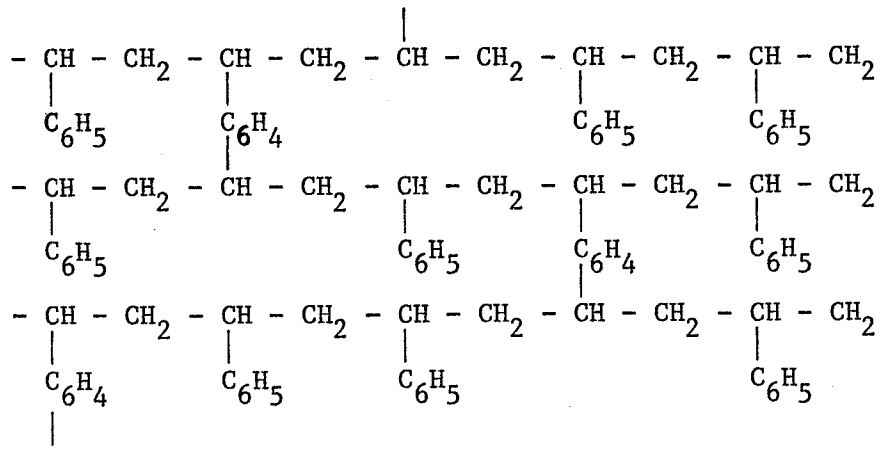
II | THE SEPARATION OF RHODIUM AND IRIDIUM BY ANION-EXCHANGE

1. INTRODUCTION

1-1. Ion-Exchange Resins

An ion-exchange resin is a crosslinked polymer containing ionized or ionizable groups such as $-SO_3H$, $-SO_3Na$, $-COOH$, $-NH_3Cl$, or $-NMe_3Cl$. The crosslinkages are necessary due to the hydrophilic nature of the ionogenic groups. These groups tend to dissolve when the resin is brought into contact with water, and since they are attached to a polymer, they tend to draw the whole polymer into solution. To prevent dissolution, the structure of the ion-exchange resin is held together with the crosslinkages thus forming a three-dimensional network polymer. The network structure suppresses the tendency of the resin to dissolve, with the result that the resin swells, but remains undissolved in water. The amount of swelling depends upon the degree of crosslinkage: the greater the degree of crosslinkage, the lesser the swelling of the resin. Resins with a large degree of crosslinage (e.g. 24%) have a dense impenetrable structure which makes it impossible for ions from the external solution to diffuse through such resins. Therefore, in this case, exchange can only occur at the surface of the resin particles, hence the specific exchange capacity of these resins is small. Ion-exchange resins with smaller degrees of crosslinkage absorb water and swell when placed in contact with water or an aqueous solution. Exchanging ions are able to diffuse through the internal water and thus all ionogenic groups of the resin can undergo exchange. The specific exchange capacity in this case may be large. Ion-exchange resins with very small degrees of crosslinkage absorb so much water that they behave like particles of soft jelly and are ill-suited for most ion-exchange reactions.

Almost all of the analytically important ion-exchange resins of the present day are synthesized by addition polymerization. The sulfonic acid form of the cationic strongly acidic type of resin is produced by the sulfonation of a copolymer of styrene with divinylbenzene (DVB). If a mixture of styrene and DVB is warmed with a catalyst such as benzoyl peroxide, the molecules of styrene form linear polymeric chains while the molecules of DVB become crosslinks between the chains.



The relative amount of DVB can be varied and commercial resins with varying degrees of crosslinking are available. The degree of crosslinking is defined in terms of the percentage of DVB added during polymerization. Most commercial resins are made from copolymers of styrene, ethylvinylbenzene and DVB, but in all respects, in this context the resins behave as styrene-DVB resins. Most commercial resins generally contain crosslinkages ranging from 1 to 12% DVB.

Small spheres of the polysturene resin are produced by emulsifying a mixture of styrene, DVB and catalyst in an aqueous solution of an emulsifying agent and heating the mixture to about 90°C. The average size of the spheres (called pearls or beads) depends on the concentration and nature of

the emulsifying agent and the vigor of the stirring.

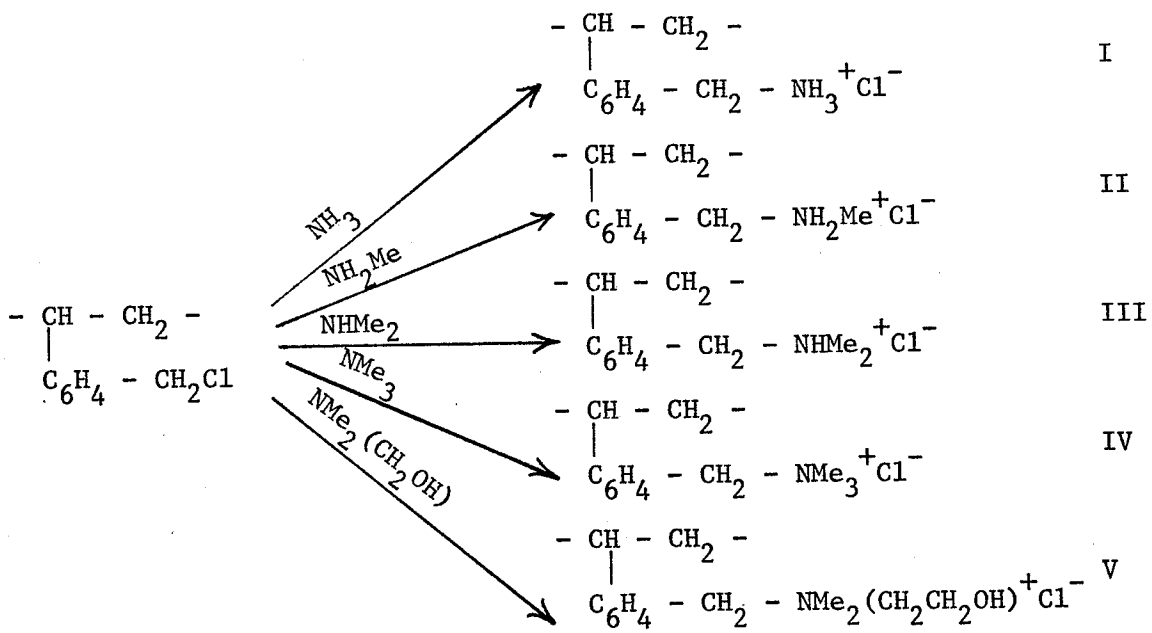
The final step in the manufacture of the strongly acidic cation-exchange resin is the sulfonation of the beads of crosslinked polystyrene. The sulfonation is made with sulfuric acid, and, on the average, about one sulfonic acid group per benzene ring may be present in commercial products of this type.

Carboxylic cation-exchange resins (a weakly acidic type) are made by the copolymerization of methacrylic acid or its esters with DVB. As in the case of polystyrene resins, the DVB serves to provide the crosslinks.

The starting point for the manufacture of anion-exchange resins is beads of crosslinked polystyrene. These beads are swollen in chloromethyl methyl ether and then reacted with the ether by the addition of a suitable catalyst such as anhydrous stannic chloride or zinc chloride. The reaction (1) causes the substitution of the

$$\begin{array}{l} -\mathrm{CH}-\mathrm{CH_2}- \\ \quad | \\ \quad \mathrm{C_6H_5} \end{array} + \mathrm{MeOCH_2Cl} \rightarrow \begin{array}{l} -\mathrm{CH}-\mathrm{CH_2}- \\ \quad | \\ \quad \mathrm{C_6H_4-CH_2Cl} \end{array} + \mathrm{MeOH} \qquad (1)$$

chloromethyl group in about 56% of the benzene rings. The beads of chloromethylated resin are then swollen in a suitable solvent and heated with excess ammonia or an aliphatic amine. All of the chloromethyl groups react according to the equations



In each case, the product is an anion-exchange resin in the chloride form. The first three of the above with primary, secondary or tertiary nitrogen atoms, are weakly basic resins. The fourth and fifth with quaternary nitrogens are strongly basic resins. They are sometimes designated as strong-base resins of types 1 and 2 respectively with the type 2 being slightly less basic than the type 1. The free-base forms of these resins can be produced by treatment of the chloride form with sodium hydroxide.

With macroporous resins, two types of pores exist. The basic structure consists of a highly crosslinked styrene divinylbenzene copolymer matrix with small pores (micropores). This dense and rigid matrix is permeated by larger pores (macropores). The dimensions of the macropores far exceed those of the low-crosslinked resins, such as those containing only 1% divinylbenzene crosslinkage. Thus, in comparison with a nominally 8% crosslinked resin, the kinetics of exchange with these resins are relatively rapid for large molecules which can enter the macropores but are relatively slow for small ions capable

of entering the micropores. These resins can be obtained in either the strongly acidic or strongly basic form.

The four fundamental types of ion-exchange materials available are essentially analogous to common acids or bases and undergo similar reactions. The primary difference, however, is that the ion-exchange materials are insoluble and actually remove constituents from solution while the common acids and bases form water-soluble salts with the constituents present in solution. These four types and their typical reactions are listed below. R_z represents the non-mobile part of the ion-exchange resin.

I Strongly Acidic Cation-Exchangers - Analogous to Sulfuric Acid.

$$R_zSO_3H + NaCl \rightleftarrows R_zSO_3Na + HCl \quad (1)$$

$$2\ R_zSO_3Na + CaCl_2 \rightleftarrows (R_zSO_3)_2Ca + 2NaCl \quad (2)$$

II Weakly Acidic Cation-Exchangers - Analogous to Acetic Acid.

$$R_zCO_2H + NaOH \rightleftarrows R_zCO_2Na + H_2O \quad (3)$$

$$2\ R_zCO_2Na + CaCl_2 \rightleftarrows (R_zCO_2)_2Ca + 2\ NaCl \quad (4)$$

III Strongly Basic Anion-Exchange Resin - Analogous to Sodium Hydroxide.

$$R_zNR_3OH + NaCl \rightleftarrows R_zNR_3Cl + NaOH \quad (5)$$

$$2\ R_zNR_3Cl + H_2SO_4 \rightleftarrows (R_zNR_3)_2SO_4 + 2HCl \quad (6)$$

IV Weakly Basic Anion-Exchange Resin - Analogous to Ammonium Hydroxide.

$$R_zNH_2 + HCl \rightleftarrows R_zNH_3Cl \quad (7)$$

$$R_zNH_3OH + HCl \rightleftarrows R_zNH_3Cl + H_2O \quad (8)$$

Reactions (1) and (5) represent the salt-splitting properties of strong-acid cation-exchange resins and strong-base anion-exchange resins. The weakly acidic and weakly basic exchangers do not undergo these reactions nor will they remove extremely weak bases or acids.

1-2. The Separation of Rhodium and Iridium by Anion-Exchange

All of the stable chloro complexes of rhodium and iridium ($RhCl_6^{3-}$, $IrCl_6^{3-}$ and $IrCl_6^{2-}$) are completely absorbed by a strongly basic anion-exchange resin. The chlororhodate and chloroiridate (III) species are not strongly retained by the resin (41) and can be easily eluted from the exchanger with dilute hydrochloric acid solution. However, the chloroiridate (IV) complex exhibits a strong affinity for the resin over a hydrochloric acid concentration range from 0.1 to 12 molar.

The strong affinity of the chloroiridate (IV) species for a strongly basic anion-exchange resin provides a method for the separation of rhodium and iridium from dilute hydrochloric acid solutions: The rhodium species can be eluted from the resin with dilute hydrochloric acid while the quadrivalent iridium complex can be retained in the resin matrix. However, one is faced with the problem of removing the iridium from the resin following the separation. In the separation by anion-exchange of iridium and platinum as their chloro complexes, Blasius and Rexin (30) eluted the quadrivalent iridium species with an iron (II) sulfate-7 M hydrochloric acid solution. The iron (II) sulfate reduced the iridium to the tervalent state which is easier to remove from the resin. No data, however, was given to indicate the efficiency of the iridium recovery. This method is also complicated by the fact that one must remove the iron from the iridium solution after elution.

To date, the best anion-exchange method of separating and recovering rhodium and iridium in both the microgram and milligram range is the method used by Berman and McBryde (23). A hydrochloric acid solution (0.8 M) containing the chlororhodate (III) and the chloroiridate (IV) species was fed onto a resin column of the chloride form of the strongly basic anion-exchange resin Amberlite IRA-400 (which had been ground to a mesh size of 70-100 mesh). The resin bed had been previously treated with cerium (IV) solution to counteract the reducing effect of the resin on the iridium (IV) species. The rhodium was eluted with 0.8 M hydrochloric acid containing the cerium (IV) ion and the iridium subsequently recovered by removing the resin from the column and Soxhlet extracting it with 6 M hydrochloric acid for one-half hour. The quantitative elution of the iridium was attributed to the increase in temperature which enhanced the reducing properties of the resin, causing the reduction of the iridium most intimately bound in the resin matrix and making it available for leaching with the hot acid solution. Marks and Beamish (26) later modified the method slightly by eliminating the need for grinding the resin by increasing the depth of the resin bed used and increasing the extraction time to one hour.

Although favorable separational results were obtained by Berman and McBryde, their method has not found wide acceptance, presumably because of the complicated method required for the removal of iridium from the resin. It was felt by this author that if some simpler method for eluting the iridium could be developed, the method would find wider application. In the present work, heated columns and acid reservoirs were used for the elution of iridium from the resin. It was believed that this method would best

simulate the conditions involved in the Soxhlet extraction of the resin and that this would simplify the iridium recovery by eliminating the need for removing the resin from the column and extracting it.

2. EXPERIMENTAL

2-1. Apparatus and Reagents

Baird-Atomic Model 530 gamma-spectrometer and Model 810C well scintillation detector with a 4.4 cm diameter by 5.1 cm thick NaI(Tl) well crystal (Baird-Atomic, Bedford, Massachusetts).

Perkin-Elmer Model 306 atomic absorption spectrophotometer with a 10 cm single slot burner and Varian rhodium and iridium lamps.

Unicam Model SP800B spectrophotometer.

Jacketed ion-exchange columns and acid reservoirs (see Fig. 1). The actual exchange columns were 0.5 cm in internal diameter and about 12 cm in height.

Haake Model FJ thermostated circulating bath (Haake Gebruder, Berlin, West Germany).

Lauda Model K2R thermostated circulating bath (Messgerate-Werk Lauda, West Germany.

An iridium solution containing 1 mg/ml iridium in 0.1 M hydrochloric acid was prepared from sodium chloroiridate ($Na_2IrCl_6 \cdot 6H_2O$) and a solution containing 1 mg/ml rhodium in 1.2 M hydrochloric acid was prepared from sodium chlororhodate ($Na_3RhCl_6 \cdot 12H_2O$), both obtained from Johnson Matthey and Mallory Limited (Toronto). Dilutions with the same acid concentration were made accordingly from the stock solutions.

Iridium-192 was obtained from Amersham-Searle Limited, Don Mills, Ontario and diluted prior to use.

All reagents used in this study were reagent grade. Water purified by double-distillation followed by double-de-ionization was used for the required dilutions and washings.

The principal resin used was an analytical grade of Amberlite IRA-400 (Rohm and Haas, Philadelphia, Pennsylvania), a strongly basic anion-exchange resin with 8% divinylbenzene crosslinkage. The resin had a wet particle size of 16-50 mesh and a listed wet exchange capacity of 1.2 meq/ml. The resin was obtained in the chloride form and this form was ensured by stirring the resin for several hours with a large excess of 3 M hydrochloric acid. At the same time the resin was freed of small bits of foreign matter which usually floated on the surface of the supernatant liquid. The resin was then Soxhlet extracted for several hours with 6 M hydrochloric acid to remove any possible contaminating ions and any easily dissolved organic matter. A glass column with a fritted glass disc on the bottom was used to contain the resin during extraction. The resin was stored in a solution of 3 M hydrochloric acid after extraction.

Two other resins were used in cursory studies:

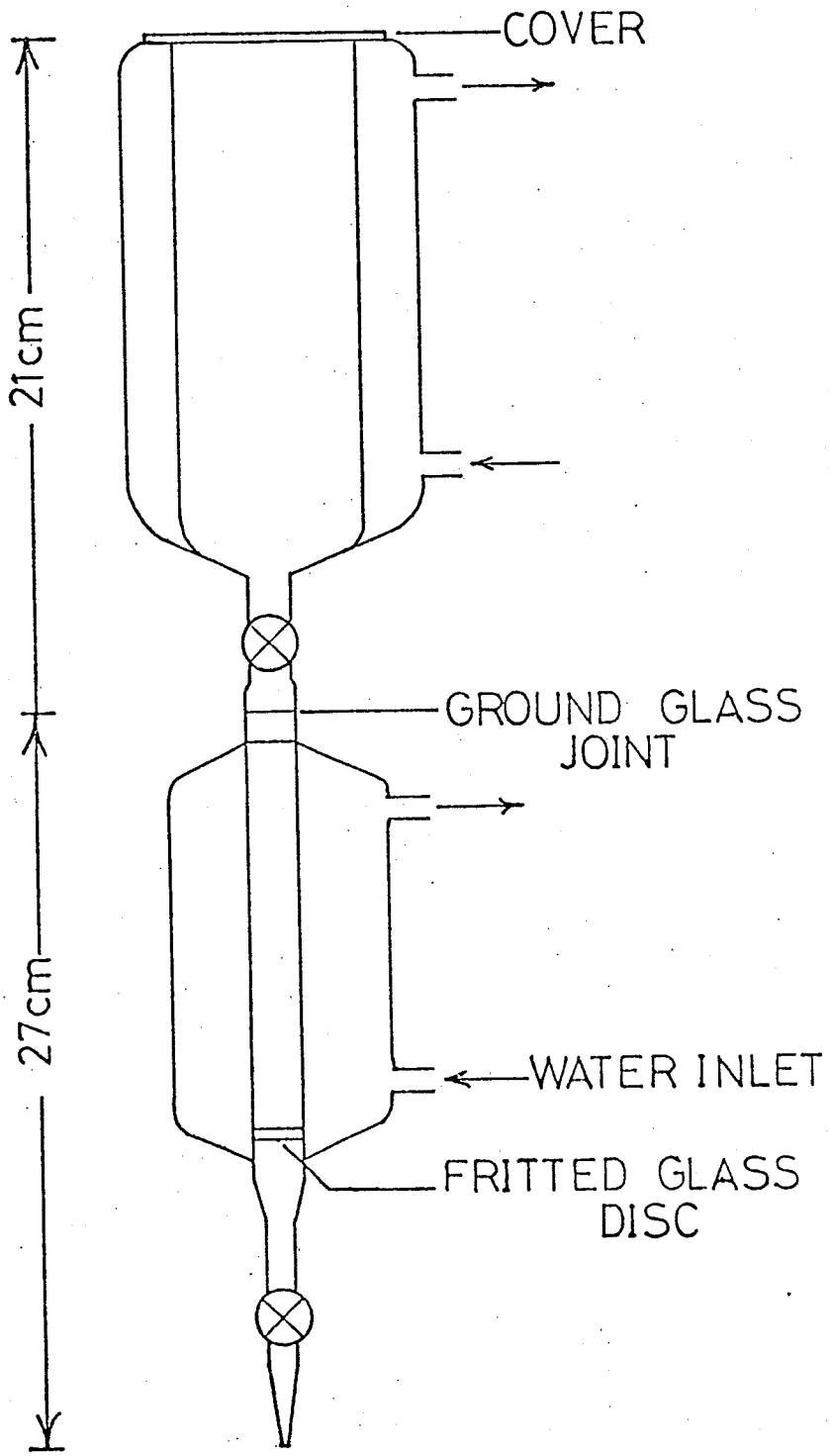
Amberlite IRA-401 (Rohm and Haas, Philadelphia, Pennsylvania), a strongly basic anion-exchange resin in the chloride form with 4% divinylbenzene crosslinkage. The resin had a wet particle size of 16-50 mesh and a listed wet exchange capacity of 0.8 meq/ml.

AGMP-1 (Bio-Rad Laboratories, Richmond, California), a macroporous, analytical grade, strongly basic anion-exchange resin in the chloride form. The wet resin particle size was 20-50 mesh and the listed wet exchange capacity was 1.0 meq/ml.

These resins were conditioned in the same manner as above.

In all of the following studies a resin bed 3 cm in length and 0.5 cm in diameter was employed except when noted otherwise.

Fig. 1. Jacketed Exchange Column and Acid Reservoir (Not to Scale).


COVER
21cm
GROUND GLASS JOINT
27cm
WATER INLET
FRITTED GLASS DISC

2-2. Radioactive Tracer Studies of Iridium Elution with Hydrochloric Acid under Various Conditions

In these preliminary studies to develop an improved method for the recovery of iridium from a strongly basic anion-exchange resin, a radioactive tracer, iridium-192 was used. The use of the tracer gave a relatively rapid method for studying the absorption of iridium into the resin matrix and its subsequent removal. These studies only involved iridium since the rhodium complex was easily eluted from the resin with dilute hydrochloric acid. Unless otherwise noted, Amberlite IRA-400 resin was used in all these studies.

