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CANADIAN THESES ON MICROFICHE

THÈSES CANADIENNES SUR MICROFICHE

NAME OF AUTHOR/NOM DE L'AUTEUR WALKER, Robert J.

TITLE OF THESIS/TITRE DE LA THÈSE The separation of palladium from the other platinum metals and associated base metals.

UNIVERSITY/UNIVERSITÉ University of Windsor, Windsor, Ontario

DEGREE FOR WHICH THESIS WAS PRESENTED /
GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE Ph.D.

YEAR THIS DEGREE CONFERRED/ANNÉE D'OBTENTION DE CE DEGRÉ 1974

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THE SEPARATION OF PALLADIUM FROM THE OTHER
PLATINUM METALS AND ASSOCIATED BASE METALS

BY

ROBERT J. WALKER

A Dissertation
Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy at the
University of Windsor

Windsor, Ontario

1974

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... 'Too well loved to ever be forgotten'

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ABSTRACT

PART I

A study of the extraction of the four symmetrical alkyl ketoxime complexes of palladium (II) chloride into chloroform is given. The effects of pH on the chloroform extraction of the 4-heptanone oxime complex of palladium (II) chloride from aqueous-alcohol solution is presented. At least 99% of the palladium (II) taken is extracted into chloroform from 1M hydrochloric acid solution while iron (III) and nickel (II) are not extracted in macroscopic amounts under the same conditions.

PART II

A procedure is outlined for the quantitative extraction of palladium (II) into chloroform as the 4-heptanone oxime complex. The effects due to hydrochloric acid, alcohol and oxime concentrations are described. Cobalt (II) and copper (II) are not extracted in macroscopic amounts under the same conditions.

PART III

A procedure is outlined for the extraction of the gold (III) chloride complex of 4-heptanone oxime into

chloroform. The effects due to hydrochloric acid concentration, oxime concentration and multiple extraction are described.

PART IV

A study of the chloroform extraction of the platinum (IV), rhodium (III), iridium (IV), iridium (III) and platinum (II) chlorides with 4-heptanone oxime is given. Trace amounts of platinum (IV) and rhodium (III) are extracted. Iridium (IV) and iridium (III) constitute a minor interference while platinum (II) constitutes a major interference.

PART V

A procedure is outlined for the quantitative separation of microgram amounts of palladium from hydrochloric acid solution and hydrochloric acid solution containing milligram amounts of platinum (IV) and microgram amounts of rhodium (III) and iridium (IV).

PART VI

A procedure is outlined for the separation of microgram amounts of palladium (II) from hydrochloric or sulphuric acid solutions containing gram amounts of the base metals copper (II), nickel (II) and iron (III). This procedure is satisfactory for each system separately

or a synthetic mixture. Results are given for the efficiency of the separation procedure as applied to a certified, standard reference matte.

ACKNOWLEDGEMENTS

I would like to thank Dr. W.J. Holland for his courteous patience and expert guidance during the course of this work.

A great deal of gratefulness is extended to my wife; Judy for her excellent typing of this dissertation and her encouragement, without which this work could not have been done.

I wish to acknowledge the financial assistance provided by a Province of Ontario Graduate Fellowship, a Teaching Assistantship and Research Assistantship from the Department of Chemistry, the University of Windsor, as well as the support of the National Research Council of Canada.



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GENERAL INTRODUCTION

The past decade has witnessed a considerable extension of analytical chemistry into adjacent specialized fields of chemistry. The greatest extension of analytical methods has resulted in a great many, new analytical tools or instruments; the great majority of today's chemical literature proves this point! Thus, the development of separational methods of analysis has not matched the ever increasing interest in determinative methods.

Even to date, some of the complex solution chemistry of many noble metals is not yet known. The basic knowledge of noble metals in solution will provide the analytical researcher with an intelligent attitude towards the problems that he may encounter. Such data as effects of acidity, salt content, stability constants and rates of reaction can pave the way to a more basic understanding of separational methods such as ion-exchange, precipitation, fire assay, chromatography and solvent extraction.

The new determinative methods such as atomic absorption, radioactivation, X-ray spectrometry and spectrochemical analysis almost always lead to the question of financial outlay. Furthermore, despite the general usefulness of these methods, the problems of interferences still

continue to make necessary good methods of separation. New methods of solvent extraction must be recorded and the deficiencies of the old ones recognized and overcome.

In the area of ore analysis the need still exists for separational methods of noble metals from naturally occurring complex matrices. Such procedures are even more necessary in the light of today's rising costs of the noble metals. Thus, the ability for quick, reliable data on the commercial usefulness of the less rich deposits becomes increasingly important.

Solvent extraction methods for the separation and purification of metals have developed considerably during the past twenty years owing to stringent requirements for the purity of metals for commercial purposes. The choice and applicability of solvent extraction, rather than alternative methods for separation or purification processes in the production of metals depends mostly on costs as well as its unique ability to achieve a high standard of purity. Compared to methods of chromatography, solvent extraction possesses such advantages as:

- a) they are suitable for continuous operation;
- b) they are capable of producing very pure products in relatively few stages;
- c) they are easy to control, and for a given size of equipment have a high throughput.

Other than the introduction of fire hazards by the use of

5

organic solvents the only disadvantage of solvent extraction is the amount of preliminary laboratory study necessary to obtain a satisfactory procedure.

For details on the theory and applications of solvent extraction in analytical chemistry, the excellent text of Morrison and Freiser (1) should be consulted.

With regards to the noble metals and their chemistry, extensive reviews have been written by F.E. Beamish (2,3) as well as an excellent book (4) to update the activities on all aspects of the noble metals.