2-2a. Sample Preparation

Samples containing the required amounts of iridium were prepared from stock iridium solutions containing sufficient iridium-192 tracer to yield a counting rate of 78×10^3 counts per minute. The sample solutions were pipetted into 30 ml beakers containing 6 mg of sodium chloride and were treated in the following manner:

Several milliliters of concentrated hydrochloric acid were added to each of the beakers and the solutions were evaporated to dryness on a steam bath. Two milliliters of aqua regia (1:3 HNO_3:HCl) was added to each dry residue. The beakers were covered with regular watch glasses and replaced on the steam bath. When the action of the aqua regia ceased, the undersides of the watch glasses were rinsed with a few milliliters of concentrated hydrochloric acid and were replaced by evaporating cover glasses. The solutions were allowed to evaporate to dryness and the residues were treated twice more with aqua regia. The aqua regia treatments were required to

ensure that the iridium was in the quadrivalent state. Following the aqua regia treatments, the samples were thrice-treated with 2 ml of concentrated hydrochloric acid and evaporated to dryness to remove any nitrates. Before being fed onto the resin beds, the samples were treated with a few drops of concentrated hydrochloric acid and were evaporated to dryness.

2-2b. Counting Technique

The test tube containing the sample was placed in the well of the scintillation counter and the activity of the sample was counted five successive times, each for a period of 100 sec and the average activity determined. The average sample activity was then corrected for background activity which was determined by taking the average of fifteen successive 100 sec counting periods. All counting was done with the lid of the well-counter closed.

2-2c. Absorption of Iridium

The fact that the resin Amberlite IRA-400 acts as a mild reducing agent towards chloroiridate (IV) (as was demonstrated by Berman and McBryde (23)) necessitated the presence of an oxidizing agent since the tervalent iridium complex does not have as strong an affinity for the resin in dilute hydrochloride acid solutions as does the quadrivalent complex (41). Without the oxidizing agent some of the iridium would be eluted with the rhodium fraction. A solution containing cerium (IV) as an oxidant in 0.8 M hydrochloric acid was used as an eluting agent for rhodium as suggested by Berman and McBryde. The use of cerium (IV) limits the acid concentration permissable to the range of 0.5 to 1 M. In acid solution below this range the cerium salts hydrolyze, while at higher concentrations, the chloride ion is

oxidized to chlorine. The oxidizing cerium solution contained 2 ml of 0.1 M cerium (IV) sulfate per 100 ml of 0.8 M hydrochloric acid.

A column containing a resin bed 3 cm deep by 0.5 cm in diameter was washed with 20 ml of water and then rinsed with 20 ml of the cerium solution. The iridium sample containing 500 μg of iridium plus radioactive iridium-192 was dissolved in 2 ml of 0.8 M hydrochloric acid and was fed onto the resin bed with a dropper. The beaker was twice-rinsed with approximately 2 ml of 0.8 M hydrochloric acid and the washings added to the column. A flow rate of approximately 25-30 ml/hr was used during the feeding of the sample onto the resin. The column was then eluted at a flow rate of approximately 50 ml/hr with an additional 250 ml of cerium solution to simulate the removal of rhodium from the resin. This volume of cerium solution was required for the elution of the largest amount of rhodium used in the actual rhodium and iridium separation studies discussed later in this work. The effluent from the column was collected in 15 ml aliquots in test tubes and the activities of the solutions determined to check for iridium leakage from the resin.

It was noted that immediately upon loading of the sample onto the resin a dark brown band 3-4 mm wide formed at the top of the resin bed. The dark brown color is indicative of the quadrivalent iridium chloro complex.

After the passage of the cerium solution through the column, the resin was removed by inverting the column over a 15 ml test tube and forcing out the resin with pressurized water introduced through the column outlet. The activity in the resin was determined in the same manner as for the effluent.

The percentage of iridium lost during the sample loading and elution of "rhodium" was determined by the relation:

$$\% \text{ iridium lost} = \frac{W}{W + I} \times 100$$

where W = total activity recovered in feed effluent and "rhodium fraction",

I = activity on the resin.

The iridium loss from the resin for a 500 μg sample with a passage of 250 ml of cerium solution through the column is shown in Table I. The majority of the iridium leakage occurred in the first 45 ml of effluent. The use of a deeper resin bed (4 cm) and increased cerium (IV) concentration (twice the normal concentration) did not decrease the iridium loss. An iridium leakage of 0.48% was obtained with the passage of 250 ml of cerium solution. The use of cerium solution instead of hydrochloric acid to dissolve the sample and to wash the beaker failed to reduce the iridium leakage from the resin. The iridium loss was 0.52%, slightly higher than that obtained by using only hydrochloric acid. Additional treatments of the iridium sample with aqua regia (a total of 5 treatments) and hydrochloric acid prior to feeding it onto the resin yielded an iridium loss of 0.50%. It would appear that the slight iridium loss from the resin was due either to difficulty in obtaining all of the iridium in the form of the chloroiridate (IV) complex or to a slight reduction of the iridium (IV) by the resin in spite of the presence of an oxidizing agent. Since no further decrease in the iridium leakage could be obtained, all further studies were performed using a cerium (IV) oxidizing solution with a concentration of 2 ml of 0.1 M ceric sulfate per 100 ml of 0.8 M hydrochloric acid and a resin bed 3 cm deep.

2-2d. Effect of Temperature

To develop a method for eluting iridium from the resin with hot acid and heated resin columns, it was felt that a study of the effect of various temperatures on the iridium removal from the resin was necessary in order to determine the optimum eluting temperature.

Table I

Iridium Loss from Resin on Elution
with Cerium Solution

Total Volume of Effluent (ml)	Total Percentage of Iridium Lost
15	0.066
30	0.12
45	0.17
60	0.20
75	0.23
90	0.27
105	0.29
120	0.32
135	0.35
150	0.37
165	0.38
180	0.40
195	0.41
210	0.42
225	0.43
240	0.44
250	0.45

The resin beds were treated as in the above study with 20 ml of water followed by 20 ml of cerium solution. The samples containing 500 μg of iridium in 0.8 M hydrochloric acid were fed onto the resin beds as before at approximately 25-30 ml/hr. The resin beds were eluted with a further 50 ml of cerium solution at a flow rate of 50 ml/hr. Only 50 ml of cerium solution was used in order to simplify the study since it had already been determined that the majority of the iridium leakage occurred in the first 45 ml of effluent. The feed and cerium wash effluent activities were determined in this study only to ascertain whether or not the sample was essentially in the chloroiridate (IV) form. The primary concern of this study was to determine the effect of acid and column temperature on the efficiency of iridium elution from the resin.

After the passage of the cerium solution through the columns, the resin beds were washed free of the cerium solution with 15 ml of 0.8 M hydrochloric acid. The column flows were then stopped and 105 ml of 6 M hydrochloric acid was added to each acid reservoir. The resin beds and acid solution were then heated to the required temperatures by circulating thermostated water through the column and reservoir jackets. A warm-up period of one-half hour was used. (A preliminary study had shown that the acid reached a temperature of 95°C within 20 minutes of heating.) The resin beds were then eluted with the acid at a flow rate of approximately 40 ml/hr and the effluents collected in 15 ml aliquots in test tubes. The activities of the effluent samples were determined as before. After the passage of the acid through the columns the resin beds were removed and the residual activity on them determined. The percentage of iridium removed from the resin was obtained by the following relation:

$$\% \text{ Iridium Removed from Resin} = \frac{A}{R + A} \times 100$$

where R = residual activity on resin after 6 M hydrochloric acid elution,

A = total activity recovered from 6 M hydrochloric acid elution of resin.

The results of the temperature study are shown in Table II. The results show that for a fixed volume of eluting acid, the percentage of iridium removed from the resin increased with increasing temperature. Presumably with the higher temperature the reducing ability of the resin increased and the hot acid was more able to leach out the reduced iridium. However, even at 95°C the 6 M hydrochloric acid was not able to remove all of the iridium from the resin. It was noted that during the elution at 95°C, some small bubbles appeared in the resin bed, probably due to dissolved gases in the hydrochloric acid solution. Elutions at temperatures greater than 95°C were not attempted due to the probability of greater bubble formation in the resin bed at higher temperatures. In any event, the increased temperature probably would not have resulted in any substantial improvement in the removal of iridium by this method, since an increase of 30° from 65° to 95° only improved the iridium removal by 1.9%.

From the results of this temperature study it was decided to carry out all further hydrochloric acid elutions of iridium from IRA-400 resin at a temperature of 95°C.

It was noted in this study that as the eluting acid was passed through the resin the dark brown band due to the chloroiridate (IV) complex at the top of the resin bed slowly disappeared. The first 30 ml of elution effluent which contained the major portion of the eluted iridium was pale yellow in color, whereas later fractions were essentially colorless - probably due to the

Table II

Effect of Temperature on Iridium Elution

Elution Temperature ^{o}C	Percentage of Iridium Removed
25	60.4[a] ± 0.2
50	88.6 ± 0.2
65	92.8 ± 0.1
95	94.7 ± 0.1

[a] mean value ± mean deviation for 2 samples

dilute iridium concentration. The pale yellow color instead of the more intense yellow-brown of the chloroiridate (IV) suggested that the iridium had been reduced to the almost colorless chloroiridate (III) by the resin.

In an attempt to identify the eluted iridium species, a spectrophotometric study was performed using non-radioactive iridium. A sample solution of $IrCl_6^{2-}$ containing 1000 μg of iridium was fed onto a resin column and eluted at 95°C with 6 M hydrochloric acid in the same manner as the above procedure. The first 15 ml aliquot of elution effluent was analyzed spectrophotometrically using 4 cm quartz cells and 6 M hydrochloric acid (which had been passed through a resin bed at 95°C) as a blank. (The solutions had first been de-oxygenated by bubbling nitrogen through them for 10 minutes. Dissolved oxygen apparently interferes with the absorption spectrum of iridium (III) complexes (57).) The ultraviolet-visible spectrum showed two weak absorption bands (approximately 0.1 absorbance) in the area of 350-360 mμ and 410-420 mμ . Although the $IrCl_6^{3-}$ species has absorption peaks at 356 mμ and 415 mμ(62), the broad, weak absorbances obtained in this study made it impossible to conclusively assign the absorption bands to the iridium (III) chloro complex. In an attempt to identify this species, the effluent sample was treated with chlorine in order to oxidize the tervalent iridium to the quadrivalent species (the quadrivalent iridium chloro complex having approximately 40 times the absorbance of the corresponding tervalent species (62,63)). Both the effluent sample and the blank were saturated with chlorine. The effluent sample turned to a yellow-brown color on treatment. The visible absorption spectrum of the oxidized eluted iridium species is shown in Fig. 2. One centimeter cells were used in the study. The spectrum was quite similar to the spectrum obtained with 1 cm cells of a solution of

$IrCl_6^{2-}$ containing 1000 μg of iridium in 15 ml of 0.8 M hydrochloric acid shown in Fig. 3. The $IrCl_6^{2-}$ sample (which had been treated with aqua regia and hydrochloric acid as described above) exhibited a visible absorption spectrum in agreement with the one obtained by Jorgensen for $IrCl_6^{2-}$ (63). Absorption maxima were obtained at 417, 433, 487 and 576 mμ as compared to maxima at 414, 431, 489 and 576 mμ obtained by Jorgensen. Although the spectrum of the oxidized eluted iridium species was quite similar to the spectrum of $IrCl_6^{2-}$, the absence of a peak at 576 mμ and the more pronounced peak at 435 mμ indicated that not all of the oxidized eluted iridium was in the form of $IrCl_6^{2-}$. This in turn meant that a small proportion of the unoxidized eluted iridium was in some form other than $IrCl_6^{3-}$. At the time of these preliminary studies, no reason could be given for the presence of more than one iridium species on elution.

2-2e. Effect of Acid Concentration

From the results of the preliminary attempts to remove the iridium from the resin by heating the ion-exchange column and eluting acid, it was decided to determine if increased acid concentration - namely 9 or 12 M (concentrated) hydrochloric acid would improve the iridium recovery.

The procedure followed was the same as described in the temperature study. It was found that with 9 M hydrochloric acid, after the passage of approximately 50 ml of eluting acid, small bubbles appeared in the resin bed which in time expanded and caused difficulty in maintaining a uniform flow rate. When attempts were made to use concentrated hydrochloric acid as an eluting agent, the acid bubbled so excessively that the elution study with this acid concentration had to be abandoned. Heating of the concentrated acid before use decreased the amount of bubbling, but did not eliminate it.

Fig. 2. Visible Absorption Spectrum of Oxidized Eluted Iridium Solution.

Eluant: 6 M Hydrochloric Acid at $95^{o}C$

Approximate Iridium Concentration: 2.6×10^{-4} M.

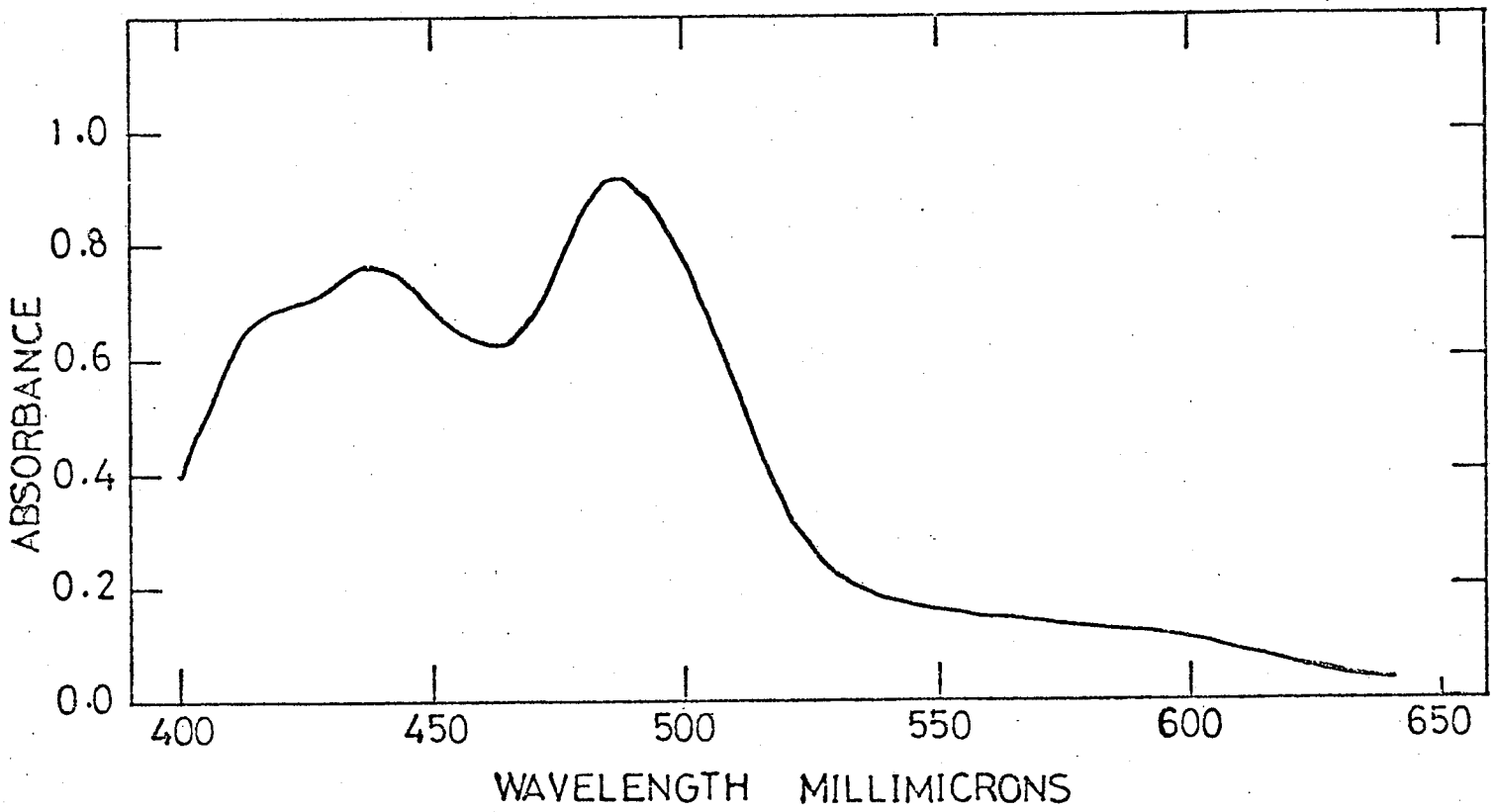
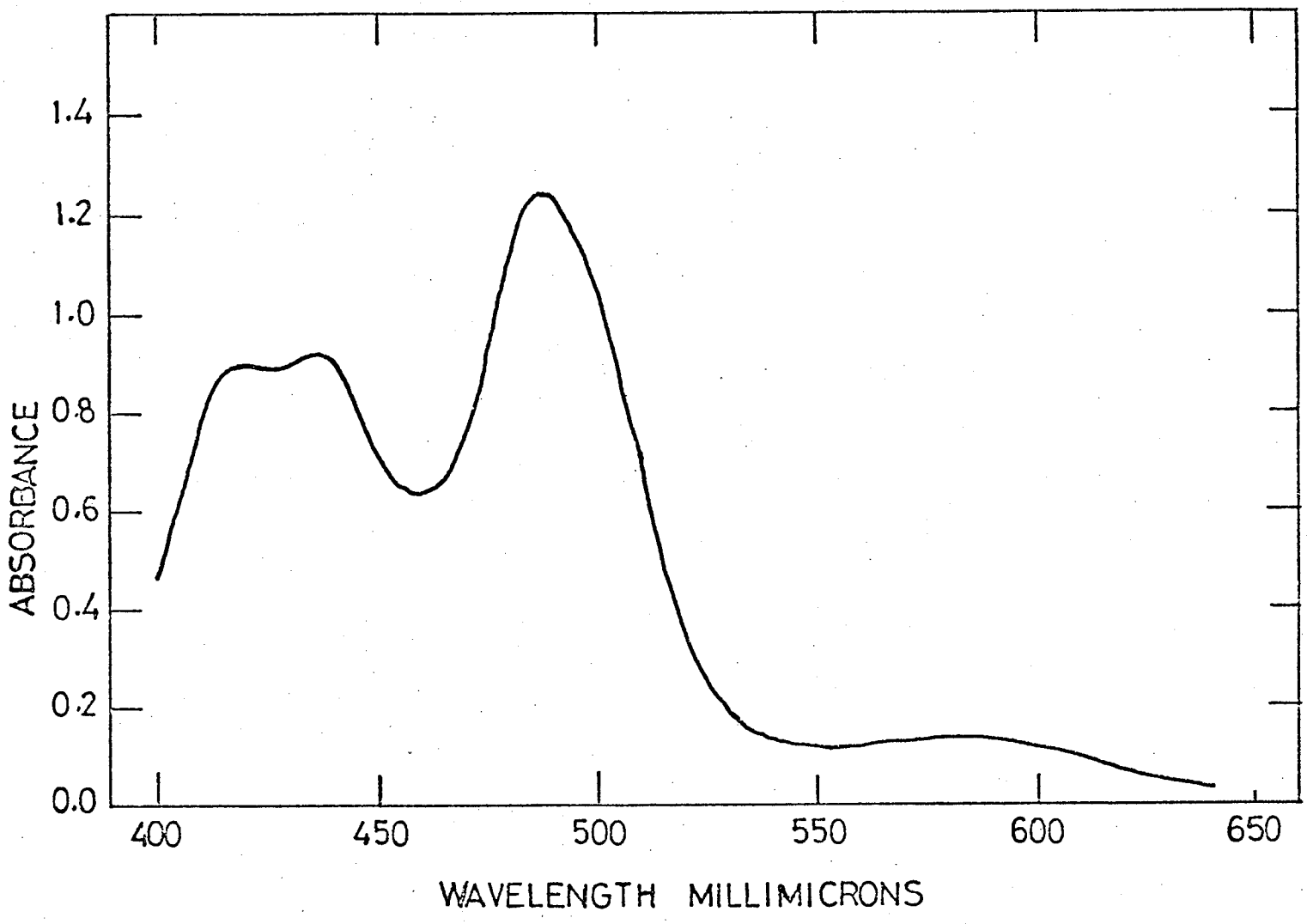

1.0
0.8
0.6
0.4
0.2
0.0
ABSORBANCE
400
450
500
550
600
650
WAVELENGTH MILLIMICRONS

Fig. 3. Visible Absorption Spectrum of Standard Iridium (IV) Chloro Complex Solution.

Iridium Concentration: 3.5×10^{-4} M in 0.8 M Hydrochloric Acid.


ABSORBANCE
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
650
WAVELENGTH MILLIMICRONS

The result of the elution study with 9 M hydrochloric acid showed that slightly more iridium was removed from the resin than with 6 M acid (96.8% vs 94.7% removed). A graphical comparison of the elution efficiency of 6 and 9 M hydrochloric acid is shown in Fig. 4. It will be noted that the percentage of iridium removed from the resin with 6 M acid gradually approached the percentage obtained with 9 M acid. Perhaps with more acid the recovery with 6 M acid would have been the same as with the higher acid concentration. The curve for the elution with 9 M hydrochloric acid was essentially horizontal after the passage of 75 ml of eluent through the column which suggested that elution with more than 105 ml of acid probably would not improve the iridium recovery from the resin.

2-2f. Effect of Reducing Agent

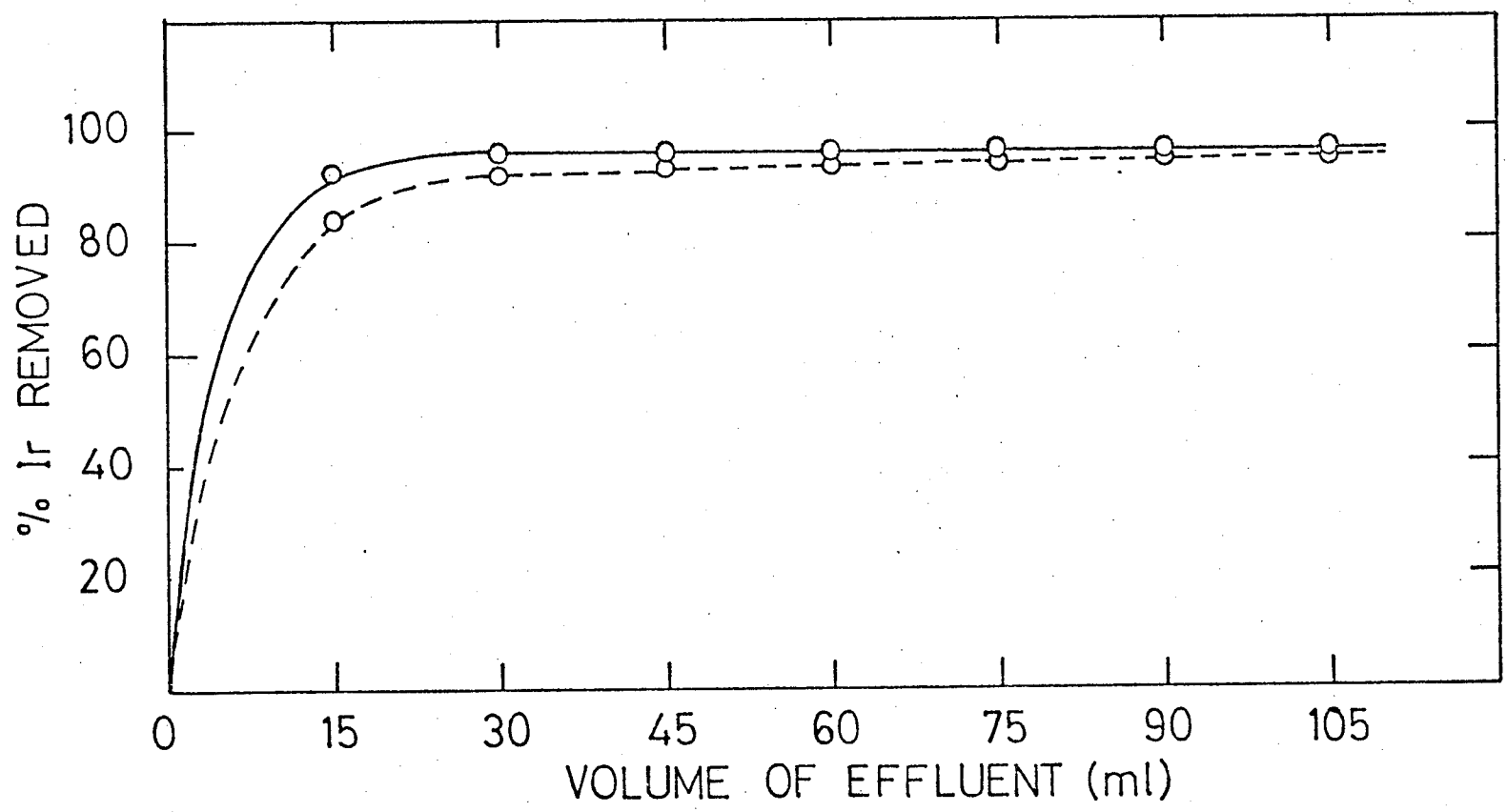
The affinity of chloroiridate (III) for the exchanger is small in hydrochloric acid solutions more concentrated than 1 M (41). Attempts had been made by Berman and McBryde (23) to reduce the quadrivalent iridium complex in the resin matrix with either hydroxylamine hydrochloride or hydrazine hydrochloride and to elute the tervalent species with hydrochloric acid. Reductions of the absorbed chloroiridate (IV) complex with 1 and 4% solutions of the reducing agents followed by elution at room temperature with a dilute solution of hydrochloric acid yielded recoveries from 88 to 96% for 454 μg iridium samples. The recoveries did not seem to depend upon the concentration of the reducing agent or the hydrochloric acid eluant. The incomplete recoveries were ascribed to the fact that some of the iridium was not readily available for reduction.

From the results of Berman and McBryde's work it was felt that

Fig. 4. Effect of Hydrochloric Acid Concentration on Elution of 500 µg of Iridium from Resin at 95°C.

——— 9 M Hydrochloric Acid.

----- 6 M Hydrochloric Acid


% Ir REMOVED
100
80
60
40
20
0
15
30
45
60
75
90
105
VOLUME OF EFFLUENT (ml)

perhaps a better iridium recovery could be obtained by passing a hot acidic solution of the reducing agent through the heated resin column. It was believed that at elevated temperatures the reduction of the chloroiridate (IV) species by both the reducing agent and the resin itself would be enhanced and that the hot hydrochloric acid would be more efficient in leaching the reduced iridium from the resin.

The same procedure for feeding a 500 μg iridium sample solution onto the resin and eluting with 50 ml of cerium solution as described previously was followed. The resin was washed free of the cerium solution with 15 ml of 0.8 M hydrochloric acid and after a half hour warm-up period, eluted with 105 ml of 4% hydroxylamine hydrochloride in 9 M hydrochloric acid at 95°C. A flow rate of approximately 40 ml/hr was used and the activities of the effluent samples were determined in the usual manner. It was noted that as soon as the solution containing the reducing agent contacted the resin, the dark brown chloroiridate (IV) band disappeared, suggesting that reduction had taken place. However, after determining the residual activity on the resin, it was found that only 82.1% of the iridium had been removed. The low iridium recovery may be due to the possible reaction of the iridium (III) chloro complex and the hydroxylamine hydrochloride at the higher temperature to form a complex which was even more difficult to remove from the resin than the original chloroiridate (IV) species. It is known that the hydroxylamine hydrochloride can serve as a ligand to form complexes such as $Zn(NH_2OH)_2Cl_3$ (44). Perhaps the iridium (III) species had formed similar anionic complexes by the exchange of chlorine atoms (which have been shown to be labile (57,58)) by hydroxylamine groups.

A spectrophotometric study of the eluted iridium species was performed using a non-radioactive $IrCl_6^{2-}$ solution containing 1000 μg iridium. The

iridium on the resin bed was reduced in the manner described above and the first 15 ml of elution effluent analyzed spectrophotometrically using 4 cm quartz cells and a 9 M hydrochloric acid solution (containing 4% hydroxylamine) which had been passed through a resin bed at 95°C as a blank. The solutions had first been de-oxygenated with nitrogen. The ultraviolet-visible spectrum showed two weak absorption bands (approximately 0.08 absorbance for both bands) in the area of 350-360 mμ and 410-420 mμ which suggested that the eluted iridium was in the form of the tervalent chloro complex. Upon oxidation with chlorine, the effluent solution turned yellow-brown and yielded the visible absorption spectrum shown in Fig. 5 with 1 cm quartz cells. The spectrum was similar to the spectrum of $IrCl_6^{2-}$ (see Fig. 3, p. 42) but the more pronounced peak at 435 mμ and the absence of a peak at 576 mμ indicated that not all of the oxidized eluted iridium was in the form of the quadrivalent chloro complex. This in turn meant that a small portion of the unoxidized eluted iridium was in some form other than $IrCl_6^{3-}$.

2-2g. Effect of Thiourea as a Complexing Agent

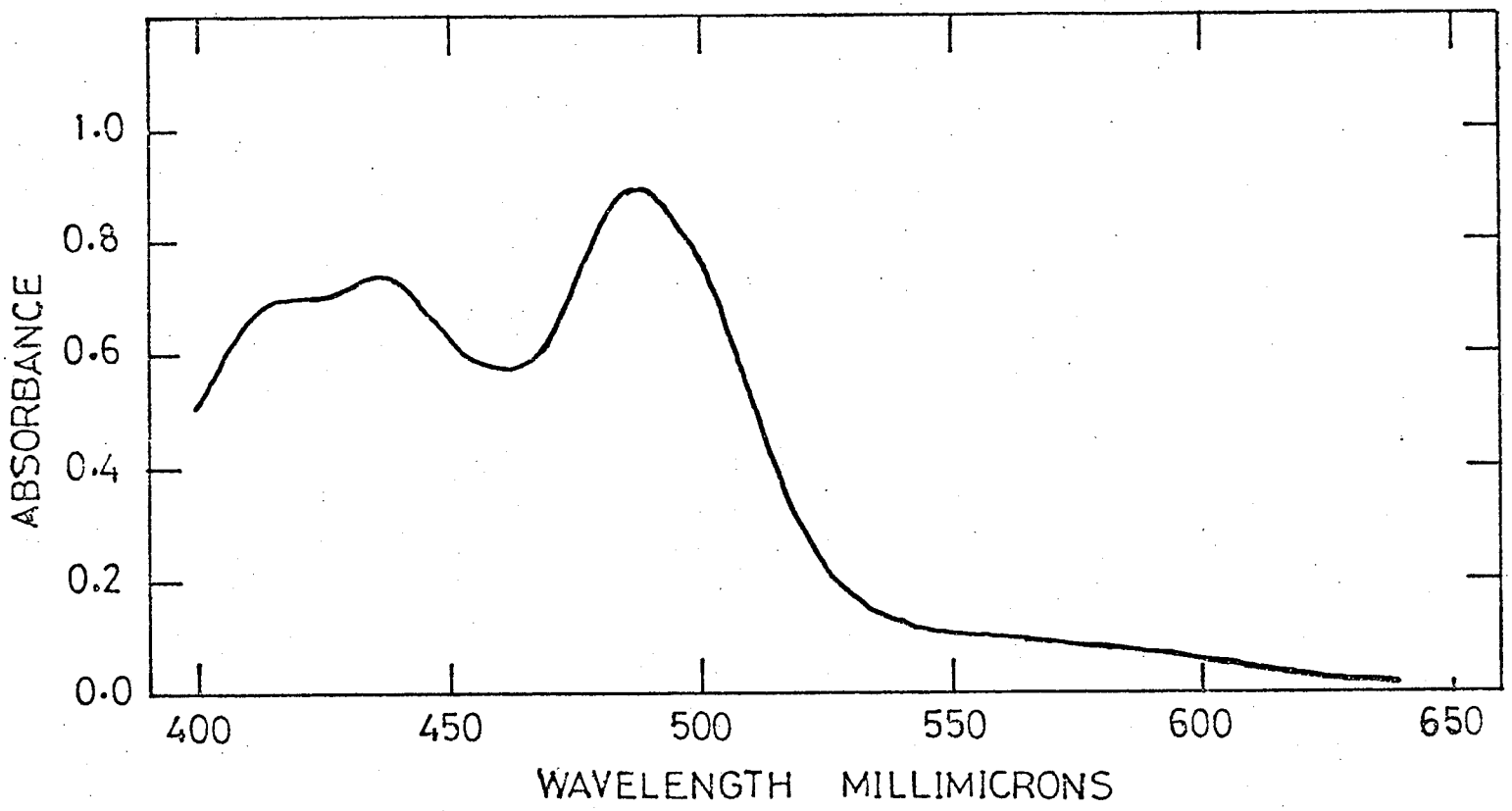
The fact that the chloroiridate (IV) species forms an anionic complex with thiourea (24) suggested that perhaps the chloroiridate (IV) absorbed into the resin matrix could be complexed by passing a hot acid solution containing thiourea through the heated resin column. It was hoped that the thiourea-iridium complex would be easier to elute from the resin than the chloroiridate (IV) species.

A 500 μg iridium sample was fed onto a resin bed in the usual manner and the resin bed washed free of cerium (IV) with hydrochloric acid. After a one-half hour warm-up period, the resin was eluted with 105 ml of a 1%

Fig. 5. Visible Absorption Spectrum of Oxidized Eluted Iridium Solution.

Eluant: 9 M Hydrochloric Acid Containing 4% Hydroxylamine Hydrochloride at 95°C.

Approximate Iridium Concentration: 2.5×10^{-4} M.


1.0
0.8
0.6
0.4
0.2
0.0
ABSORBANCE
400
450
500
550
600
650
WAVELENGTH MILLIMICRONS

thiourea solution in 9 M hydrochloric acid at 95°C using a flow rate of approximately 30 ml/hr. The activity of the effluent was determined in the usual manner. The dark brown iridium absorption band disappeared as soon as the thiourea solution made contact with it, indicating either that the colorless iridium-thiourea complex was formed, or that the iridium had been simply reduced. Determination of the residual activity on the resin showed that 95.8% of the iridium was removed. This was one percent less than that removed with only 9 M hydrochloric acid heated to 95°C. It would appear that the introduction of thiourea to the column produced an iridium-thiourea complex which was more difficult to remove from the resin than the original chloroiridate (IV) complex.

In a spectrophotometric study of the elution of iridium by the above procedure using a non-radioactive $IrCl_6^{2-}$ solution containing 1000 µg iridium, the first 15 ml aliquot of effluent showed slight absorption peaks (approximately 0.03 absorbance units for a 4 cm path length) in the area of 350-360 mµ and 410-420 mµ. This indicated that not all of the eluted iridium was in the form of the iridium-thiourea complex and that some of it was in the tervalent state. When the iridium solution was oxidized with chlorine to produce a yellow solution, it was found that the color was not stable with time and quickly faded. This suggested that the iridium in the tervalent state was oxidized by the chlorine and had then formed the colorless iridium (IV)-thiourea complex.

2-2h. Effect of Zinc Chloride on Iridium Elution

Berman and McBryde (41) had used the affinity of zinc chloride toward anion-exchangers to recover the platinum (IV) chloro complex from IRA-

400 resin. Quantitative recoveries of platinum had been achieved by passing a 9 M hydrochloric acid solution containing 15% (w/v) zinc chloride through a resin column surrounded with a hot-water jacket at 95°C. It was felt that perhaps the high affinity of zinc chloride for the resin could be used in the present work to facilitate the removal of iridium from the resin.

A 500 μg iridium sample was eluted in the usual manner at 40 ml/hr with a 105 ml solution of 9 M hydrochloric acid containing 15% (w/v) zinc chloride at 95°C and the residual activity in the resin determined. It was found that the percentage of iridium removed from the resin was slightly less than that obtained with only 9 M hydrochloric acid (95.3 vs 96.8%). The presence of zinc chloride had actually decreased the iridium recovery slightly in some manner.

In a spectrophotometric study of the eluted iridium species employing the above elution procedure using a non-radioactive $IrCl_6^{2-}$ solution containing 1000 μg iridium, the first 15 ml aliquot of oxidized effluent exhibited the visible absorption spectrum shown in Fig. 6 with 1 cm cells. The spectrum had the same appearance as that obtained from the oxidized effluent of a 1000 μg iridium sample eluted with 6 M hydrochloric acid (Fig. 2, p. 41). The more pronounced peak at 435 mμ and the absence of a peak at 576 mμ indicated that a small portion of the oxidized eluted iridium was not in the form of the quadrivalent chloro complex. This in turn meant that not all of the unoxidized eluted iridium was in the form of the tervalent chloro complex.

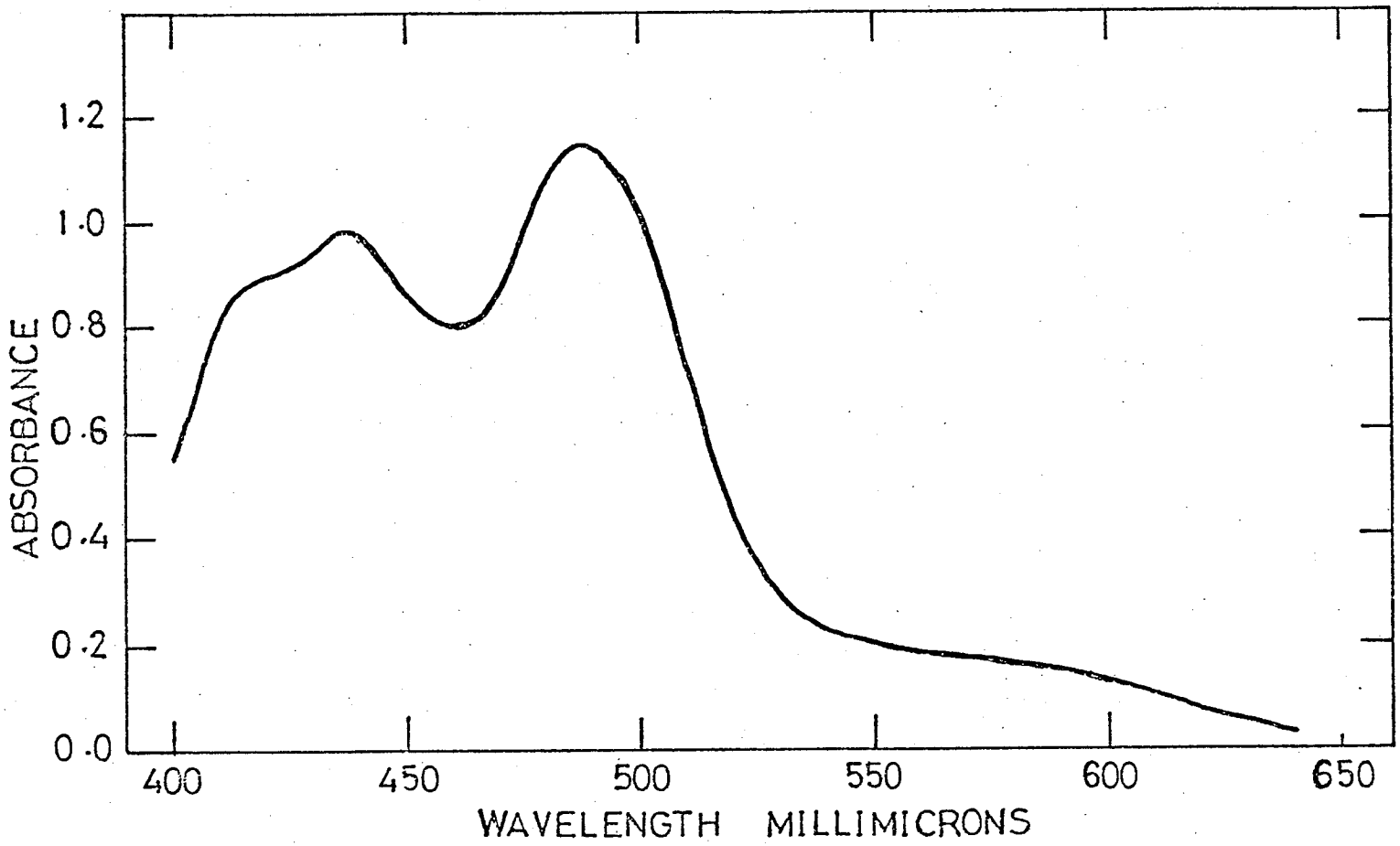
2-2i. Effect of Resin Crosslinkage and Porosity

Cursory studies on the recovery of iridium from the resin were done with Amberlite IRA-401, a strongly basic anion-exchange resin with 4% divinylbenzene crosslinkage, and Bio-Rad AGMP1, a macroporous anion-exchange resin.

Fig. 6. Visible Absorption Spectrum of Oxidized Eluted Iridium Solution.

Eluant: 15% Zinc Chloride in 9 M Hydrochloric Acid at 95°C.

Approximate Iridium Concentration: 3.2×10^{-4} M.


ABSORBANCE
1·2
1·0
0·8
0·6
0·4
0·2
0·0
400
450
500
550
600
650
WAVELENGTH MILLIMICRONS

The IRA-401 resin was used to determine whether the decreased crosslinkage (4% vs 8% for IRA-400) had any effect on iridium recovery. The macroporous resin was used in the hope that increased resin porosity would enable the eluting acid to leach out the iridium more easily. In both cases the usual 500 μg iridium samples were eluted at 40 ml/hr with 6 M hydrochloric acid heated to 95°C in the usual manner. In both studies the results were not as good as those obtained with IRA-400 resin under the same conditions as shown in Table III.

2-3. Radioactive Tracer Studies of Iridium Elution with Nitric Acid under Various Conditions

The study of iridium elution with 9 M hydrochloric acid at 95°C showed that a maximum of about 97% of the iridium could be removed from the resin. It did not appear that any better iridium recoveries could be accomplished with hydrochloric acid. In addition, there was the problem of bubble formation in the resin bed at this temperature. Since it is known that polystyrene resins are susceptible to attack by hot nitric acid (42), it was felt that perhaps hot nitric acid would be able to leach out the iridium found deep in the resin matrix which could not be leached out with hydrochloric acid. Also, it was hoped that the greater affinity of the nitrate ion as compared to the chloride ion for the resin (43) would make it easier to displace the iridium from the exchange sites in the resin matrix and improve its recovery. The iridium sample preparation and counting technique employed were the same as mentioned in the hydrochloric acid elution studies. Amberlite IRA-400 resin was used in all the studies.