It is a fact that no proved wet procedure, as applied to ores and concentrates has ever been recorded, but theoretically wet methods will make available for accurate determination each of the platinum metals. A practical problem exists when dealing with, even the high grade ores of Northern Ontario, which dilute about 200-400 µg of total platinum metals in about 30 g of crude ore. The methods most often employed are methods grouped under the heading of 'en masse'. Of these methods the one which receives most acclaim in analytical separations of noble metals is fire assay. Such technologies as formation of fluxes, lead-alloy collection and silver bead collection are included under fire assay techniques.

Even the assayer who requires the highest accuracy obtainable must inevitably become acquainted with the most suitable wet separational methods. Gilchrist and

Wichers (5) proceeded to develop a method of separation (which is the most generally effective separation thus far recorded) to isolate all six of the platinum metals. Unfortunately this method is not applicable to ores or to small amounts of platinum metals in the presence of large proportions of base metals.

Gilchrist's procedure is outlined in Figure 1.

From solutions of the hexabromosmate or solutions made by caustic fusions, osmium is quickly distilled in the presence of a 10% (volume) nitric acid solution. Ruthenium is next isolated by distilling its tetroxide from a solution of the sulphates in diluted sulfuric acid to which sodium bromate is added. Platinum is separated by precipitation as the sulphide and determined after ignition to the metal. In acidified medium, palladium is separated with dimethylglyoxime and then determined by ignition to the metal. Rhodium is separated from iridium by reducing it to the metal with titanous chloride in a boiling solution of the sulphates in sulphuric acid. The rhodium is then precipitated as the sulphide and then reduced to the metal. Iridium is thus separated from titanium with cupferron and the hydrated oxide precipitated and ignited to the metal. This method of Gilchrist's is recommended for amounts of platinum metals of the order of about 100mg or more, thus limiting its application.

A complete procedure for the separation and

determination of the platinum metals on a microscale was recorded by Westland and Beamish (6) and a schematic description is presented in Figure 2. After collective distillations of both osmium and ruthenium, thiourea formed additive products that were extractable with chloroform. Platinum and palladium were isolated from iridium and rhodium with tellurium powder, after fuming with sulphuric acid. The platinum and palladium were then determined using p-nitrosodimethylamine. Rhodium was then separated from iridium by boiling a sulphuric acid solution with antimony dust, and thus precipitating the rhodium. The rhodium was then determined with 2-mercapto-4,5-dimethylthiazole and the iridium determined by the stannous bromide method.

Figure 1. Separation of macro amounts of platinum metals.