2-3a. Effect of Acid Concentration

Samples containing 500 μg of iridium were fed onto the columns in

Table III

Effect of Resin Crosslinkage and Porosity on Elution of Iridium with 6 M Hydrochloric Acid at 95°C

Resin	Resin Characteristic	Percentage of Iridium Removed
IRA-400	8% divinylbenzene crosslinkage	94.7
IRA-401	4% divinylbenzene crosslinkage	89.5
AGMP1	Macroporosity	91.2

the usual manner and were eluted with 50 ml of cerium solution. The resin beds were then washed with 15 ml of 0.8 M hydrochloric acid to remove the ceric ion followed by 10 ml of water to remove the hydrochloric acid. After a one-half hour warm-up period, the resin beds were eluted at a flow rate of approximately 40 ml/hr with 105 ml of either 8 or 12 M nitric acid at 95°C. The effluents from the columns were collected in 15 ml aliquots and the activities determined. After passage of the acid, the resin activities were checked.

The percentage of iridium removed after the passage of 105 ml of acid was the same for both 8 and 12 M nitric acid - 97.6%. However, as is shown in Fig. 7, the more concentrated acid was more efficient in removing the iridium from the resin. The recovery of iridium was approximately 1% better with nitric acid than with the same volume of 9 M hydrochloric acid.

In a spectrophotometric study of the elution of iridium by the above procedure using a non-radioactive $IrCl_6^{2-}$ solution containing 1000 μg of iridium, the first 15 ml aliquot of effluent obtained by elution with 12 M nitric acid yielded the visible absorption spectrum shown in Fig. 8 with 1 cm quartz cells. Comparison with the spectrum for $IrCl_6^{2-}$ (Fig. 3, p. 42) indicated that most of the iridium was eluted as the quadrivalent chloro complex. However, the more pronounced peak at 435 mμ and the absence of a peak at 576 mμ suggested that a small portion of the eluted iridium was in another form.

2-3b. Effect of Temperature

During the elution with nitric acid at 95°C, bubbles formed in the resin bed in the same manner as in the hydrochloric acid studies. An iridium elution study was performed at 74°C with the expectation that a decrease in

Fig. 7. Effect of Nitric Acid Concentration on Elution of 500 µg of Iridium from Resin at 95°C.

——— 12 M Nitric Acid.

----- 8 M Nitric Acid.

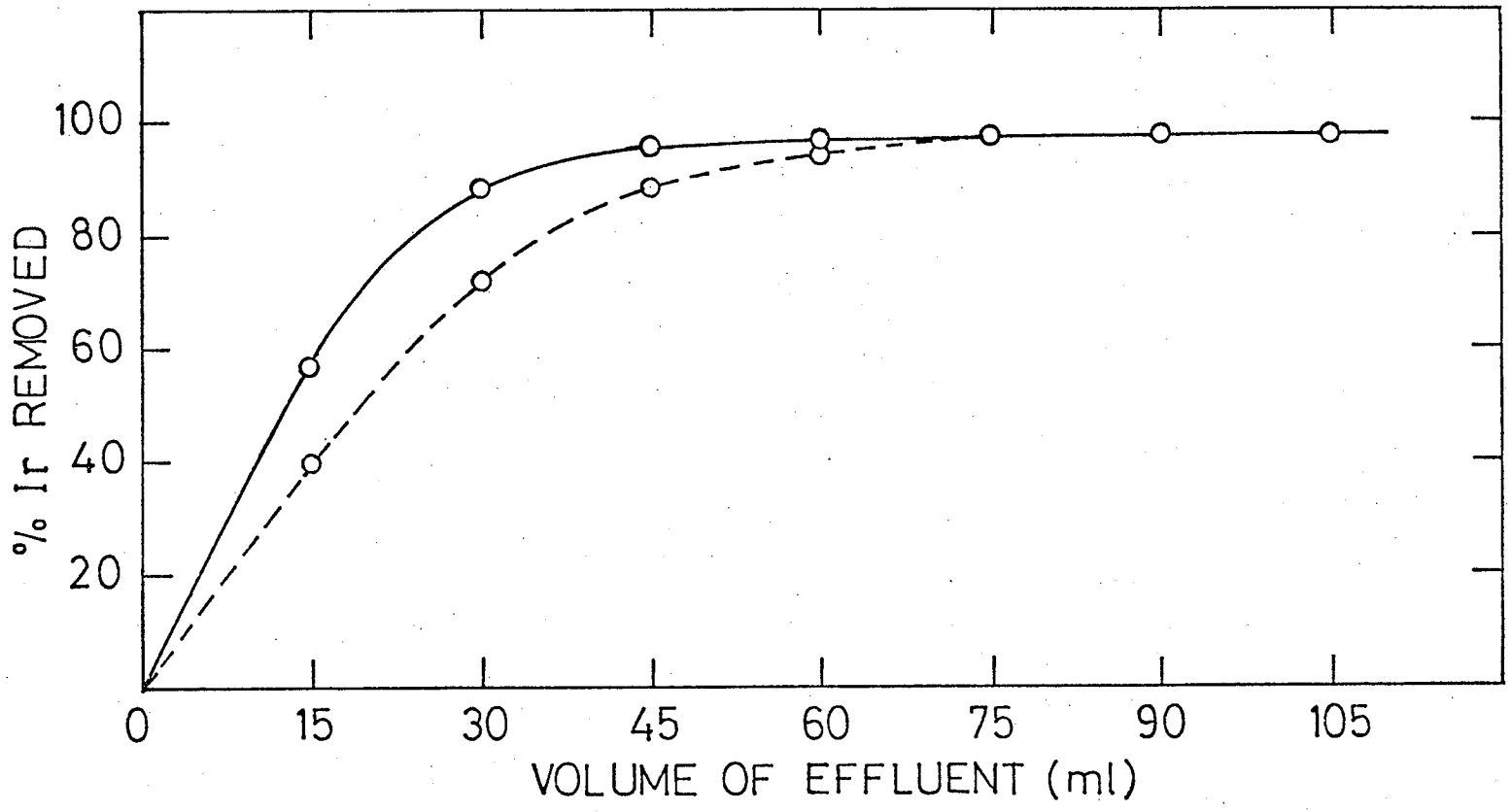
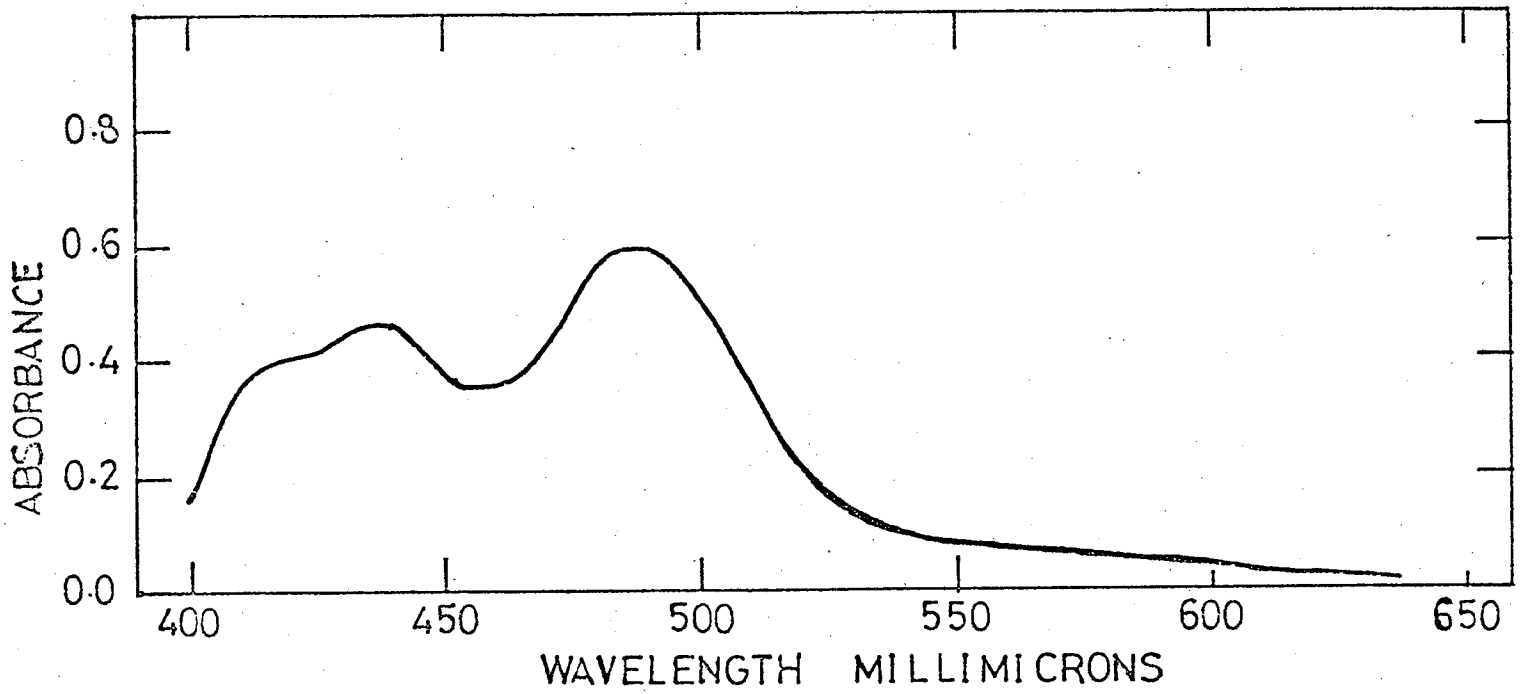

100
80
60
40
20
% Ir REMOVED
0
15
30
45
60
75
90
105
VOLUME OF EFFLUENT (ml)

Fig. 8. Visible Absorption Spectrum of Eluted Iridium Solution.

Eluant: 12 M Nitric Acid at 95°C.

Approximate Iridium Concentration: 1.7×10^{-4} M.


0·8
0·6
0·4
0·2
0·0
ABSORBANCE
400
450
500
550
600
650
WAVELENGTH MILLIMICRONS

temperature would eliminate the problem of bubble formation. A volume of 105 ml of 12 M nitric acid was used to remove the 500 µg iridium sample from the resin.

The results of this study were interesting. The decreased temperature eliminated the bubbling as expected. However, it was found that the percentage of iridium removed from the resin was 98.3% - 0.7% more than that removed at 95°C with the same concentration of acid. A decrease in iridium recovery and not an increase would have been expected at the lower temperature. A comparison of the effect of temperature on the efficiency of 12 M nitric acid in removing iridium from the resin is shown in Fig. 9. It will be noted that up to a volume of 60 ml of acid, a greater percentage of iridium was removed with the acid at 95°C as would be expected. However, from 60 ml onwards, a greater percentage of iridium was removed at 74°C than at 95°C.

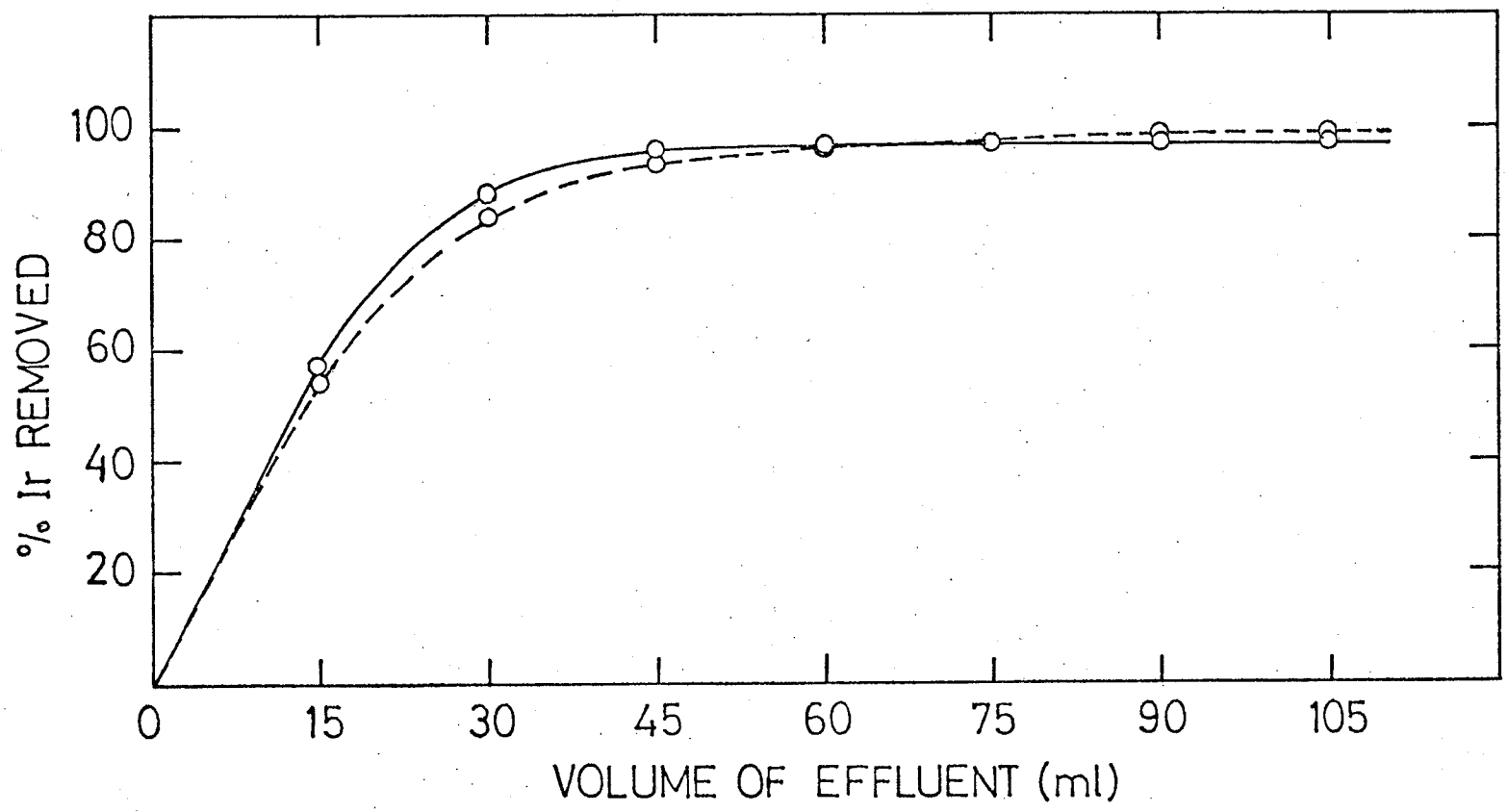
The increased iridium recovery at the lower temperature can be explained in the following manner:

When the resin column was washed free of the ceric ion and hydrochloric acid, the absorbed quadrivalent iridium chloro complex was no longer in the presence of an oxidizing agent and was now susceptible to reduction to the tervalent form by the resin. The elevated temperatures during the one-half hour warm-up period would have increased the rate of reduction of iridium by the resin. This quantity of tervalent iridium chloro complex, being more reactive kinetically than the quadrivalent species (57), was able to undergo an aquation reaction in the essentially aqueous medium to form a small amount of the first aquation product $Ir(OH_2)Cl_5^{2-}$ (57). (Although the presence of small amounts of the second and third aquation products, $Ir(OH_2)_2Cl_4^-$ and

Fig. 9. Effect of Elution Temperature on Removal of 500 µg of Iridium from Resin with 12 M Nitric Acid.

——— 95°C.

----- 74°C.


% Ir REMOVED
100
80
60
40
20
0
15
30
45
60
75
90
105
VOLUME OF EFFLUENT (ml)

$Ir(OH_2)_3Cl_3$ were possible, it was highly unlikely since their rates of formation are 15 and 66 times slower, respectively, than that for the first aquation product (57,58).) The tervalent aquated iridium species was then oxidized to the corresponding quadrivalent species on contact with the nitric acid. The presence of this oxidized aquated species was indicated in a comparison of the spectrum obtained for the iridium eluted with 12 M nitric acid (Fig. 8, p. 55) with the spectrum given for $Ir(OH_2)Cl_5^-$ (Fig. 10, p. 59) by Chang and Garner (58). The more pronounced peak at 435 mμ and the absence of a peak at 576 mμ (as compared to the spectrum of $IrCl_6^{2-}$) in the present nitric acid study was probably due to a small amount of $Ir(OH_2)Cl_5^-$ present in the $IrCl_6^{2-}$ solution. If the oxidized aquated species was more difficult to remove from the resin than the original quadrivalent chloro complex, the better iridium recovery at the lower temperature could be accounted for. The rate of reduction and aquation would be faster at 95°C than at 74°C and hence a larger portion of the absorbed iridium would be aquated at the higher temperature, resulting in a larger amount of oxidized aquated product on contact with the nitric acid.

Comparison of the spectra previously obtained for the oxidized iridium solutions eluted with hydrochloric acid under various conditions (Figs. 2, 5 and 6, pp. 41, 47, and 50) with the spectrum given for $Ir(OH_2)Cl_5^-$ (Fig. 10, p. 59) by Chang and Garner (58) suggested that the more pronounced peaks at 435 mμ and the absence of peaks at 576 mμ (as compared to the spectrum of $IrCl_6^{2-}$) in the hydrochloric acid elution studies were due to a small amount of $Ir(OH_2)Cl_5^-$ present in the $IrCl_6^{2-}$ solutions. This would indicate that a small amount of $Ir(OH_2)Cl_5^{2-}$ was formed by the reduction-aquation reactions described above during the one-half hour warm-up period. If the aquated species,

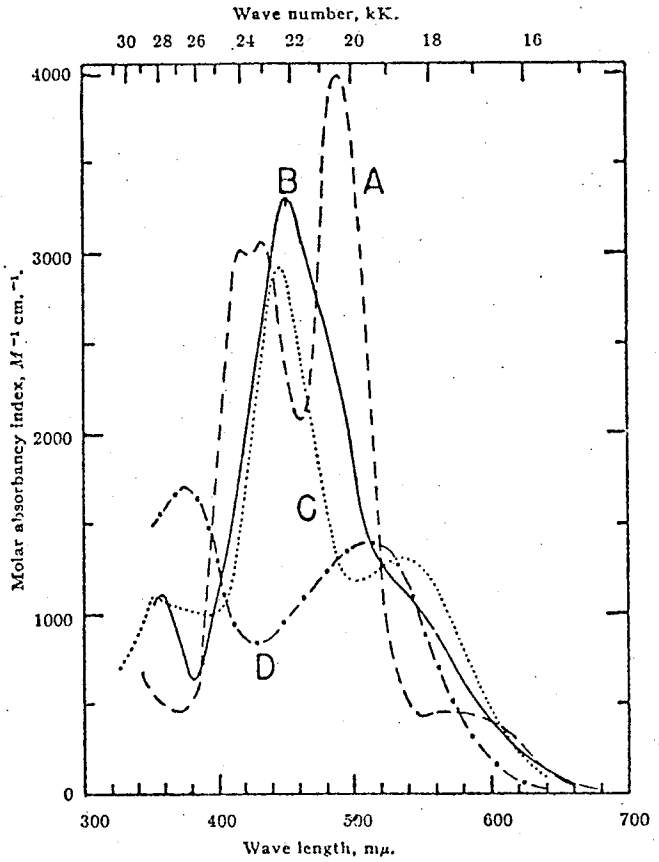
Fig. 10. Visible Absorption Spectra of Hexachloro and Aquopentachloro Complexes of Iridium (IV) in Cl_2-Saturated 2.5 F $HClO_4$-1.2 F $NaClO_4$ at 25°C (58).

A: $IrCl_6^{2-}$

B: $Ir(OH_2)Cl_5^-$

C: $Ir(OH_2)_2Cl_4$

D: $Ir(OH_2)_3Cl_3^+$


Wave number, kK.
30 28 26 24 22 20 18 16
4000
3000
2000
1000
0
Molar absorbancy index, M^{-1} cm.$^{-1}$.
B
A
C
D
300 400 500 600 700
Wave length, mμ.

$Ir(OH_2)Cl_5^{2-}$, was more difficult to remove from the resin than the tervalent chloro complex, the incomplete iridium recoveries on elution with hydrochloric acid could be accounted for.

It was felt that by eliminating the aquation conditions, better iridium recoveries from the resin could be expected on elution with either nitric or hydrochloric acid. This was determined in the following studies.

2-3c. Effect of Elimination of Aquation Conditions on Iridium Recoveries

A 500 µg iridium sample was fed onto the resin bed and eluted with 50 ml of cerium solution in the usual manner. The resin was washed free of ceric ion with 15 ml of 0.8 M hydrochloric acid and the column flow stopped. A 15 ml portion of 12 M nitric acid at room temperature was then passed through the resin bed at 40 ml/hr. An additional 90 ml of 12 M nitric acid was added to the acid reservoir and the acid passed through the column without stoppage in flow while water heated to 75°C was circulated through the jackets of the acid reservoir and the resin column. The acid flow through the column could not be stopped on heating because bubbles due to the formation of nitrogen dioxide disrupted the resin bed. As long as the flow rate was not stopped, no bubbling occurred in the resin bed. The acid in the reservoir reached its equilibrium temperature of 74°C within 15 minutes of heating. The effluent from the column was collected in 15 ml aliquots and the activity determined. The activity of the resin was checked after passage of the acid solution.

It was found by this method that 99.1% of the iridium was removed from the resin with 12 M nitric acid. A study done with the same volume of concentrated nitric acid (16 M) further improved the iridium recovery to 99.6%. It would appear that the improved iridium recoveries were due to the elimination

of the aquation conditions.

A study using 150 ml of concentrated nitric acid at room temperature to remove the iridium from the resin showed that 92.7% of the 500 μg iridium sample was removed. Evidently the hot nitric acid was more efficient in leaching out the iridium deep in the resin matrix.

The addition of nitric acid to the resin at room temperature turned the resin dark brown in color and caused a slight swelling of the resin bed, which suggested a partial degradation of some of the crosslinking in the resin matrix. On passage of hot acid through the column, the resin quickly reverted back to a golden-brown color and the dark brown chloroiridate (IV) band quickly disappeared.

The effluent for approximately the first 30 milliliters was yellow-brown in color due to both the eluted iridium and the presence of nitrogen dioxide in the acid solution. Further aliquots of the effluent gradually became colorless as more acid was passed through the column. When the total effluent was evaporated to dryness on a steam bath, a dark blue-green residue remained (probably a hydrated oxide of iridium). After successive additions and evaporations, each with several milliliters of concentrated hydrochloric acid, the residue was easily dissolved in 1 M hydrochloric acid.

A spectrophotometric study of the iridium eluted from the resin was performed using the concentrated nitric acid elution procedure at 74°C discussed above, and a non-radioactive chloro complex solution containing 1000 μg of iridium. Following the passage of the first 15 ml of concentrated nitric acid through the resin bed, a 15 ml aliquot of effluent was collected as 75°C water was circulated through the jackets of the resin column and acid reservoir. The visible spectrum of this aliquot was obtained using 1 cm cells and a

concentrated nitric acid solution (which had been passed through a jacketed resin column treated in the same manner as the sample) as a blank. See Fig. 11. The spectrum was essentially identical to that obtained for $IrCl_6^{2-}$ (see Fig. 3, p. 42), indicating that the presence of more than one eluted iridium species in the previous spectrophotometric study of the iridium elution with nitric acid was due to the slight aquation of the chloro complex as discussed above.

In the iridium elution study employing 9 M hydrochloric acid and a 500 μg iridium sample, the resin was first eluted at room temperature with 15 ml of 9 M hydrochloric acid at a flow rate of 40 ml/hr. The column flow was then stopped and, after a one-half hour warm-up period, the resin was eluted at 95°C with an additional 90 ml of 9 M hydrochloric acid. The same flow rate of 40 ml/hr was used. It was found that 98.6% of the iridium could be removed in this manner. This was an improvement of almost 2% over that obtained by the usual method of elution.

In a spectrophotometric study of the eluted iridium species employing the above hydrochloric acid elution procedure using a non-radioactive $IrCl_6^{2-}$ solution containing 1000 μg iridium, the first 15 ml aliquot of odixized effluent eluted at 95°C exhibited the visible absorption spectrum shown in Fig. 12 with 1 cm cells. The spectrum was identical to the one obtained for $IrCl_6^{2-}$ (Fig. 3, p. 42)indicating that the presence of more than one oxidized eluted iridium species in the spectrophotometric studies discussed previously had been due to the slight aquation of the tervalent chloro complex and the subsequent oxidation of this aquated product, $Ir(OH_2)Cl_5^{2-}$, to its quadrivalent form with chlorine.

Although better than 98% of the iridium could be recovered in this manner, no further studies were performed with hydrochloric acid since even better

Fig. 11. Visible Absorption Spectrum of Eluted Iridium Solution.

Eluant: Concentrated Nitric Acid at $74^{o}C$.

Approximate Iridium Concentration: 1.2×10^{-4} M.

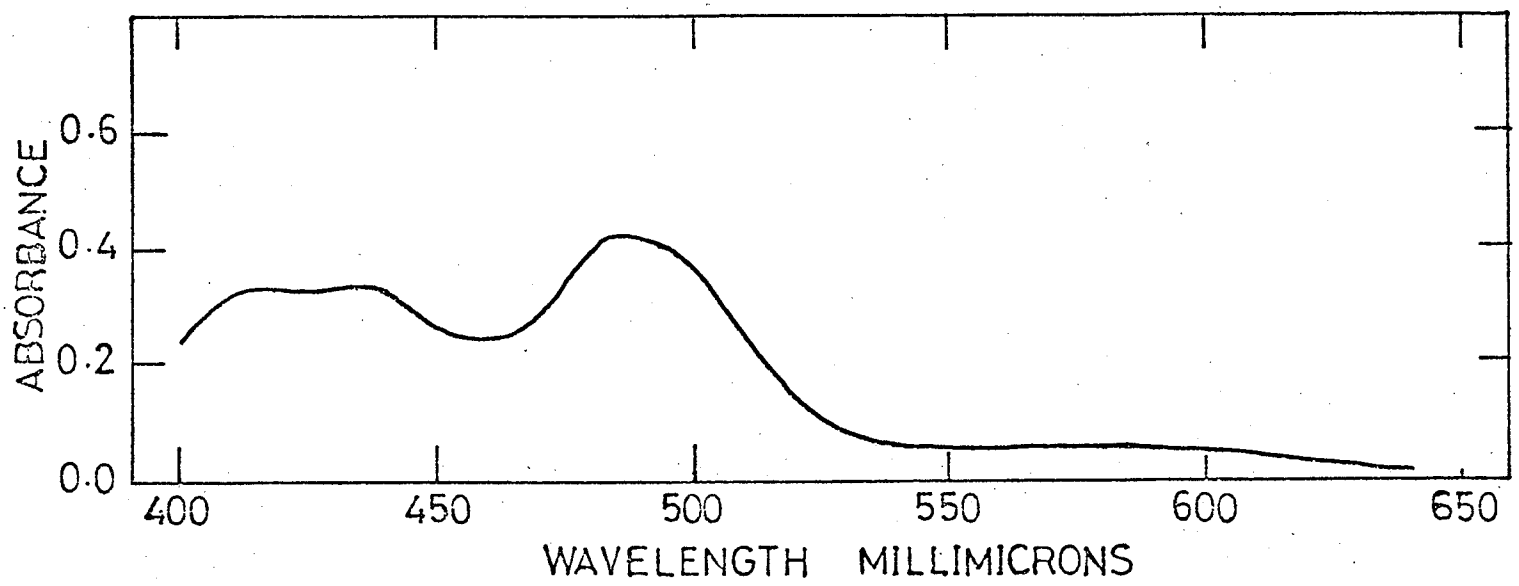
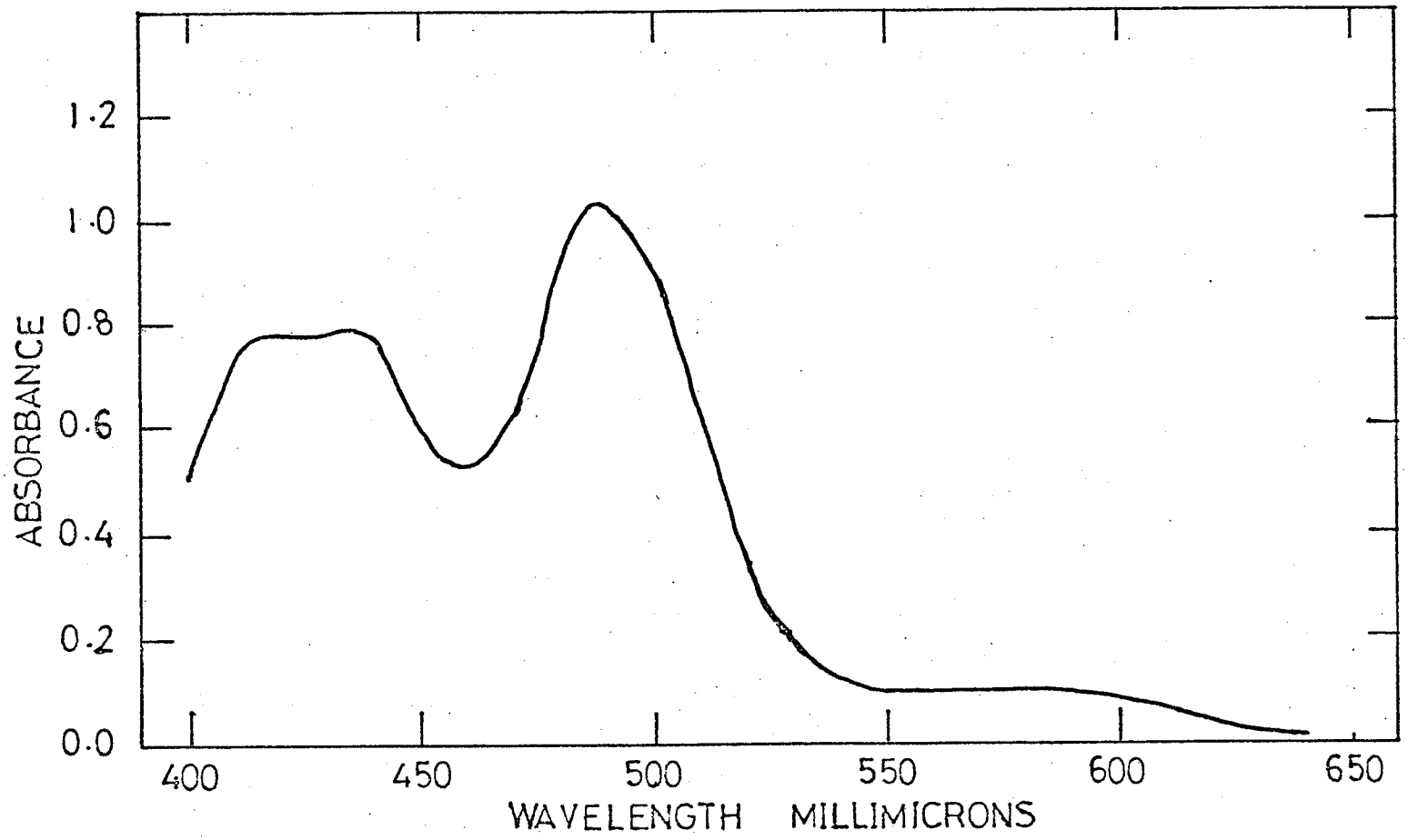

ABSORBANCE
0.6
0.4
0.2
0.0
400
450
500
550
600
650
WAVELENGTH MILLIMICRONS

Fig. 12. Visible Absorption Spectrum of Oxidized Eluted Iridium Solution (After Elimination of Aquation Conditions).

Eluant: 9 M Hydrochloric Acid at 95°C.

Approximate Iridium Concentration: 2.9×10^{-4} M.


1·2
1·0
0·8
0·6
0·4
0·2
0·0
ABSORBANCE
400
450
500
550
600
650
WAVELENGTH MILLIMICRONS

recoveries were obtained with nitric acid without any bubble formation in the resin bed.

The improved iridium recovery with nitric acid as compared to hydrochloric acid was probably due to several factors. Some iridium was probably recovered due to a slight dissolution of the resin upon partial degradation of the resin crosslinkage. However, the main reason for better recovery was likely due to the greater affinity of the nitrate ion over the chloride ion for the resin exchange sites. This greater affinity probably made the removal of iridium from the exchange sites easier. Although the perchlorate ion has even a greater affinity than the nitrate ion, studies involving perchloric acid were not carried out due to difficulties in working with perchloric acid in the presence of organic matter at elevated temperatures.

2-3d. Absorption and Recovery of Various Amounts of Iridium

A study involving iridium samples of 100, 500 and 1000 μg was made to determine the effect of the amount of sample on iridium leakage from the resin during the sample loading and "rhodium elution". The efficiency of 150 ml of concentrated nitric acid in removing various quantities of iridium was determined also.

The samples were dissolved in 2 ml of 0.8 M hydrochloric acid and were fed with droppers onto the resin beds which had been previously washed, first with 20 ml of water, then by 20 ml of cerium solution. (2 ml of 0.1 M ceric sulfate per 100 ml of 0.8 M hydrochloric acid) The beakers were twice-rinsed with several milliliters of 0.8 M hydrochloric acid and the washings added to the columns. The flow rate used during the feeding of the samples onto the resin beds was approximately 25-30 ml/hr. The columns were then eluted at a flow rate of 50 ml/hr with 250 ml of cerium solution to simulate the elution of rhodium

from the resin. Effluent samples were taken in 15 ml aliquots and their activities determined. Following the "rhodium elution", the resin beds were washed free of ceric ion with 15 ml of 0.8 M hydrochloric acid.

The iridium was removed from the resin beds by first passing a 15 ml portion of concentrated nitric acid at room temperature through the columns followed by an additional 135 ml of acid while water heated to 75°C was circulated through the jackets of both the resin columns and the acid reservoirs. The circulating water heated the acid to its equilibrium temperature of 74°C in about 20 minutes. The elution flow rate was approximately 40 ml/hr. The effluent and resin activities were determined in the usual manner.

The results of the study are shown in Table IV. The percentage of iridium lost during the "rhodium elution" and the percentage of iridium remaining on the resin after the nitric acid elution were determined by the following relations:

$$\% \text{ Iridium Lost from Resin} = \frac{W}{W + A + R} \times 100$$

$$\% \text{ Iridium Remaining on Resin} = \frac{R}{W + A + R} \times 100$$

where W = total activity recovered during "rhodium elution" and hydrochloric acid wash,

A = total activity recovered during nitric acid elution of resin,

R = residual activity on resin after nitric acid elution.

The total iridium not recovered represented the amount which would not be recovered in the iridium fraction of an actual rhodium-iridium separation. The results show that essentially quantitative recoveries of the iridium fed onto the resin were obtained. The total percentage of iridium not recovered was less

Table IV

Leakage and Recovery of Iridium from Resin

Sample (μg)	% Ir Lost in "Rhodium Elution" and Hydrochloric Acid Wash	Ir Lost in "Rhodium Elution" and Hydrochloric Acid Wash (μg)	% Ir Remaining on Resin after 16 M Nitric Acid Elution	Total % Ir Not Recovered	Total Ir Not Recovered (μg)
100	0.79	0.8	1.18	1.97	2.0
500	0.53	2.6	0.28	0.81	4.0
1000	0.44	4.4	0.69	1.13	11.3

than 2% over the entire range studied. The total amount of iridium not recovered increased with increasing amounts of iridium, as did the iridium loss during the "rhodium elution" (the loss representing approximately half of the total iridium not recovered).

Table V shows the efficiency of concentrated nitric acid in removing the various concentrations of iridium from the resin. The percentage of iridium removed was calculated from the equation:

$$\text{Total \% Iridium Removed} = \frac{A_v}{A + R} \times 100$$

where A_v = total activity recovered after the passage of v ml of nitric acid through the column.

From the results it was evident that 150 ml of nitric acid was sufficient to remove the maximum amount of iridium from the resin over the entire range studied.

2-4. Spectrophotometric Studies of the Rhodium Chloro Complex in 6 and 0.8 M Hydrochloric Acid Solutions

Two samples of the rhodium chloro complex, each containing 1500 µg rhodium, were treated with aqua regia and hydrochloric acid in the same manner as iridium samples used in the radioactive tracer studies discussed above. The first sample residue was dissolved in 15 ml of 6 M hydrochloric acid and its visible absorption spectrum obtained using 4 cm quartz cells. The absorption spectrum (see Fig. 13-a) with peaks at 410 and 519 mµ indicated that the rhodium was in the form of the chloro complex $RhCl_6^{3-}$ (62). The spectrum remained constant for at least 24 hours. The spectrum for the second sample dissolved in 15 ml of 0.8 M hydrochloric acid and allowed to stand for 20 minutes before

Table V

Efficiency of Concentrated Nitric Acid
in Removing Iridium from Resin

Total Acid Volume (ml)	Sample: 100 µg Ir Total % Ir Removed	Sample: 500 µg Ir Total % Ir Removed	Sample: 1000 µg Ir Total % Ir Removed
15	38.5	31.9	28.2
30	74.5	71.2	67.5
45	90.9	90.6	86.7
60	96.5	96.6	95.0
75	98.1	98.8	97.9
90	98.6	99.4	98.9
105	98.7	99.6	99.2
120	98.8	99.6	99.2
135	98.8	99.7	99.3
150	98.8	99.7	99.3

measuring is shown in Fig. 13-b. The two absorption bands had moved towards shorter wavelengths (402 and 509 mμ). Jorgensen (62) has shown that this movement by the absorption bands of $RhCl_6^{3-}$ with time was due to the exchange of chloride with water and that in a 1 M hydrochloric acid solution at 18°C, the shift in absorption bands continued for several weeks until a steady state condition was achieved. The final aquated product was calculated to be $RhCl_{4.4}(H_2O)^{1.4-}$. Jorgensen also noted that in 6 M hydrochloric acid solutions, the rhodium chloro complex did not exhibit any change in absorption bands over a period of one month.

The results of the present spectrophotometric study indicated that the rhodium eluted from the ion-exchange resin would be in the form of mixed chloride complexes of the general form $RhCl_n(H_2O)_{6-n}^{3-n}$ where n = 0 - 6.

2-5. Separation of Rhodium from Iridium

From the radioactive tracer studies it was shown that iridium could be quantitatively removed from the resin with concentrated nitric acid at 74°C. A complete study of the separation of various ratios of rhodium and iridium in amounts ranging from 100 to 1000 micrograms was now performed using atomic absorption spectrophotometry for the analysis of both rhodium and iridium.

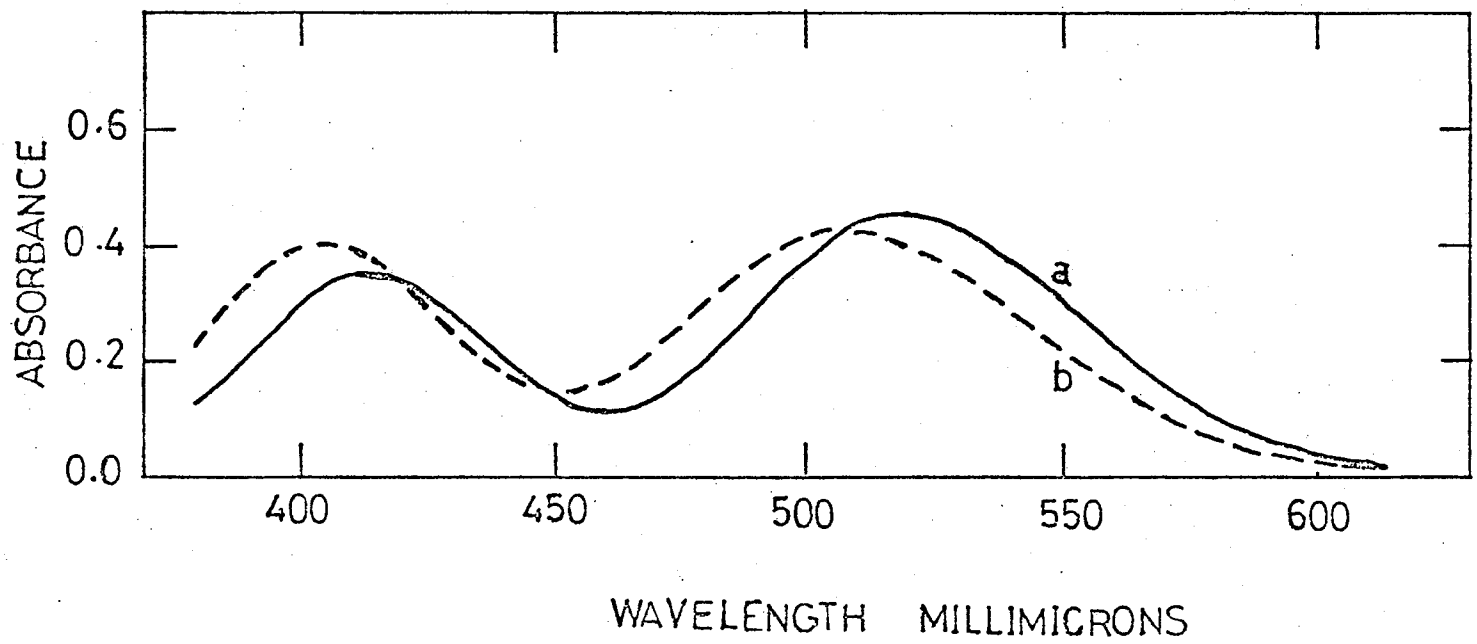
2-5a. Procedure

Sample solutions containing the required amounts of rhodium and iridium were pipetted into 30 ml beakers containing 6 mg of sodium chloride. Several milliliters of concentrated hydrochloric acid were added to each sample and the samples evaporated to dryness on a steam bath. The samples were thrice-

Fig. 13. Visible Absorption Spectra of the Rhodium Chloro Complex in 6 and 0.8 M Hydrochloric Acid Solutions.

a. 6 M Hydrochloric Acid.

b. 0.8 M Hydrochloric Acid.