Figure 1

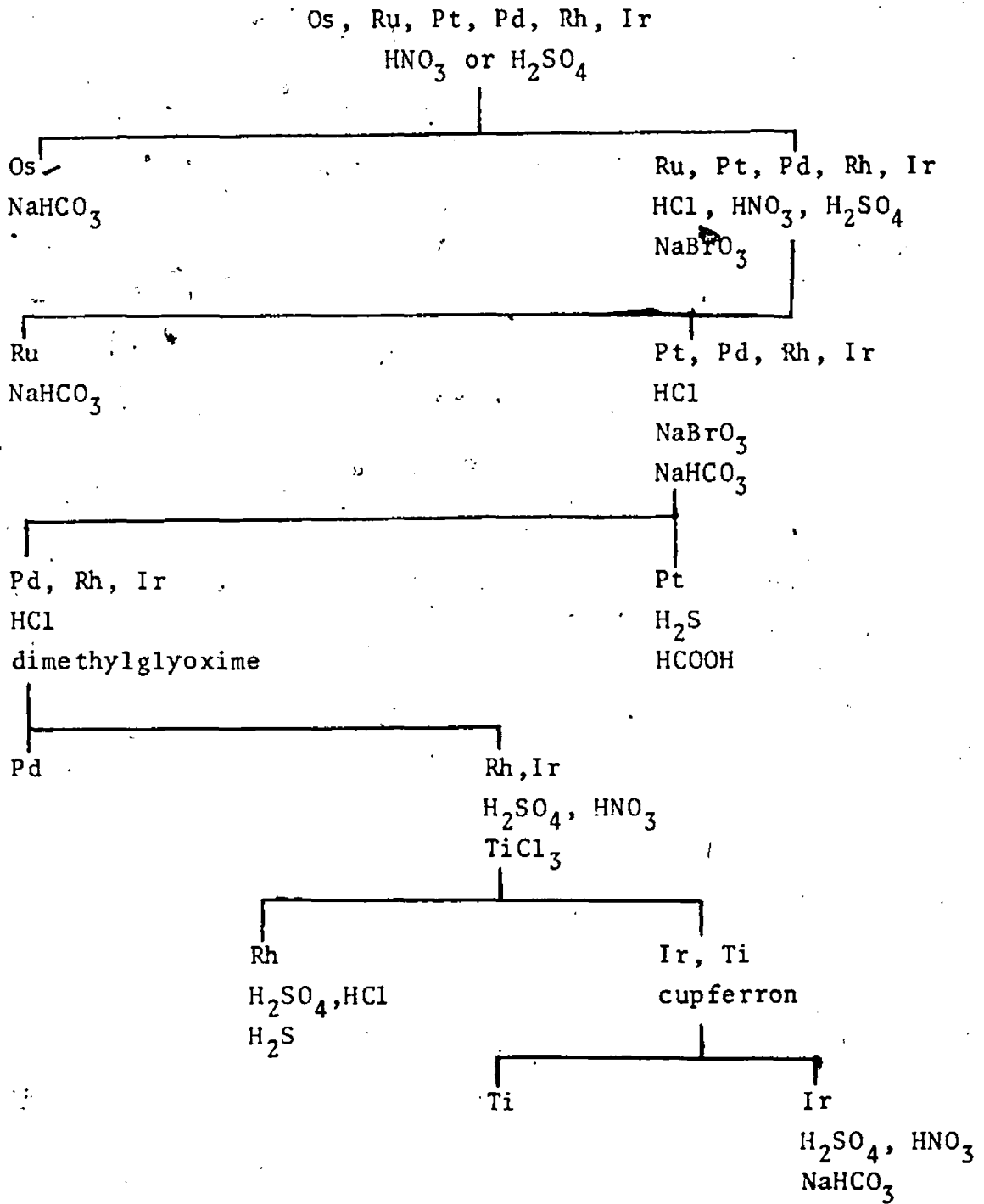
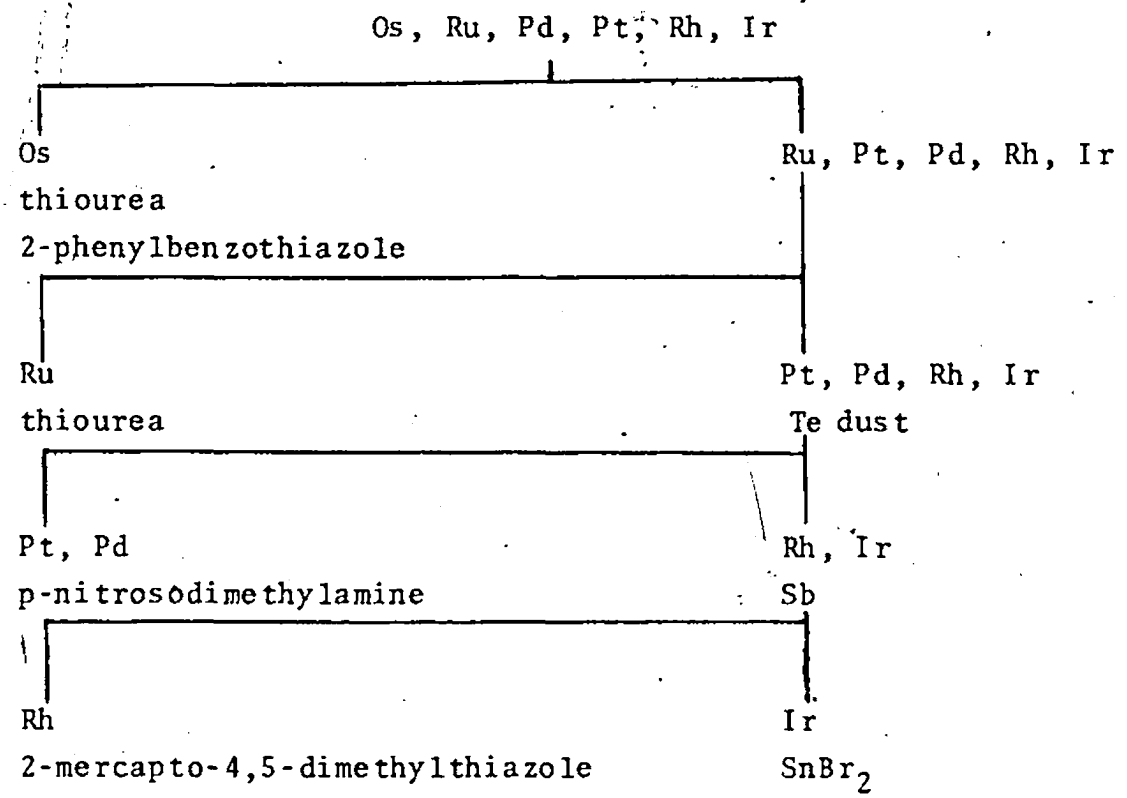


Figure 2. Separation of micro amounts of platinum metals.

Figure 2



Since these workers, many attempts have been made to improve the separation methods that would be applied directly to complex mixtures. The work that is described in the following document is an attempt to find a solvent extraction procedure (starting with a study on palladium) using oximes which can be applied to some type of complex matrix and still achieve acceptable separations.

PART I

THE CHLOROFORM EXTRACTION OF THE
ALKYL KETOXIME COMPLEXES OF
PALLADIUM (II) CHLORIDE

CHAPTER I

INTRODUCTION

Undoubtedly the most important types of organic reagents for palladium are those containing the oxime group.

A great many of these have been studied for use with palladium but most of these are used in conjunction with a spectrophotometric determinative procedure.

Probably the greatest find of all oximes was dimethylglyoxime. Its application to quantitative analysis was first recorded by Duparc (7) and by Wunder and Thuringer (8-10) who found that it quantitatively precipitated palladium and nickel under different conditions. The fact that palladium can be practically completely converted to the dimethylglyoxime complex is attested by its application, through solvent extraction, to micro determinations.

Benzoylmethylglyoxime was proposed by Hanus, Julek and Lukas (11) and later by Holzer (12). Gold interfered, but the remaining platinum metals did not; nor was there interference from a large number of cations including iron, cobalt and nickel. The usual claims of all reagents competing with dimethylglyoxime are made, namely a greater water solubility of the reagent, a more favourable gravimetric factor and a precipitate of improved physical characteristics.

Similar claims are made for such reagents as 1,2-cyclohexanedione dioxime (nioxime) (13) as well as others such as β -furaldoxime (14), α -benzoinoxime (15) and oxalenediamidoxime (16).

Salicylaldoxime (17) was used for trace separations of palladium from rhodium by extraction into 4-methyl-2-pentanone.

Some of the non-oxime reagents used for separating palladium are as follows: triphenylphosphine, -arsine and -stibine (18), tri-n-octylamine (19), isobutyl methyl ketone for separation of palladium as the iodide (20), dimethyl ether with tetraiodopalladate (II) into methylene chloride (21), isopropenylacetylene (22) and Reineckes' salt (23) which separates palladium from gold and platinum with reasonable accuracy.

Holland and co-workers have extended the use of oximes to spectrophotometric procedures for palladium. Such reagents as 2,2'-dipyridyl ketoxime (24) and 2,2'-diquinolyl ketoxime (25) were proposed. As well 2,2'-dithienyl ketoxime (26) was used for the gravimetric separation of palladium. Holland utilized the fact that no separation of isomers was required when symmetrical ketoximes were synthesized.

With the idea of using symmetrical ketoximes as analytical reagents, the possibility of isolating complexes of palladium (II) with 2-propanone oxime, 3-pentanone oxime, 4-heptanone oxime and 5-nonanone oxime was accomplished

by DiMenna (27). It was discovered that these complexes showed extremely high solubilities in chloroform. The possibility of utilizing these oximes for solvent extraction purposes of milligram amounts of palladium became increasingly evident.

The present work constitutes an investigation into the extractability of these complexes of palladium. A study of 4-heptanone oxime yields results of the effect of pH on the percent palladium(II) extracted from an aqueous-alcohol solution, a statistical study of the amount of palladium(II) extracted from an aqueous-alcohol solution 1.0M in hydrochloric acid and an investigation of the extraction of iron(III), and nickel(II) from an aqueous-alcohol solution 1.0M in hydrochloric acid.

CHAPTER II

EXPERIMENTAL

A. APPARATUS AND MATERIALS

1) Instrument

A Sargent Model - D R pH meter was used for all pH measurements.

2) 4-Heptanone Oxime

The oxime was prepared by refluxing 4-heptanone with hydroxylamine hydrochloride in an alkaline alcohol-water mixture, evaporating the excess alcohol, drying the oily top layer over anhydrous calcium chloride and distilling under vacuum.

3) Standard Palladium (II) Chloride Solution

A stock solution was prepared by dissolving anhydrous palladium (II) chloride in 30 ml of concentrated hydrochloric acid, diluting to 1 liter with distilled water and standardizing gravimetrically with di-2-pyridyl ketoxime (28) to give a solution containing 45 mg of palladium (II) per 25 ml of stock solution.

4) Diverse Cation Solutions

Reagent grade chloride salts of nickel (II) and iron (III) were used.

5) Miscellaneous Reagents

The chloroform, ethanol, hydrochloric acid and

sodium hydroxide were A.C.S. grade.

6) Palladium(II) Chloride

Purified anhydrous palladium(II) chloride was obtained from Fisher Scientific Company.

B. PROCEDURES

1) Extraction Procedure Used to Study the Series of Aliphatic Oximes

A 25 ml aliquot of the standard palladium (II) chloride solution was transferred to a 150 ml beaker and the pH adjusted to 3.0 by the addition of sodium hydroxide solution. The solution was transferred to a 250 ml graduated separatory funnel. To a 100 ml beaker was added 0.010 mole of the alkyl ketoxime, 12 ml of alcohol and 2 ml of distilled water. After adjusting the pH to 3.0 by the addition of dilute hydrochloric acid, the oxime solution was added to the separatory funnel. The electrodes were rinsed with 1 ml of alcohol and the rinsings added to the separatory funnel. The solution in the separatory funnel was diluted to 100 ml with distilled water of pH 3.0, shaken and then allowed to stand for 20 minutes and extracted with three 30 ml portions and one 10 ml portion of chloroform. The chloroform extracts were collected in a 250 ml beaker and evaporated to dryness on a steam bath.

2) Palladium Analysis of the Chloroform Layer

To the residue in the beaker were added 10 ml of aqua regia and the solution was evaporated to dryness. The aqua regia digestion was repeated once more and

10 ml of concentrated hydrochloric acid were added to the residue. The solution was evaporated to near dryness. After the addition of 25 ml of distilled water, the solution was filtered into a 250 ml beaker. The filter paper, containing a small amount of insoluble matter, was dried and ignited in a porcelain crucible. To the residue were added a few drops of formic acid (29) and the crucible heated to dryness on a hot plate. The very small amount of palladium was dissolved in a few ml of concentrated hydrochloric acid containing a few drops of concentrated nitric acid. The solution in the crucible was transferred to the beaker containing the original filtrate and the palladium content determined gravimetrically with di-2-pyridyl ketoxime (28).

The results are summarized in Table I.

3) Palladium Analysis of the Water Layer

To the water layer were added 10 ml of aqua regia and the solution evaporated to dryness. The aqua regia digestion was repeated once more, the residue brought into solution by the addition of 50 ml of distilled water and the palladium determined gravimetrically with di-2-pyridyl ketoxime.

The results of the analyses are summarized in Table I.

4) Procedure for the Study of the Effect of Acidity on the Extraction of the 4-Heptanone Oxime Complex of Pd (II).

A 25 ml aliquot (~45 mg) of the standard palladium (II) chloride solution was transferred to a 150 ml beaker

and the pH adjusted by the addition of sodium hydroxide or hydrochloric acid solution. The solution was transferred to a 250 ml graduated separatory funnel. To a 100 ml beaker was added 0.010 mole of 4-heptanone oxime, 13 ml of alcohol and 2 ml of distilled water. After adjusting the pH to the same value as the palladium (II) chloride solution, the oxime solution was added to the separatory funnel. The mixture was diluted to the 100 ml mark with distilled water of the same pH, shaken and allowed to stand for 20 minutes then extracted with three 30 ml and one 10 ml portion of chloroform.