ABSORBANCE
0.6
0.4
0.2
0.0
400
450
500
550
600
a
b
WAVELENGTH MILLIMICRONS

treated with aqua regia as described previously on page 31 and evaporated to dryness after each treatment. The samples were then treated four times each with several milliliters of concentrated hydrochloric acid to remove any nitrates. The last acid treatment was made immediately prior to the samples being fed onto the resin columns.

The samples were dissolved in 2 ml of 0.8 M hydrochloric acid and were fed onto 3 cm resin beds with droppers. The beakers were twice-rinsed with several milliliters of 0.8 M hydrochloric acid and the washings fed onto the columns. The resin beds had been previously washed with 20 ml of water followed by 20 ml of cerium solution (2 ml of 0.1 M ceric sulfate per 100 ml of 0.8 M hydrochloric acid). The flow rate used while loading the samples onto the resin was approximately 25-30 ml/hr. The rhodium was then eluted at a flow rate of 50 ml/hr with either 150 or 250 ml of cerium solution, depending upon the amount of rhodium. (A volume of 150 ml of cerium solution had been previously found to be sufficient for the elution of 100-500 μg rhodium whereas 250 ml was required for 1000 μg samples). The effluents were collected in either 250 or 400 ml beakers. Upon elution of the rhodium, the resin beds were washed free of ceric ion with 15 ml of 0.8 M hydrochloric acid and the wash effluents collected in the beakers containing the rhodium fractions. The rhodium effluents were then evaporated to dryness on a steam bath and the rhodium determined by atomic absorption spectrophotometry.

Following the rhodium elution, the iridium was removed by first passing 15 ml of concentrated nitric acid at room temperature through the resin beds at a flow rate of approximately 40 ml/hr, followed by an additional 135 ml of acid as the resin columns and acid reservoirs were being heated with water at 75°C.

The effluents were collected in 150 ml beakers to which 10 μg of sodium chloride had been added, and were evaporated to dryness. The iridium was then determined by atomic absorption.

Rhodium Analysis

The rhodium residues were dissolved by adding 15 ml of 1 M hydrochloric acid to each and gently heating on a steam bath for approximately one-half hour. The solutions were allowed to cool and were then transferred to 50 ml volumetric flasks (to which 4 ml of 37.5% (w/v) sodium hydrogen sulfate in 1 M hydrochloric acid had been added), and diluted to the mark with 1 M acid. The addition of 3% sodium hydrogen sulfate (as shown by Kallmann and Hobart (45)) removed any interference effects from the sulfate ion of the cerium sulfate solution. The sodium hydrogen sulfate also enhanced the rhodium absorbance values approximately twofold. The effect of 3% sodium hydrogen sulfate on the absorbance of a 20 ppm rhodium solution is shown in Table VI. All samples were in a 1 M hydrochloric acid medium. The instrument settings used according to the Perkin-Elmer Handbook (46) were:

Fuel flow rate : 3 l/min

Air flow rate : 24 l/min

Wavelength : 3435 $\mathring{A}$

Slit width : 2 $\mathring{A}$

Lamp current : 16 ma

The rhodium concentration in the samples was determined by comparison with appropriate standards prepared in the same manner as the samples. The absorbance for the samples containing 100 μg rhodium were scale-expanded approximately twofold to give absorbance values of 0.150. A standard calibration

Table VI

Effect of Sodium Hydrogen Sulfate
on Rhodium Absorbance

Sample	Absorbance
20 ppm rhodium solution	0.316
20 ppm rhodium solution containing 3% sodium hydrogen sulfate	0.615
20 ppm rhodium solution containing 3% sodium hydrogen sulfate and 5 ml of 0.1 M cerium sulfate	0.615

curve for the concentration range studied is shown in Fig. 14.

A preliminary study had shown that the presence of up to 25% iridium had essentially no effect on the rhodium absorbance values. A 4 ppm rhodium solution and a solution containing 4 ppm rhodium plus 1 ppm iridium had absorbances of 0.101 and 0.100 respectively.

Iridium Analysis

The iridium residues were treated a total of 4 times with approximately 5 ml portions of concentrated hydrochloric acid and evaporated to dryness after each addition in order to reconvert the iridium to the easily dissolved chloro complex. The residues were then dissolved in 10 ml of 1 M hydrochloric acid solution containing 20,000 ppm copper in the form of copper nitrate. (The use of 20,000 ppm copper had been found by Houzé (47) to enhance the iridium absorbance fivefold and to eliminate any interference effect from up to 2000 ppm sodium and 100 ppm rhodium on the absorbance of a 20 ppm iridium solution.) The solutions in the beakers were aspirated directly and their iridium concentration determined by comparison to similarly prepared standards. The absorbance values for the 100 µg samples were scale-expanded approximately fivefold to 0.085. The instrument settings were as follows:

Fuel flow rate	: 4 l/min
Air flow rate	: 24 l/min
Wavelength	: 2639 Å
Slit width	: 2 Å
Lamp Current	: 25 ma

A standard calibration curve for the concentration range studied is shown in Fig. 15.

Fig. 14. Calibration Curve for Rhodium Determination By Atomic Absorption.

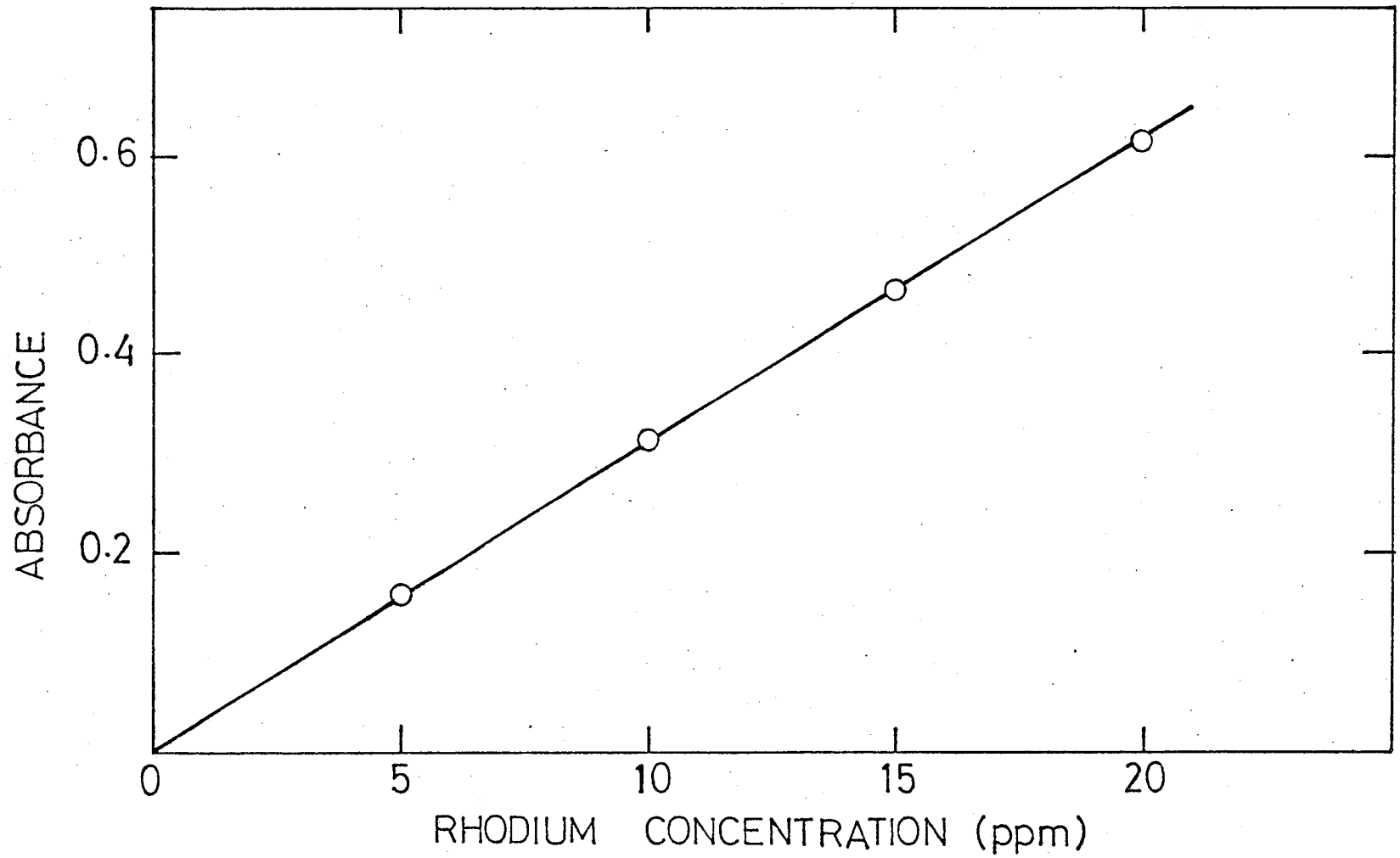
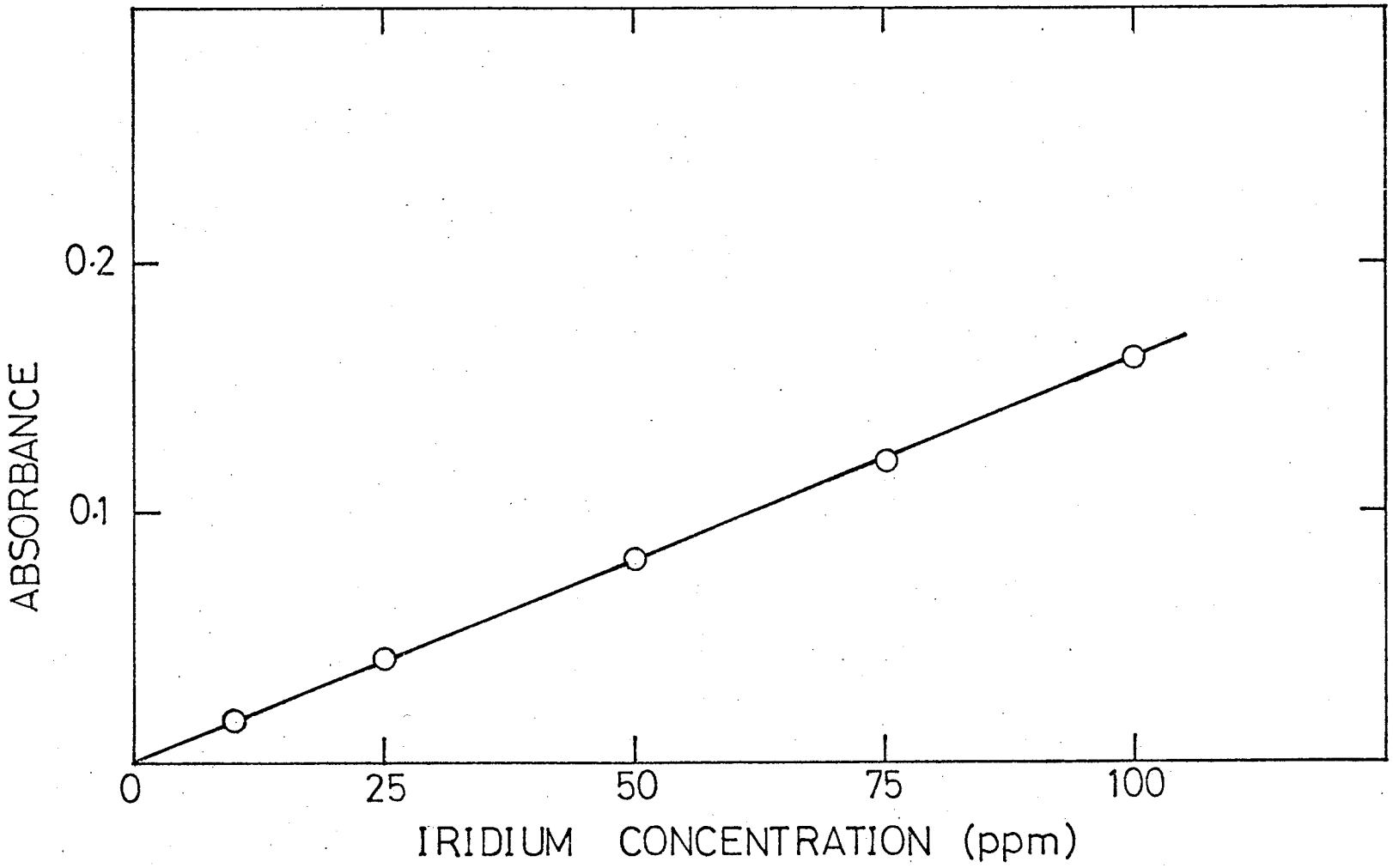

ABSORBANCE
0.6
0.4
0.2
0
5
10
15
20
RHODIUM CONCENTRATION (ppm)

Fig. 15. Calibration Curve for Iridium Determination by Atomic Absorption.


ABSORBANCE
0·2
0·1
0
25
50
75
100
IRIDIUM CONCENTRATION (ppm)

2-5b. Results and Discussion

The results of the separation of various amounts of rhodium and iridium are shown in Table VII. A summary of the mean values is given at the end of the table.

The recoveries for both rhodium and iridium were 98% or greater over the entire range studied. In the case of rhodium, the percentage recovery in general increased with increasing amounts of rhodium. The small amount of rhodium not recovered with the larger rhodium samples (500 and 1000 μg) suggested that when the Rh:Ir ratio was five or greater the iridium fraction would contain about 5% rhodium. When the Ir:Rh ratio was greater than five, the rhodium fraction would contain approximately 4% iridium due to iridium leakage from the resin as was shown in the radioactive tracer studies.

2-5c. Summary of Separation Procedure Employed

Sample solutions containing rhodium and iridium as their tervalent and quadrivalent chloro complexes respectively were first treated with aqua regia and concentrated hydrochloric acid to ensure that the iridium was in the form of the quadrivalent chloro complex. The dry sample residues were dissolved in 0.8 M hydrochloric acid and were fed onto jacketed ion-exchange resin columns of Amberlite IRA-400 resin. The resin beds had previously been treated with a 0.8 M hydrochloric acid solution containing 2 ml of 0.1 M ceric sulfate per 100 ml of acid to prevent the reduction of the iridium. The rhodium was eluted from the resin with additional 0.8 M hydrochloric acid containing ceric sulfate. Upon elution of the rhodium, the resin beds were washed free of ceric ion with 0.8 M hydrochloric acid. The iridium was removed from the resin by passing 15 ml of concentrated nitric acid at room temperature through the resin beds, followed by additional acid as the resin columns and acid reservoirs were being heated

Table VII

The Separation of Various Amounts
of Rhodium and Iridium

Iridium Added (µg)	Rhodium Added (µg)	Iridium Recovered (µg)	Rhodium Recovered (µg)
100	100	98	99
100	100	99	98
100	100	96	98
100	100	102	100
Mean and mean deviation:		99 ± 2	99 ± 1
100	500	99	490
100	500	98	500
100	500	100	500
100	500	96	490
Mean and mean deviation:		98 ± 1	495 ± 5
100	1000	95	993
100	1000	100	996
100	1000	101	995
100	1000	98	991
Mean and mean deviation:		98 ± 2	994 ± 2
500	100	494	99
500	100	500	98
500	100	494	98
500	100	506	99
Mean and mean deviation:		498 ± 4	98 ± 0.5

Iridium Added (µg)	Rhodium Added (µg)	Iridium Recovered (µg)	Rhodium Recovered (µg)
500	500	500	494
500	500	494	496
500	500	500	492
500	500	494	496
Mean and mean deviation:		497 ± 3	494 ± 2
500	1000	506	995
500	1000	500	997
500	1000	494	998
500	1000	500	993
Mean and mean deviation:		500 ± 3	996 ± 2
1000	100	987	98
1000	100	987	97
1000	100	1000	99
1000	100	994	98
Mean and mean deviation:		992 ± 5	98 ± 0.5
1000	500	994	493
1000	500	987	491
1000	500	987	498
1000	500	994	496
Mean and mean deviation:		990 ± 4	494 ± 2

Iridium Added (µg)	Rhodium Added (µg)	Iridium Recovered (µg)	Rhodium Recovered (µg)
1000	1000	994	997
1000	1000	987	997
1000	1000	987	993
1000	1000	994	992
Mean and mean deviation:		990 ± 4	995 ± 2
	Summary		
100	100	99[a] ± 2	99[a] ± 1
100	500	98 ± 1	495 ± 5
100	1000	98 ± 2	994 ± 2
500	100	498 ± 4	98 ± 0.5
500	500	497 ± 3	494 ± 2
500	1000	500 ± 3	996 ± 2
1000	100	992 ± 5	98 ± 0.5
1000	500	990 ± 4	494 ± 2
1000	1000	990 ± 4	995 ± 2

[a]mean value of four samples ± mean deviation

with water at 75°C.

2-5d. Conclusion

The quantitative elution of microgram and milligram quantities of iridium from a strongly basic anion-exchanger with hot concentrated nitric acid has been shown to be feasible. The procedure involved is simpler than the Soxhlet extraction method previously employed but requires slightly more time. However, the eluted iridium can be analyzed directly in the same vessel used to collect the effluent, thus minimizing the chance of sample loss on transferring the solution from one vessel to another as is the case in the Soxhlet extraction method. By eliminating the necessity of removing the resin from the column, the procedure described above may find wider application than the Soxhlet extraction method for the recovery of iridium from a strongly basic anion-exchanger.

Essentially quantitative separations and recoveries of rhodium and iridium were possible over the entire 100 - 1000 μg range studied. However, when the ratio of one metal to the other was five or greater, the portion with the lesser amount of metal contained a small amount of the other metal.

III | THE SEPARATION OF IRIDIUM FROM RHODIUM BY SOLVENT EXTRACTION WITH THE LIQUID ANION-EXCHANGER TRI-n-OCTYLAMINE

1. INTRODUCTION

1-1. Liquid Ion-Exchangers

Since the publication in 1948 of a paper by Smith and Page (48) entitled "The Acid-Binding Properties of Long-Chain Amines", increasing interest has been shown in the use of high molecular weight acids and bases as extractants. These acids and bases have a low water solubility and a high solubility in water-immiscible solvents. Two extensive review articles published by Green (49,50) cover the various uses of liquid ion-exchangers in inorganic analysis.

Liquid ion-exchange is a special case of solvent extraction in that it involves the selective transfer of solute between two immiscible phases. Solvent extraction, however, involves the formation of a neutral species, whether a chelate, an ion-pair or a non-dissociating compound. Liquid ion-exchange, on the other hand, refers only to the formation of ion-pairs with special reference to the exchange of one ion for another between the aqueous and organic phase. The degree of ion-exchange transfer is directly proportional to the concentration of the exchanger in the solvent, and the distribution coefficients may be obtained in a manner similar to those obtained in solvent extraction. Changes in the selectivity and in the values for the distribution coefficients are related to changes in pH, temperature, salt concentration, charge on the ions involved, the presence of complexing and competing ions and the organic solvent employed. Liquid ion-exchange has been compared with resin ion-exchange because the

behaviour of the analogous functional groups in the two systems is frequently similar. Therefore, by reference to the literature on separations with ion-exchange resins, it is possible to predict the likely course of a liquid ion-exchange extraction.

Compared with resinous exchangers, separations of the required ionic species with liquid ion-exchangers are much more rapid. Diffusion is faster in an organic solution of a liquid exchanger than in a swollen ion-exchange resin and this leads to faster exchange reactions.

Acids that are insoluble in water and soluble in organic solvents serve as liquid cation-exchangers. The most useful of these are di-(2-ethylhexyl) orthophosphoric acid (referred to as D2EHPA, DEHPA or HDEHP by various authors) and dinonylnaphthalene sulfonic acid (DNS). Solutions of these acids in organic solvents can undergo extraction reactions with cations in aqueous solutions in the following manner:

$$(HX)_o + B_a^+ + Cl_a^- \rightleftarrows (BX)_o + H_a^+ + Cl_a^-$$

where HX = a high molecular weight acid,

B^+ = a cation such as Na^+,

o = organic phase,

a = aqueous phase.

Although actual extraction reactions are usually more complex, the above equation illustrates the formal similarity between liquid and resinous cation-exchangers.

Liquid anion-exchangers are based on high molecular weight primary, secondary and tertiary amines and quaternary ammonium salts.

The high molecular weight ensures low solubility in aqueous solutions and high solubility in most water-immiscible organic solvents. Various solvents, such as aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, high molecular weight alcohols and petroleum distillates are suitable. The extraction reactions are of the following ion-association type:

1. The organic solvent containing the amine can extract an aqueous acid to form an amine salt in the organic phase:

$$(Amn)_o + H_a^+ A_a^- \rightleftarrows (AmnH^+A^-)_o$$

where Amn = a high molecular weight amine,

A^- = anion of either a simple acid or a complex metal acid such as $FeCl_4^-$,

o = organic phase,

a = aqueous phase.

2. An amine salt in the organic phase can undergo anion-exchange with an ion in the aqueous phase:

$$(AmnH^+A^-)_o + B_a^- \rightleftarrows (AmnH^+B^-)_o + A_a^+$$

If the amine salt is treated with an alkaline solution, the extraction is reversed and the free amine is obtained.