The amount of palladium in the chloroform extracts was determined gravimetrically as palladium metal by the following procedure.

The chloroform extracts were collected in a 250 ml beaker, evaporated on a steam bath and the residue transferred to a tared porcelain crucible. The crucible was heated on a hot plate to destroy the complex, ignited over a burner and cooled. A few drops of formic acid were added to reduce any surface oxide to the metal. The crucible was then placed in an oven at 125°C for approximately 1 hour, cooled and weighed.

The results are summarized in Table II and illustrated in Figure 3.

5) Statistical Study of the Amount of Palladium (II) Extracted from an Aqueous-Ethanol Solution 1M in Hydrochloric Acid

The extraction procedure outlined above (section 4) was followed. All solutions were 1M in hydrochloric acid. The chloroform extracts were evaporated on a steam bath. Nitric and sulphuric acids were added to the residue and the beaker heated on a hot plate until dense white fumes appeared. Dilute hydrochloric acid was added and the palladium determined gravimetrically with di-2-pyridyl ketoxime.

The results are presented in Table III.

6) Extraction of Iron (III) and Nickel (II) from an Aqueous-alcohol Solution 1M in Hydrochloric Acid

The extraction procedure given above (section 4) was followed using approximately 4.2×10^{-4} mole each of ferric chloride hexahydrate and nickel (II) chloride hexahydrate. The aqueous layers were collected in 400 ml beakers and the organic matter destroyed by digestion with sulphuric acid and hydrogen peroxide. Iron (III) was determined gravimetrically with 8-hydroxyquinoline and the nickel (II) was determined gravimetrically with dimethylglyoxime.

The results are summarized in Table IV.

TABLE I

Palladium Analyses - Palladium Taken, 44.9 mg.

Oxime	Palladium Found in Water Layer mg	Palladium Found in Chloroform Layer mg	Total Palladium Recovered mg	% Palladium Extracted
Acetoxime	4.3	40.0	44.3	88.9
	4.2	40.1	44.3	89.3
3-Pentanone Oxime	0.2	44.3	44.5	98.7
	0.0	44.9	44.9	100
4-Heptanone Oxime	0.1	44.5	44.6	99.1
	0.1	44.9	45.0	100
5-Nonanone Oxime	0.1	44.3	44.4	98.9
	0.1	44.5	44.6	99.1

TABLE II

Effect of pH on the Amount of Palladium Extracted

pH	Palladium Taken, mg	Palladium found in Chloroform Extract, mg	% Palladium Extracted
2.51	44.9	45.2	100.7
2.50	44.9	44.5	99.1
2.00	44.9	44.4	98.9
2.01	44.9	44.5	99.1
1.49	44.9	44.9	100.0
1.50	44.9	44.5	99.1
0.54	44.9	44.6	99.3
0.54	44.9	44.5	99.1
0.0 (1M HCl)	45.0	44.6	99.1
0.0 (1M HCl)	45.0	44.7	99.3
-0.18 (1.5M HCl)	45.0	44.4	98.7
-0.18 (1.5M HCl)	45.0	44.4	98.7
-0.48 (3.0M HCl)	45.0	39.5	87.8
-0.48 (3.0M HCl)	45.0	39.1	86.9
-0.70 (5.0M HCl)	45.0	15.3	34.0
-0.70 (5.0M HCl)	45.0	15.1	33.6

TABLE III

Amount of Pd Extracted from Aqueous-alcohol
 Solution 1M in Hydrochloric Acid
 Pd Taken 45.0 mg

Run	Palladium Found in Chloroform Extract, mg	% Palladium Extracted
1	45.0	100.0
2	44.6	99.1
3	45.1	100.2
4	44.9	99.8
5	44.8	99.6
6	44.9	99.8
Average	44.9	99.8
Standard Deviation	+0.2	+0.4

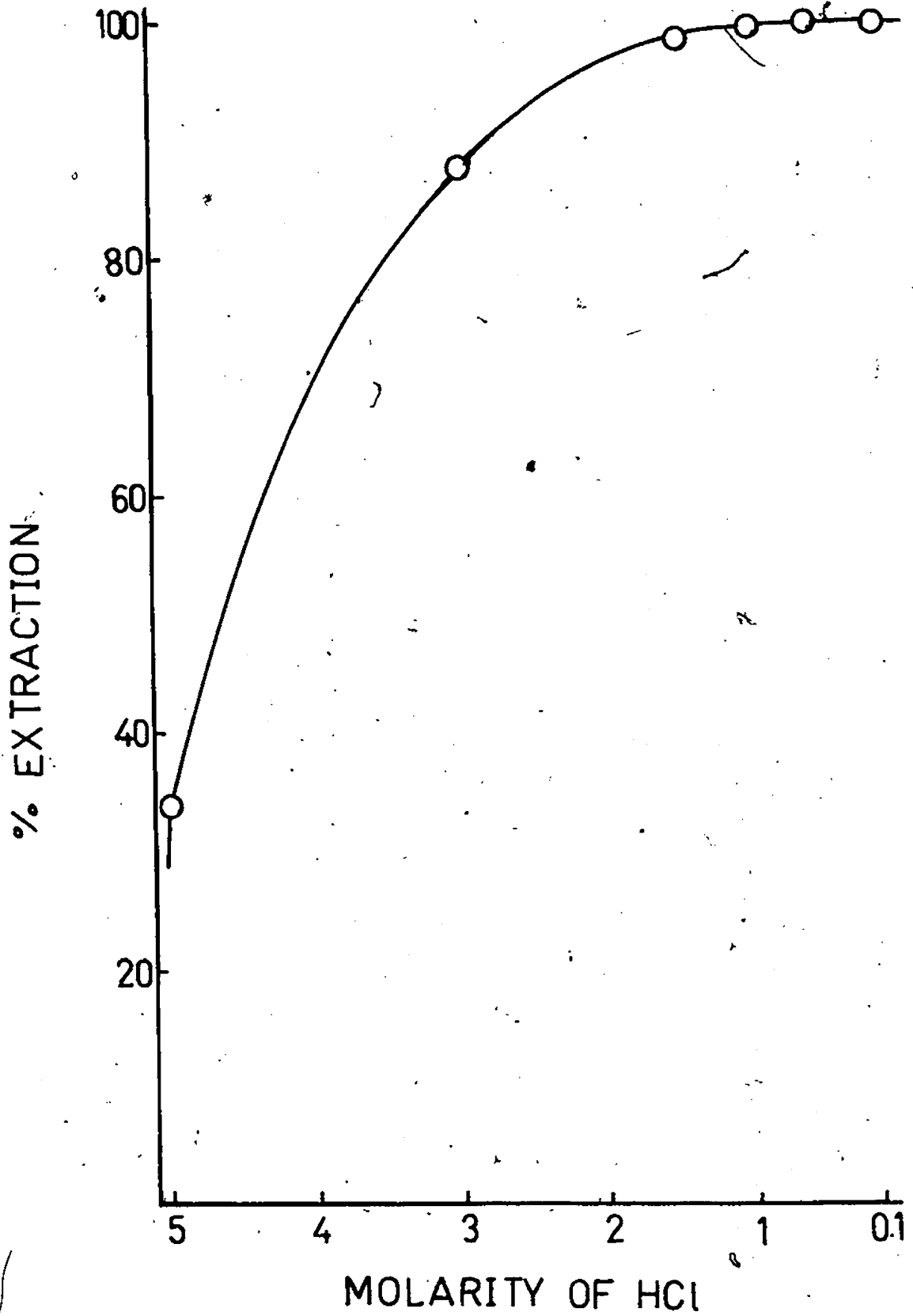
TABLE IV
Extraction of Iron (III) and Nickel (II)
from Aqueous-alcohol Solutions
1M in Hydrochloric Acid

Fe (III) taken, mg	Fe (III) found in aqueous layer,mg	Ni (II) taken, mg	Ni (II) found in aqueous layer, mg
23.6	23.5	25.8	25.6
23.5	23.4	26.0	25.9

Figure 3. Effect of Acidity on the Amount of Palladium Extracted.



FIGURE 3



CHAPTER III

RESULTS AND DISCUSSION

From the conception of the idea of using symmetrical alkyl ketoximes as complexing agents for palladium (II) comes the following results. The results of the original chloroform extraction study indicate that relatively large amounts of palladium (II) chloride may be extracted into chloroform after reaction with symmetrical alkyl ketoximes in aqueous-alcohol solution at pH 3.0.

The study of scanning the four aliphatic oximes, revealed that in the case of 3-pentanone oxime, 4-heptanone oxime and 5-nonanone oxime, the extraction appears to be quantitative. The results seem to indicate that a lengthening of the aliphatic chain may lead to a more quantitative reaction and extraction. This probably will be counteracted by the fact that the solubilities in water of the aliphatic oximes would become lower as the chain length is increased, thus limiting the reactivity in an aqueous media.

The choice of further studying 4-heptanone oxime is made since it appears to be quantitative in extracting palladium (II) as the chloride complex into chloroform. Since this oxime does not seem to be at the critical point in chain length to effect differing extractabilities

and since it is appreciably soluble in aqueous-alcohol, solutions to give satisfactory reaction conditions it was chosen to be studied at different acidities.

The results of the study of the effect of acidity on the amount of palladium (II) extracted (Table II) seem to indicate that 99 to 100% of the milligram amounts (45mg) of palladium (II) may be extracted into 100 ml of chloroform after reaction with 4-heptanone oxime in 100 ml of an aqueous-alcohol solution over the pH range 0 - 2.5.

The acidity in this range seems not to be critical. Since one objective of this work is to study the separation of palladium (II) from the base metals by chloroform extraction of the alkyl ketoxime complexes of palladium (II) chloride, it was considered necessary to determine the greatest hydrochloric acid concentration that could be used and still effect 99 - 100% extraction. Low acid concentrations could result in separation difficulties due to hydrolysis of the associated base metals as well as palladium itself.

As can be seen from the results presented in Table III, greater than 99% of the palladium (II) taken can be extracted from 1M hydrochloric acid solutions. The average percent extracted is 99.8% with a standard deviation of 0.4%. From Table IV it can be seen that macroscopic amounts of iron (III) and nickel (II) are not extracted at this high acid concentration under

the same conditions. The stability of both the oxime and the palladium oxime complex at this high acid concentration is somewhat surprising since it does not form a chelate that might add to its stability.

In a private communication (30) it was discovered that under the 1M hydrochloric acid conditions, 4-heptanone oxime did not hydrolyse completely in the recommended twenty minute waiting period for reaction. At times longer than twenty minutes the oxime was hydrolysed appreciably back to the ketone and hydroxylamine hydrochloride, and thus was not available to react with the palladium (II).