1-2. The Separation of Iridium from Rhodium with Tri-n-octylamine

Tri-n-octylamine, (TOA), is one of the most widely employed liquid anion-exchangers. When dissolved in an organic solvent, TOA reacts with an aqueous acid to first form an amine salt in the organic phase. The amine salt then undergoes anion-exchange with an ion in the aqueous phase. This anion-exchanger has been used in extraction studies of rhodium and iridium as well as other noble metals.

The extraction of platinum (IV) and rhodium (III) by TOA hydrochloride was reported by Gindin and Ivanova (51). Extractions with 0.5 M exchanger in toluene showed decreasing extraction with increasing hydrochloric acid concentration. The separation of the two metals was found to be possible in 2 M hydrochloric acid with platinum extracting into the organic phase.

The extractibility of both the rhodium (III)-tin (II) complex and rhodium (III) chloro complex from hydrochloric acid solutions by 0.2 M TOA in benzene was studied by Khattak and Magee (52). By heating rhodium (III) with tin (II) in 7-11.6 M hydrochloric acid, a yellow rhodium (III)-tin (II) complex was formed in the aqueous phase, which could be extracted with TOA. The extractabilities of the rhodium (III)-hydrochloric acid, platinum (IV)-hydrochloric acid, and palladium (II)-hydrochloric acid systems by TOA were studied and were found to be dependent on the hydrochloric acid concentration. It was found that rhodium could not be extracted with TOA from solutions 4 molar or greater in hydrochloric acid concentration whereas platinum and palladium were extractable under these conditions. Therefore, rhodium could be separated from platinum and palladium and the rhodium concentration determined spectrophotometrically by means of the extracted yellow rhodium-tin complex.

Fedorenko and Ivanova (39) studied the extraction of iridium (III), iridium (IV) and rhodium (III) separately with tri-n-octylamine in benzene from 1-12 M hydrochloric acid solutions using a Kirk-Danielson extractor (61). The noble metals were present in the solutions as their complex chlorides. The tervalent ions were extracted only to a slight extent, and iridium (IV) was extracted with a high distribution coefficient,

but was partially reduced to iridium (III) on contact with the organic phase. The iridium could be kept in the quadrivalent state if the extraction was carried out while chlorine was bubbled through the solution. Calculation of the separation factor for the pair, iridium (IV)-rhodium (III), indicated the possibility of a separation using 6 M hydrochloric acid although no experimental results were reported.

The work of Fedorenko and Ivanova (39) suggested that TOA could be used as a rapid method for separating iridium from rhodium by solvent extraction. The present work involved an extraction with 6 M hydrochloric acid and TOA solution using conventional separatory funnels rather than the more complicated Kirk-Danielson extractor and presented quantitative results which were previously lacking. Separation studies were performed with both microgram and milligram amounts of rhodium and iridium since some other successful solvent extraction separation methods such as the tin bromide-isopentyl alcohol method (36) and the 4,5-dimethyl-2-mercaptothiazole method (35) have been applied to relatively restricted quantities. In addition, a study was made of the recovery of iridium from the organic phase using ammonium hydroxide.

2. EXPERIMENTAL

2-1. Apparatus and Reagents

Baird-Atomic Model 530 gamma-spectrometer and Model 810C well scintillation detector with a 4.4 cm diameter by 5.1 cm thick NaI(Tl) well crystal (Baird Atomic, Bedford, Massachusetts).

Perkin-Elmer Model 306 atomic absorption spectrophotometer with a 10 cm single slot burner and Varian rhodium lamp.

A Burrell "Wrist-Action" shaker (Burrell Corporation, Pittsburg, Pennsylvania) was used for the equilibration of the amine solution with hydrochloric acid.

An iridium solution containing 1 mg/ml iridium in 0.1 M hydrochloric acid was prepared from sodium chloroiridate ($Na_2IrCl_6 \cdot 6H_2O$) and a solution containing 1 mg/ml rhodium in 1.2 M hydrochloric acid was prepared from sodium chlororhodate ($Na_3RhCl_6 \cdot 12H_2O$), both obtained from Johnson Matthey and Mallory Limited (Toronto).

Iridium-192 was obtained from Amersham-Searle Limited, Don Mills, Ontario and diluted prior to use.

Tri-n-octylamine (TOA) (practical) (Eastman Kodak, Rochester, New York) was used without further purification. A 0.2 M solution of the amine in thiophene-free benzene was equilibrated on the shaker for one hour with four times its volume of 6 M hydrochloric acid before use.

All other chemicals used were reagent grade. Water purified by double-distillation followed by double-de-ionization was used for the required dilutions.

2-2. Procedure for Study

The extraction study was performed in two stages. The extractability of iridium in the presence of rhodium was studied by using iridium-192 as a tracer in conjunction with non-radioactive rhodium. The extent of iridium extraction was determined by the activity of the iridium tracer in the aqueous and organic phase. Because there was no rhodium isotope of sufficient purity available, the rhodium extractability was studied separately employing non-radioactive iridium and rhodium and by determining the change in rhodium concentration in the aqueous phase by atomic absorption spectrophotometry. (The iridium concentration in the aqueous phase after extraction could not be determined by atomic absorption due to its poor sensitivity and the presence of benzene caused erratic absorbance values when the organic phase was aspirated). The separation of iridium from rhodium was determined from the combined results of the two separate studies.

2-3. Preliminary Studies of Iridium Extraction

A number of preliminary studies were required in order to determine the optimum conditions for the extraction and recovery of iridium. No rhodium was present in the solutions used for these studies.

2-3a. Sample Preparation

Samples containing the required amounts of iridium were prepared from a stock solution containing sufficient iridium-192 tracer to yield a counting rate of 13×10^3 counts per minute. The samples were treated in the following manner:

Several milliliters of concentrated hydrochloric acid were added to the beakers containing the iridium solutions. The beakers were covered

with evaporating cover glasses and the solutions evaporated to dryness on a steam bath. Two milliliters of aqua regia (1:3 HNO_3: HCl) were added to each dry residue. The beakers were covered with regular watch glasses and replaced on the steam bath. When the action of the aqua regia ceased, the undersides of the watch glasses were rinsed with a few milliliters of concentrated hydrochloric acid and were replaced with evaporating cover glasses. The solutions were allowed to evaporate to dryness and the residues treated twice more with aqua regia. The aqua regia treatments were required to ensure that the iridium was in the quadrivalent state. Following the aqua regia treatments, the samples were thrice-treated with 2 ml of concentrated hydrochloric acid and evaporated to dryness to remove any nitrates. Before using, the samples were treated with a few drops of concentrated hydrochloric acid and were evaporated to dryness. Only 500 μg iridium samples were used in the preliminary studies.

2-3b. Counting Technique

The radioactive counting procedure used was to determine each sample in a test tube five successive times for a period of 100 sec and to use the average activity after correcting for the background which was obtained from the average of fifteen successive 100 sec measurements. The average deviation for the major iridium-containing phase was $\pm$ 0.6%. All determinations were done with the lid of the well-counter closed to minimize the background activity.

2-3c. Effect of Chlorine on Iridium Extraction

Because the iridium (IV) chloro complex is partially reduced to the less-extractable iridium (III) form in the presence of tri-n-octylamine

during extraction, chlorine has to be bubbled through the solution in order to maintain the iridium in the quadrivalent state (39). In the present work, studies were performed to determine the optimum amount of chlorine required to obtain maximum iridium extraction.

Three dry sample residues were dissolved in 15 ml of 6 M hydrochloric acid and each transferred to a 100 ml separatory funnel to which 15 ml of equilibrated 0.2 M TOA solution was then added. Chlorine from a cylinder was bubbled (40 ml/min) through the solutions in two of the separatory funnels with a bubbler fashioned from a piece of 8 mm glass tubing drawn to a capillary. In one case the chlorine was bubbled until a slight haziness appeared in the organic phase, while in the other case, the solution was completely saturated with chlorine (requiring approximately 1 minute of bubbling). The third sample was not treated with chlorine. All three separatory funnels were then shaken by hand for two minutes and the phases allowed to separate. The aqueous and organic phases were drained into separate test tubes and their activities determined in the cavity of the well-counter.

The study showed that an excessive amount of chlorine did not improve the extraction of iridium into the organic phase. The percentage of iridium extracted was 99.3% - the same as was extracted by using only enough chlorine to cause a slight haziness in the organic phase. However, in the absence of chlorine, only 75.1% iridium was extracted.

All further extraction studies were performed using only enough chlorine to cause a slight haziness in the organic phase.

2-3d. Effect of Shaking Time

Studies were carried out on two samples to determine the effect of the shaking time on the iridium extraction. The samples were treated in the same manner as in the above study. After the bubbling of chlorine through the solutions, one sample was shaken by hand for two minutes while the other was shaken for four minutes. Upon separation of the phases, the activities of the two phases in each case was counted in order to determine the extraction efficiency.

The results showed that a doubling of the shaking time did not improve the extraction efficiency. The percentage of iridium extracted was 99.2 and 99.1% for the shaking times of two and four minutes respectively. All further extractions were therefore performed using a two minute shaking time.

2-3e. Effect of Multiple Extractions

Since complete iridium extraction was not possible with a single extraction, the effect of multiple extractions was investigated.

After the initial extraction and determination of the activity in the aqueous and organic phases, the aqueous phase was transferred to a clean separatory funnel and a second extraction was performed in the same manner as the first. The resulting activity in the aqueous and organic phases was determined and the aqueous phase transferred to another clean separatory funnel for a third extraction and the activity of both phases again measured.

The effect of multiple extractions on the extractability of iridium is shown in the results given in Table I. Although more than one

extraction increased the percentage of iridium extracted to a slight extent, complete extraction was not possible even after three extractions. In fact, the percentage of iridium extracted after three extractions was only slightly greater than that found for two extractions.

Attempts were made to improve the iridium extraction by evaporating to dryness the aqueous phase containing the iridium remaining after a single extraction and treating the residue with aqua regia as described in the procedure for sample treatment. The residue was dissolved in 6 M hydrochloric acid and extracted with TOA as before. This procedure yielded better results than a second extraction of the original sample. Approximately 75% of the iridium remaining in the aqueous phase was extracted when the sample was treated with aqua regia as compared to approximately 50% when the original sample was extracted a second time. It would appear that reduction of iridium (IV) to iridium (III) occurs during the extraction even in the presence of chlorine, thus preventing complete extraction.

2-3f. Effect of Backwashing

After a single extraction of a sample and the determination of the activity in both phases, the organic phase was transferred to a clean separatory funnel and backwashed with 15 ml of 6 M hydrochloric acid using chlorine in the same manner as the original extraction. After the phases separated, the aqueous phase was drained into a test tube and the activity of the solution was counted in order to determine the loss of iridium from the organic phase on backwashing. It was found that there was a loss of 0.2% iridium from the organic phase on backwashing with the acid.

TABLE I

Effect of Multiple Extractions on the

Extractability of Iridium

Iridium Present (µg)	Total Number of Extractions	Extent of Iridium Extraction (%)
500	1	99.3
	2	99.7
	3	99.8

2-3g. Recovery of Iridium from the Organic Phase with Ammonium Hydroxide.

Studies were made on the effect of various concentrations of ammonium hydroxide used tostrip the extracted iridium from the organic phase. Fifteen milliliter aliquots of 14 M, 7 M and 1 M ammonium hydroxide were added to three separatory funnels containing the organic phase with the extracted iridium. The separatory funnels were shaken for two minutes and the phases allowed to separate. An emulsion formed when 14 M ammonium hydroxide was used and further studies with this concentration were discontinued. The aqueous phases of the other two samples were drained into test tubes and their activities determined. The organic phases of these two samples were then stripped twice more with ammonium hydroxide and the activities in the aqueous phases determined, followed by the counting of the activity in the organic phase after the three strippings.

The results for the recovery of iridium using 7 M ammonium hydroxide are shown in Table II. After three strippings, 99.0% of the iridium could be recovered from the organic phase. Additional strippings with ammonium hydroxide failed to recover more iridium. Strippings with 1 M ammonium hydroxide only recovered approximately 10% of the extracted iridium with the same number of strippings.

2-4. Extractability of Iridium in the Presence of Rhodium

2-4a. Sample Preparation

Samples containing the required amounts of iridium and rhodium were prepared from a stock solution containing sufficient iridium-192 tracer to yield a counting rate of 13×10^3 counts per minute and a stock non-radioactive rhodium solution. The samples were treated with aqua regia

Table II

Recovery of Iridium from Organic Phase

with 7 M Ammonium Hydroxide

Iridium Present (μg)	Total Number of Strippings	Total % Iridium Recovered from Organic Phase
500	1	96.5
	2	98.8
	3	99.0

and hydrochloric acid in the same manner as in the preliminary studies with iridium.

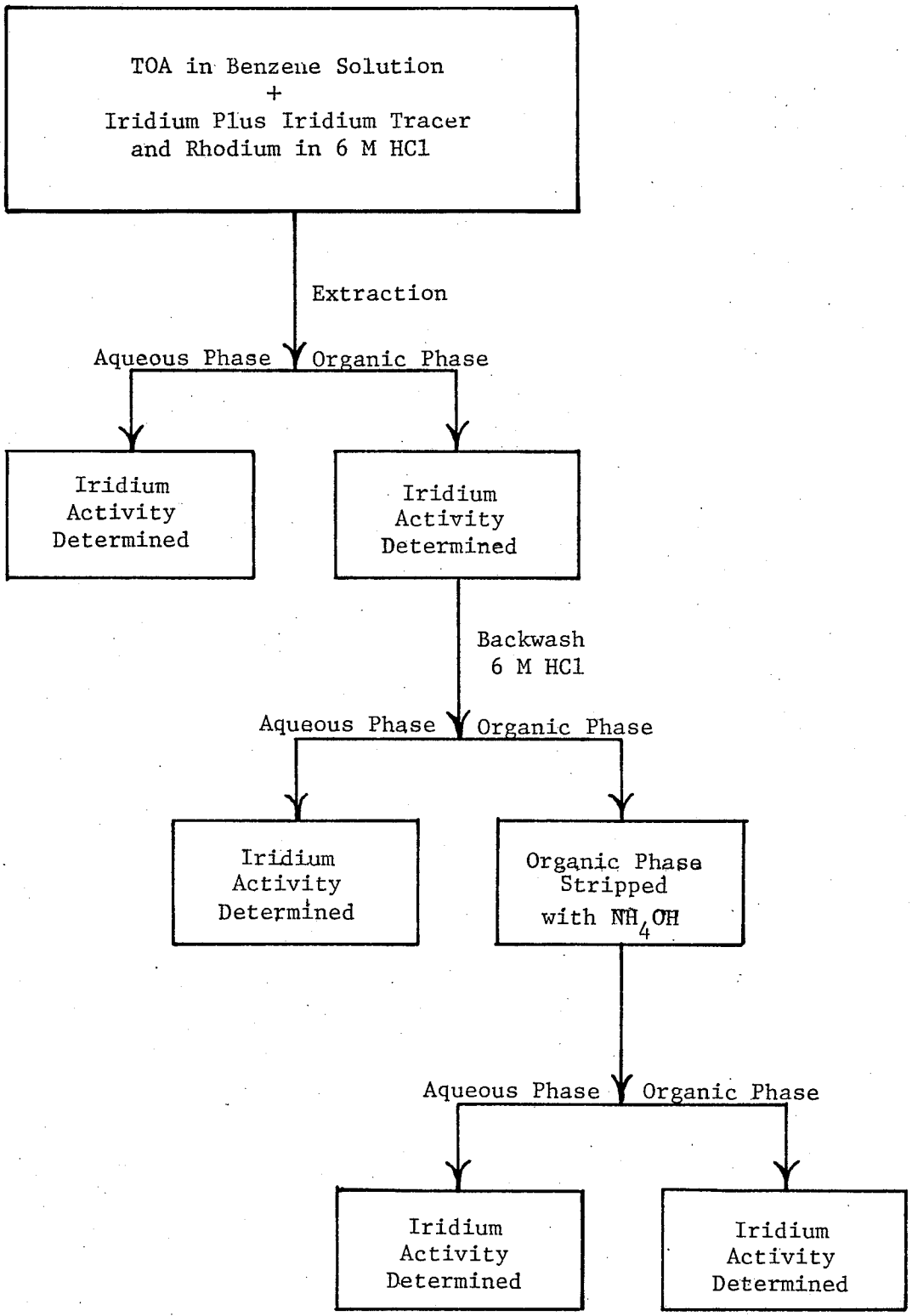
2-4b. Procedure

A schematic of the procedure employed in the tracer study of the extractability of iridium in the presence of rhodium and the recovery of the iridium from the organic phase is shown in Fig. 1. In each case, the dry sample residue was dissolved in 15 ml of 6 M hydrochloric acid and the sample transferred to a 100 ml separatory funnel to which 15 ml of equilibrated 0.2 M TOA solution was then added. Sufficient chlorine from a cylinder was bubbled (40 ml/min) through the solution with a bubbler (fashioned from a piece of 8 mm glass tubing drawn to a capillary) until a slight haziness appeared in the organic phase. The separatory funnel was then shaken by hand for two minutes and the phases allowed to separate. The aqueous and organic phases were drained into test tubes and their activities determined in the cavity of the well-counter as in the preliminary studies.

After its activity was determined, the organic phase was transferred to a clean separatory funnel and backwashed with 15 ml of 6 M hydrochloric acid using chlorine in the same manner as the original extraction. After the phases separated, the aqueous phase was drained into a test tube and the activity of the solution was counted in order to determine the loss of iridium from the organic phase on backwashing.

The organic phase remaining in the separatory funnel after the backwash was stripped with three 15 ml portions of 7 M ammonium hydroxide in order to remove the iridium. The aqueous phases were drained into test tubes and their activities determined. Finally, the activity of the organic

Fig. 1. Procedure Employed in the Iridium Tracer Study of the Extractability of Iridium in the Presence of Rhodium and the Recovery of Iridium from the Organic Phase.


TOA in Benzene Solution
+
Iridium Plus Iridium Tracer
and Rhodium in 6 M HCl
Extraction
Aqueous Phase
Organic Phase
Iridium Activity Determined
Iridium Activity Determined
Backwash 6 M HCl
Aqueous Phase
Organic Phase
Iridium Activity Determined
Organic Phase Stripped with NH_4OH
Aqueous Phase
Organic Phase
Iridium Activity Determined
Iridium Activity Determined

phase after three strippings was determined.

2-4c. Results and Discussion

The results showing the extent of iridium extraction in the presence of rhodium and the extent of iridium recovery from the organic phase are given in Table III. A summary of the complete study is given at the end of the table.

For the 100 to 1500 µg iridium sample range studied, 98 to 99% of the iridium was extracted into the organic phase with a single extraction. The backwashing of the organic phase caused an iridium loss of 0.5% or less from the organic phase. The percentage of iridium extracted increased slightly (1%) with increasing amounts of iridium. Within a series of samples containing fixed quantities of iridium, the percentage of iridium extracted decreased slightly (0.7% or less) with increasing amounts of rhodium.

The percentage of iridium recovered from the organic phase by stripping with ammonium hydroxide varied between 97 and 99% depending on the amount of iridium present. Lower percentage recoveries were obtained for samples containing the greatest amount of iridium (1500 µg).