CHAPTER IV

SUMMARY AND CONCLUSIONS

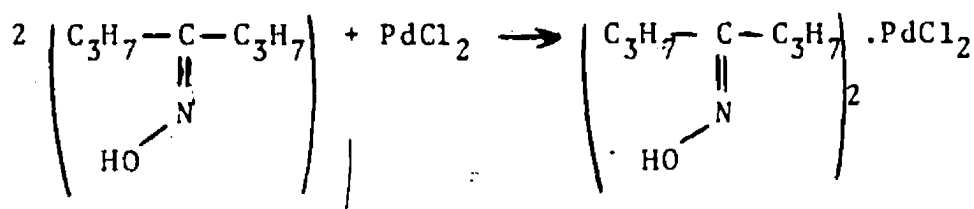
A study of the extraction of the four symmetrical alkyl ketoxime complexes of palladium (II) chloride into chloroform is given. The choice of 4-heptanone oxime as the reagent to study is rationalized. A study of the effect of pH on the chloroform extraction of the 4-heptanone oxime complex of palladium (II) chloride from aqueous-alcohol solution is presented. At least 99% of the palladium (II) taken is extracted into chloroform from 1M hydrochloric acid solution while iron (III) and nickel (II) are not extracted in macroscopic amounts under the same conditions.

A condensed version of this work has been published (27,31).

PART II
THE QUANTITATIVE EXTRACTION OF THE 4-HEPTANONE
OXIME COMPLEX OF PALLADIUM (II)
CHLORIDE INTO CHLOROFORM

CHAPTER I
INTRODUCTION

Continued studies should illuminate the reaction that occurs between palladium (II) chloride and 4-heptanone oxime and its subsequent extractability.



The previous work described in Part I showed results that give promise in the fact that a procedure might be developed in which a truly quantitative method (i.e. > 99.9%) of extraction could be effected.

In order to attempt this, the amount of palladium (II) taken was reduced from 45 mg to 18 mg. It is with this reduction the hope for quantitative extraction can be achieved.

The purpose of the present work is to investigate the application of a double extraction technique in order to effect a quantitative extraction of palladium(II). An investigation of the extraction of cobalt (II) and copper (II) under this developed procedure is also given.

CHAPTER II

EXPERIMENTAL

A. APPARATUS AND MATERIALS

1) Instruments

Spectral studies were made with a Beckman D B spectrophotometer equipped with a Sargent Model - SRL recorder and 1.00 cm matched silica cells. A Sargent Model - DR pH meter was used for pH measurements.

2) 4-Heptanone Oxime

This reagent was prepared as outlined previously (27) by reaction of hydroxylamine hydrochloride with 4-heptanone.

3) Palladium (II) Chloride

Purified anhydrous palladium (II) chloride was obtained from Fisher Scientific Company.

4) Diverse Cation Solutions

Reagent grade chloride salts of cobalt (II) and copper (II) were used in these studies.

5) Standard Palladium (II) Chloride Solution

A stock solution was prepared by dissolving anhydrous palladium (II) chloride in 30 ml of concentrated hydrochloric acid, diluting to 1 litre with distilled water and standardizing with di-2-pyridyl ketoxime (28). The solution contained 18.2 mg palladium (II) per 10 ml aliquot.

6) Miscellaneous Reagents

The chloroform, ethanol and hydrochloric acid were A.C.S. grade. The 4-heptanone was obtained from the Aldrich Chemical Company and was redistilled before use. The hydroxylamine hydrochloride was obtained from the Mallinckrodt Chemical Works.

B. PROCEDURES

1) Recommended Procedure

Transfer a 10 ml aliquot of palladium (II) chloride solution containing approximately 18 mg of palladium (II) to a 250 ml graduated separatory funnel. Add sufficient concentrated hydrochloric acid so that the solution, upon dilution to 100 ml mark is 1M in hydrochloric acid. Transfer 0.30 ml of 4-heptanone oxime to the separatory funnel and shake. Allow the solution to stand for 10 minutes and shake again. Let this stand an additional 10 minutes and extract with two 25 ml portions of chloroform. Transfer the chloroform extracts to a suitable container. Repeat the above procedure with the residual water layer. Combine the chloroform extracts (total of 100 ml) which contain more than 99.9% of the palladium taken.

2) Palladium Analysis of the Water Layer

The water layer was transferred to a 400 ml beaker. The separatory funnel was then rinsed with 5 ml of concentrated nitric acid to dissolve any trace amounts of palladium that may have adhered to the glassware. The solution was evaporated to a small volume and concentrated hydrochloric acid was added repeatedly to eliminate the oxides of nitrogen in solution. The palladium is then determined spectrophotometrically with di-2-pyridyl ketoxime (32).

3) Effect of Hydrochloric Acid Concentration

The recommended procedure described above was used with exception to the following changes. The total volume of 4-heptanone oxime reagent used was 1.4 ml. This was administered in two additions of 0.7 ml each instead of the recommended value of 0.3 ml. This study was undertaken in the presence of 13 ml of 95% ethanol. Instead of the recommended value of 1M in hydrochloric acid, these values were varied from 0.75M to 3.00M in hydrochloric acid. The results of this study are given in Table V.

4) Effect of Total Volume of 4-Heptanone Oxime

The recommended procedure described above was used in this study except the extractions were done in the presence of 13 ml of 95% ethanol. The recommended 1M hydrochloric acid concentration was kept constant as required and the total volume of 4-heptanone oxime varied from 1.0 to 0.2 ml. This amount of oxime again was added in double additions (i.e. 2 X 0.1 ml). The results of this study are summarized in Table VI.

5) Effect of Volume of Alcohol

The recommended procedure described above was used in this study except that the volume of 95% ethanol present in the extracting solution was varied from 0 to 10 ml. The results of this study are summarized in Table VII.