Table III

Extraction of Iridium in the Presence of Rhodium

Ir Present (μg)	Rh Present (μg)	% Ir Extracted into Organic Phase after Single Extraction	% Ir in Organic Phase after Backwash	% Ir Recovered from Organic Phase
100	0	98.7	98.4	98.9
100	0	98.0	97.6	98.6
100	0	98.2	97.7	98.7
Mean and Mean Deviation:		98.3 ± 0.3	97.9 ± 0.3	98.7 ± 0.1
100	93	98.2	97.8	98.8
100	93	98.4	98.1	98.9
100	93	97.8	97.4	98.5
Mean and Mean Deviation:		98.1 ± 0.2	97.8 ± 0.2	98.7 ± 0.2
100	465	98.3	97.8	98.9
100	465	98.0	97.5	99.1
100	465	97.9	97.4	98.6
Mean and Mean Deviation:		98.1 ± 0.2	97.6 ± 0.2	98.9 ± 0.2

Ir Present (μg)	Rh Present (μg)	% Ir Extracted into Organic Phase after Single Extraction	% Ir in Organic Phase after Backwash	% Ir Recovered from Organic Phase
100	1438	97.7	97.3	99.0
100	1438	97.8	97.2	99.2
100	1438	98.2	97.7	98.9
100	1438	97.9	97.5	98.0
Mean and Mean Deviation:		97.9 ± 0.2	97.4 ± 0.2	98.8 ± 0.4
500	0	99.3	99.1	99.1
500	0	99.1	98.9	99.0
500	0	99.2	99.0	98.9
Mean and Mean Deviation:		99.2 ± 0.1	99.0 ± 0.1	99.0 ± 0.1
500	93	99.1	98.9	98.5
500	93	99.2	99.0	99.3
500	93	99.0	98.8	98.5
Mean and Mean Deviation:		99.1 ± 0.1	98.9 ± 0.1	98.8 ± 0.4

Ir Present (μg)	Rh Present (μg)	% Ir Extracted into Organic Phase after Single Extraction	% Ir in Organic Phase after Backwash	% Ir Recovered from Organic Phase
500	465	98.9	98.4	98.9
500	465	98.6	98.2	98.1
500	465	98.9	98.6	98.2
500	465	98.6	98.3	98.0
Mean and Mean Deviation:		98.8 ± 0.2	98.4 ± 0.1	98.3 ± 0.3
500	1438	98.6	98.0	97.9
500	1438	98.6	98.4	97.5
500	1438	98.3	97.8	98.7
Mean and Mean Deviation:		98.5 ± 0.1	98.0 ± 0.2	98.0 ± 0.4

Ir Present (μg)	Rh Present (μg)	% Ir Extracted into Organic Phase after Single Extraction	% Ir in Organic Phase after Backwash	% Ir Recovered from Organic Phase
1500	0	99.3	99.1	97.9
1500	0	99.3	99.1	98.0
1500	0	99.2	99.0	97.3
1500	0	99.2	99.0	96.9
Mean and Mean Deviation:		99.2 ± 0.1	99.0 ± 0.1	97.5 ± 0.4
1500	93	99.3	99.0	98.1
1500	93	99.2	99.0	98.0
1500	93	99.2	98.9	97.9
1500	93	99.3	99.1	98.1
Mean and Mean Deviation:		99.2 ± 0.1	99.0 ± 0.1	98.0 ± 0.1

Ir Present (μg)	Rh Present (μg)	% Ir Extracted into Organic Phase after Single Extraction	% Ir in Organic Phase after Backwash	% Ir Recovered from Organic Phase
1500	465	99.2	99.0	96.8
1500	465	99.1	98.8	97.2
1500	465	99.2	99.0	97.1
1500	465	99.0	98.8	96.1
Mean and Mean Deviation:		99.1 ± 0.1	98.9 ± 0.1	96.8 ± 0.4
1500	1438	98.7	98.2	97.6
1500	1438	98.9	98.6	97.8
1500	1438	99.0	98.9	97.8
1500	1438	99.1	98.9	97.8
Mean and Mean Deviation:		98.9 ± 0.1	98.7 ± 0.2	97.7 ± 0.1

Ir Present (µg)	Rh Present (µg)	% Ir Extracted into Organic Phase after Single Extraction	% Ir in Organic Phase after Backwash	% Ir Recovered from Organic Phase
100	0	98.3[a] ± 0.3	97.9[a] ± 0.3	98.7[a] ± 0.1
100	93	98.1 ± 0.2	97.8 ± 0.2	98.7 ± 0.2
100	465	98.1 ± 0.2	97.6 ± 0.2	98.9 ± 0.2
100	1438	97.9 ± 0.2	97.4 ± 0.2	98.8 ± 0.4
500	0	99.2 ± 0.1	99.0 ± 0.1	99.0 ± 0.1
500	93	99.1 ± 0.1	98.9 ± 0.1	98.8 ± 0.4
500	465	98.8 ± 0.2	98.4 ± 0.1	98.3 ± 0.3
500	1438	98.5 ± 0.1	98.0 ± 0.2	98.0 ± 0.4
1500	0	99.2 ± 0.1	99.0 ± 0.1	97.5 ± 0.4
1500	93	99.2 ± 0.1	99.0 ± 0.1	98.0 ± 0.1
1500	465	99.1 ± 0.1	98.9 ± 0.1	96.8 ± 0.4
1500	1438	98.9 ± 0.1	98.7 ± 0.2	97.7 ± 0.1

[a] mean value of at least three samples ± mean deviation

2-5. Extractability of Rhodium in the Presence of Iridium

2-5a. Sample Preparation

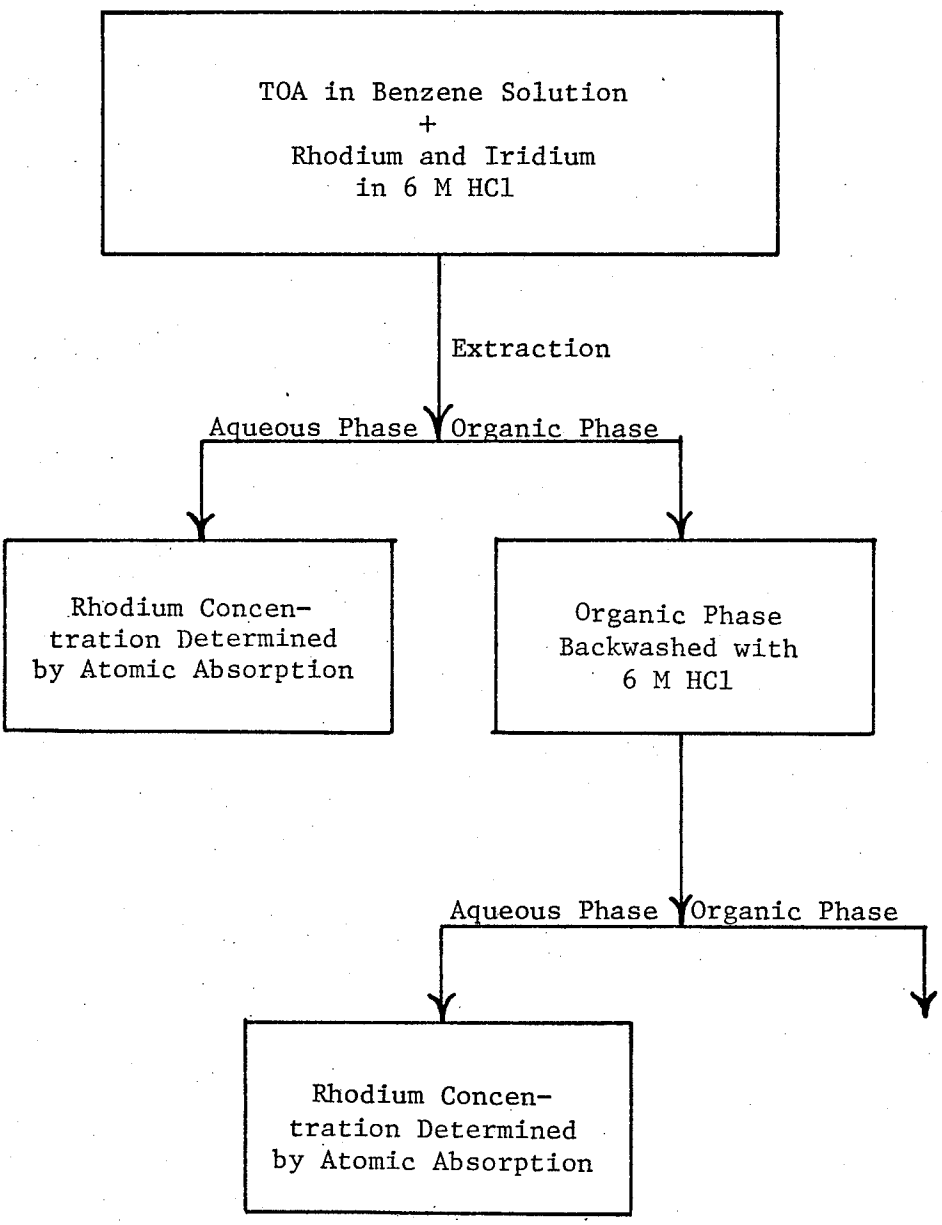
The samples were prepared in the same manner as described above except that both non-radioactive iridium and rhodium were used. Reference samples containing only rhodium were used to determine the amount of rhodium initially present.

2-5b. Procedure

A schematic of the procedure employed in the atomic absorption study of the extractability of rhodium in the presence of iridium is shown in Fig. 2. The extractions were performed as in the iridium study. The aqueous phase was drained into a test tube for the subsequent rhodium determination by atomic absorption. The organic phase remaining in the separatory funnel was transferred to a clean separatory funnel and back-washed with acid as described previously. Backwashing was necessary to recover some of the small amount of rhodium extracted with the iridium. The acid backwash was transferred to a test tube and its rhodium content determined by atomic absorption.

A cursory study of the effect of multiple extractions on the extractability of rhodium was also made. Samples containing only rhodium were extracted three times with fresh portions of TOA solution and the rhodium content in the aqueous phase determined as above. The combined organic phases were backwashed with 15 ml of acid and the rhodium content in the backwash determined.

Fig. 3. Procedure Employed in the Atomic Absorption Study of the Extractability of Rhodium in the Presence of Iridium


TOA in Benzene Solution
+
Rhodium and Iridium
in 6 M HCl
Extraction
Aqueous Phase
Organic Phase
Rhodium Concentration Determined by Atomic Absorption
Organic Phase Backwashed with 6 M HCl
Aqueous Phase
Organic Phase
Rhodium Concentration Determined by Atomic Absorption

2-5c. Rhodium Analysis

The following instrument settings were used according to the Perkin-Elmer Handbook (46):

Fuel flow rate	:	3 l/min
Air flow rate	:	24 l/min
Wavelength	:	3435 Å
Slit width	:	2 Å
Lamp current	:	16 ma

It was felt that there would be no interference from small amounts of iridium on the determination of rhodium by atomic absorption and this was demonstrated to be true for up to twice the concentration of iridium normally found in the aqueous phase after the extraction procedure. Sample solutions containing 6 ppm rhodium and 6 ppm rhodium plus 1 ppm iridium both gave the same absorbance reading of 0.106.

Sample solutions containing 1438 µg of rhodium were diluted to about 20 ppm in 6 M hydrochloric acid while more dilute samples were analyzed directly. The backwash samples were analyzed using threefold scale expansion. The rhodium concentration of the samples was compared to rhodium standards prepared in 6 M hydrochloric acid.

2-5d. Results and Discussion

The extent of rhodium extraction in the presence of iridium is shown by the results in Table IV. A summary of the complete rhodium study is given at the end of the table.

The results show the necessity for backwashing the organic phase with acid after extraction. The single backwash yielded at least 2% of

the rhodium present in the samples. Further backwashing did not recover any more rhodium.

Except for one case, little or no loss of rhodium from the aqueous phase was observed after the extraction and backwashing procedure for samples containing 93 to 465 µg rhodium and 100-1500 µg iridium. Samples containing 93 µg of rhodium and 1500 µg of iridium exhibited a 10% loss of rhodium. It would appear that this loss was due to the large amount of iridium present in the samples. In the case of samples containing 1438 µg rhodium, a rhodium loss of approximately 4% was observed.

A cursory study with 465 µg rhodium samples on the effect of multiple extractions on the extractability of rhodium showed that there was a slight increase in the loss of rhodium from the aqueous phase as compared to a single extraction. Three extractions and a backwash of the combined organic phases yielded a recovery of 455 µg of rhodium in the aqueous phase as compared to 461 µg with a single extraction and backwash.

Table IV

Extraction of Rhodium in the Presence of Iridium

Rh Present (µg)	Ir Present (µg)	Rh Found in Aqueous Phase after Single Extraction (µg)	Rh Found in Backwash (µg)	Total Rh in Aqueous Phase (µg)	% Rh in Aqueous Phase
93	0	95	3	98	105
93	0	93	2	95	102
93	0	93	1	94	101
93	0	98	3	101	109
Mean and Mean Deviation:		95 ± 2	2 ± 0.8	97 ± 2	104 ± 3
93	100	96	2	98	105
93	100	94	3	97	104
93	100	93	3	96	103
93	100	99	1	100	108
Mean and Mean Deviation:		96 ± 2	2 ± 0.8	98 ± 1	105 ± 2

Rh Present (µg)	Ir Present (µg)	Rh Found in Aqueous Phase after Single Extraction (µg)	Rh Found in Backwash (µg)	Total Rh in Aqueous Phase (µg)	% Rh in Aqueous Phase
93	500	89	2	91	98
93	500	91	3	94	101
93	500	89	2	91	98
93	500	91	3	94	101
Mean and Mean Deviation:		90 ± 1	2 ± 0.5	92 ± 2	100 ± 2
93	1500	78	3	81	87
93	1500	81	4	85	91
93	1500	80	6	86	92
93	1500	76	6	82	88
Mean and Mean Deviation:		79 ± 2	5 ± 1	84 ± 2	90 ± 2

Rh Present (μg)	Ir Present (μg)	Rh Found in Aqueous Phase after Single Extraction (μg)	Rh Found in Backwash (μg)	Total Rh in Aqueous Phase (μg)	% Rh in Aqueous Phase
465	0	450	12	462	99.4
465	0	453	10	463	99.6
465	0	453	10	463	99.6
465	0	447	10	457	98.3
Mean and Mean Deviation:		451 ± 2	10 ± 0.5	461 ± 2	99.2 ± 0.4
465	100	450	10	460	98.9
465	100	456	14	470	101.1
465	100	448	12	460	98.9
465	100	456	10	466	100.2
Mean and Mean Deviation:		452 ± 4	12 ± 2	464 ± 4	99.8 ± 0.9

Rh Present (µg)	Ir Present (µg)	Rh Found in Aqueous Phase after Single Extraction (µg)	Rh Found in Backwash (µg)	Total Rh in Aqueous Phase (µg)	% Rh in Aqueous Phase
465	500	444	12	456	98.1
465	500	453	12	465	100.0
465	500	456	12	468	100.5
465	500	444	12	456	98.1
Mean and Mean Deviation:		449 ± 5	12 ± 0	461 ± 5	99.2 ± 0.9
465	1500	447	13	460	98.7
465	1500	450	12	462	99.4
465	1500	444	12	456	98.1
465	1500	452	11	463	99.6
Mean and Mean Deviation:		448 ± 3	12 ± 0.5	460 ± 3	99.0 ± 0.6

Rh Present (µg)	Ir Present (µg)	Rh Found in Aqueous Phase after Single Extraction (µg)	Rh Found in Backwash (µg)	Total Rh in Aqueous Phase (µg)	% Rh in Aqueous Phase
1438	0	1350	32	1382	96.1
1438	0	1328	32	1360	94.6
1438	0	1335	40	1375	95.6
1438	0	1365	30	1395	97.0
Mean and Mean Deviation:		1344 ± 13	34 ± 4	1378 ± 10	95.8 ± 0.7
1438	100	1350	30	1380	96.0
1438	100	1335	30	1365	94.9
1438	100	1350	32	1382	96.1
1438	100	1365	30	1395	97.0
Mean and Mean Deviation:		1350 ± 8	30 ± 0.5	1380 ± 8	96.0 ± 0.6

Rh Present (μg)	Ir Present (μg)	Rh Found in Aqueous Phase after Single Extraction (μg)	Rh Found in Backwash (μg)	Total Rh in Aqueous Phase (μg)	% Rh in Aqueous Phase
1438	500	1365	30	1395	97.0
1438	500	1350	30	1380	96.0
1438	500	1350	32	1382	96.1
1438	500	1328	32	1360	94.6
Mean and Mean Deviation:		1348 ± 10	31 ± 1	1379 ± 13	95.9 ± 0.7
1438	1500	1358	30	1388	96.5
1438	1500	1335	32	1367	95.1
1438	1500	1350	32	1382	96.1
1438	1500	1358	30	1388	96.5
Mean and Mean Deviation:		1350 ± 8	31 ± 1	1381 ± 7	96.0 ± 0.5

Summary

Rh Present (μg)	Ir Present (μg)	Rh Found in Aqueous Phase after Single Extraction (μg)	Rh Found in Backwash (μg)	Total Rh in Aqueous Phase (μg)	% Rh in Aqueous Phase
93	0	95[a] ± 2	2[a] ± 0.8	97[a] ± 2	104[a] ± 3
93	100	96 ± 2	2 ± 0.8	98 ± 1	105 ± 2
93	500	90 ± 1	2 ± 0.5	92 ± 2	100 ± 2
93	1500	79 ± 2	5 ± 1	84 ± 2	90 ± 2
465	0	451 ± 2	10 ± 0.5	461 ± 2	99.2 ± 0.4
465	100	452 ± 4	12 ± 2	464 ± 4	99.8 ± 0.9
465	500	449 ± 5	12 ± 0	461 ± 5	99.2 ± 0.9
465	1500	448 ± 3	12 ± 0.5	460 ± 3	99.0 ± 0.6
1438	0	1344 ± 13	34 ± 4	1378 ± 10	95.8 ± 0.7
1438	100	1350 ± 8	30 ± 0.5	1380 ± 8	96.0 ± 0.6
1438	500	1348 ± 10	31 ± 1	1379 ± 13	95.9 ± 0.7
1438	1500	1350 ± 8	31 ± 1	1381 ± 7	96.0 ± 0.5

[a]mean value of four samples ± mean deviation

2-6. Separation of Iridium from Rhodium

The separation of iridium from rhodium was determined from the combination of the results of the two separate rhodium and iridium extraction studies mentioned above.

2.6a. Results and Discussion

Results showing the separation of 100 to 1500 µg of iridium from 93 to 1438 µg of rhodium are given in Table V. The results shown are for a single extraction and backwash.

For samples containing 100 to 1500 µg of iridium in the presence of 93 to 465 µg of rhodium, essentially rhodium-free iridium was obtained except in one case. The samples containing 1500 µg of iridium and 93 µg of rhodium exhibited a 10% loss of rhodium to the organic phase on extraction. It would appear that the maximum ratio of iridium to rhodium which can be tolerated without serious rhodium losses is between five and fifteen.

With respect to the iridium samples containing 1438 µg of rhodium, about 4% rhodium was extracted into the organic phase with the iridium.

Iridium-free rhodium could not be obtained with a single extraction and backwash. Approximately 1 to 3% iridium was found in the aqueous phase.

2-6b. Summary of Separation Procedure Employed

Sample solutions containing rhodium and iridium as their tervalent and quadrivalent chloro complexes respectively were first treated with aqua regia and concentrated hydrochloric acid to ensure that the iridium was in the form of the quadrivalent chloro complex. The dry sample residues

Table V

Separation of Iridium from Rhodium

with Single Extraction and Backwash

Iridium Present (µg)	Rhodium Present (µg)	% Iridium in Organic Phase	% Rhodium in Aqueous Phase
100	93	97.8[a] ± 0.2	105[a] ± 2
500	93	98.9 ± 0.1	100 ± 2
1500	93	99.0 ± 0.1	90 ± 2
100	465	97.6 ± 0.2	99.8 ± 0.9
500	465	98.4 ± 0.1	99.2 ± 0.9
1500	465	98.9 ± 0.1	99.0 ± 0.6
100	1438	97.4 ± 0.2	96.0 ± 0.6
500	1438	98.0 ± 0.2	95.9 ± 0.7
1500	1438	98.7 ± 0.2	96.0 ± 0.5

[a]mean value of at least three samples ± mean deviation

were dissolved in 6 M hydrochloric acid and transferred to separatory funnels to which 0.2 M TOA was then added. Chlorine was bubbled through the solutions until a slight haziness appeared in the organic phase. The chlorine prevented the reduction of the iridium to the less-extractable tervalent chloro complex. The separatory funnels were then shaken by hand for two minutes and the phases allowed to separate. The aqueous phase containing the rhodium was drained and the organic phase backwashed with additional 6 M hydrochloric acid (again using chlorine) to recover most of the small amount of rhodium co-extracted with the iridium. The extracted iridium in the organic phase was recovered by stripping with three portions of 7 M ammonium hydroxide.

2-6c. Conclusion

The procedure used and given in summary above provides a reasonably fast separational method for rhodium and iridium using standard equipment. The method gives quantitative recovery of rhodium and 98 to 99% recovery of iridium when using samples in the 100 - 500 μg range.

IV | SUMMARY

Two methods have been developed for the separation of the chloro complexes of rhodium and iridium in an attempt to provide simplified procedures for separating the two noble metals: anion-exchange with strongly basic resin, and solvent extraction involving the use of tri-n-octylamine (TOA) as a liquid anion-exchanger. The two separation methods were applied to a wide concentration range of rhodium and iridium.

The anion-exchange method was used to separate and quantitatively recover 100 to 1000 µg quantities of both metals in various ratios. The use of hot concentrated nitric acid to elute the iridium from the resin bed eliminated the necessity for the Soxhlet extraction of the resin or the use of excessive amounts of salts and acids to remove the iridium from the resin as recorded by previous workers (23,25) in other anion-exchange separations of the two metals. The anion-exchange method developed in this study has an advantage over some cation-exchange separations (24,27,28) in that organic complexes of rhodium and iridium do not have to be formed prior to their separation.

The solvent extraction procedure developed, using TOA as a liquid anion-exchanger, provided a reasonably fast and simple separational method for rhodium and iridium using standard equipment. Quantitative recovery of rhodium and 98 to 99% recovery of iridium was achieved when using samples in the 100-500 µg range. This method has the advantage that the separated noble metals are not contaminated by other metals as is the case in both the tin bromide-isopentyl

alcohol (36) and the 4,5-dimethyl-2-mercaptothiazole (35) extraction methods. In the tin bromide-isopentyl alcohol method, both rhodium and iridium are present as their tin (II) bromide complexes whereas in the 4,5-dimethyl-2-mercaptothiazole method the iridium in the aqueous phase is contaminated by either tin or chromium which are used as reducing agents.

This study has also served to emphasize the difficulties involved in developing satisfactory separational procedures for rhodium and iridium due to the complicated nature of the solution chemistry of these two metals.

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