6) Extraction of Cobalt (II) and Copper (II)

The recommended procedure was followed using 4.2×10^{-4}

mole each of cobaltous chloride hexahydrate and cupric chloride dihydrate. The aqueous layers were collected in 400 ml beakers and the organic matter (in the case of the cupric system) was destroyed by the addition of 10 ml concentrated nitric acid and 30 ml of concentrated hydrochloric acid. Repeated additions of hydrochloric acid after evaporating the system to a small volume caused all oxides of nitrogen to be expelled. The copper (II) was then determined gravimetrically with α -benzoin oxime (33). In the case of the cobaltous system the organic matter was destroyed by digestion with concentrated sulphuric acid and the cobalt (II) then determined gravimetrically with sodium anthranilate (34) that was prepared from anthranilic acid.

The results are summarized in Table VIII.

TABLE V

Effect of Hydrochloric Acid Concentration

Palladium taken, 18.2 mg; Total volume of 4-heptanone oxime, 1.4 ml (2 X 0.7); volume of alcohol, 13 ml.

Run	Molarity of Hydrochloric Acid	Palladium Found in Water Layer, mg	% Palladium in Water Layer
1	0.75	0.001	0.005
	0.75	0.002	0.01
2	1.00	0.010	0.06
	1.00	0.009	0.05
3	1.25	0.010	0.05
	1.25	0.008	0.04
4	1.50	0.009	0.05
	1.50	0.008	0.04
5	2.00	0.012	0.07
	2.00	0.012	0.07
6	3.00	0.5	3
	3.00	0.5	3

TABLE VI
Effect of Total Volume of 4-Heptanone Oxime

Palladium taken, 18.2 mg; Volume of alcohol, 13 ml;
Hydrochloric acid concentration, 1M.

Run	Total Volume of oxime, ml	Palladium Found in Water Layer, mg	% Palladium Found in Water Layer
1	1.0	0.003	0.02
	1.0	0.008	0.04
2	0.6	0.006	0.03
	0.6	0.002	0.01
3	0.4	0.011	0.06
	0.4	0.008	0.04
4	0.2	0.154	0.85
	0.2	0.166	0.91

TABLE VII
Effect of Volume of Alcohol

Palladium taken 18.2 mg; Total volume of 4-heptanone oxime, 0.6 ml (2 X 0.3); Hydrochloric acid concentration 1M.

Run	Volume of alcohol, ml	Palladium Found in Water Layer, mg	% Palladium Found in Water Layer
1	10	0.007	0.04
	10	0.003	0.02
2	5	0.001	0.005
	5	0.003	0.02
3	3	0.006	0.03
	3	0.005	0.03
4	1	0.009	0.05
	1	0.010	0.05
5	0	0.006	0.03
	0	0.006	0.03
6	0	0.007	0.04
	0	0.005	0.03
7	0	0.012	0.07
	0	0.011	0.06
8	0	0.002	0.01
	0	0.002	0.01

TABLE VIII

Extraction of Copper (II) and Cobalt (II)

According to the Recommended Procedure

For Palladium (II)

Cu (II) taken, mg	Cu (II) found in Aqueous layer, mg	Co (II) taken, mg	Co (II) found in Aqueous layer, mg
30.9	30.8	28.4	28.4
30.9	30.8	28.4	28.3

CHAPTER III RESULTS AND DISCUSSION

The possibility of developing a procedure for the quantitative separation of palladium (II) became evident from previous studies (Part I). The choice of reducing the level of palladium (II) taken, from 45 mg to 18 mg proved very successful in the light of the results obtained from the above studies.

From the results obtained in Table V it can be seen that the concentration of the hydrochloric acid is not critical over the concentration range 0.75M to 2.00M. Over this range greater than 99.9 percent of the palladium (II) forms a complex with 4-heptanone oxime that is extractable into chloroform.

From this study, the 1M hydrochloric acid condition was chosen for further studies since this point would not be a critical factor in determining how much palladium could be extracted.

The study dealing with the effects of the total volume of oxime was then conducted at the 1M hydrochloric acid condition. The results of Table VI indicate that greater than 99.9% of the palladium (II) taken is extracted when a total of 0.4 to 1.0 ml of the oxime is used. Since this too, gave a range in which the extractability was

not critical, it was chosen to use the total volume of 0.6 ml (i.e. 2 X 0.3 ml) for further studies.

The next variable to study is the effect of varying the amount of 95% ethanol used to solubilize the oxime in aqueous media for better reaction conditions. The results of this study (Table VII) indicate that more than 99.9% of the palladium (II) taken is extracted when 0 to 13 ml of alcohol is used. In the recommended procedure using 18 mg of palladium (II) per 100 ml, no alcohol is required as a result of this study. The study of palladium at the 45 mg per 100 ml level used the alcohol in order to increase the solubility in water for the larger amounts of oxime used. This should be avoided because in some cases ethanol can act as a reducing agent which would be detrimental in any extraction procedure requiring a particular oxidation state of a metal in solution.

The results of the study of extraction of copper (II) and cobalt (II) under the recommended procedure for palladium are given in Table VIII. These results indicate that macroscopic amounts of copper (II) and cobalt (II) are not extracted using the recommended procedure. These results as well as the results of the other base metals, iron and nickel, give rise to the idea of how large amounts of these base metals can be tolerated. Later studies will reveal the extractability of palladium in the presence of larger proportions of base metals.

CHAPTER V
SUMMARY AND CONCLUSIONS

A procedure is outlined utilizing a double extraction procedure to effect a quantitative extraction (i.e. >99.9%) of palladium (II). The extraction involves the formation of the 4-heptanone oxime complex of palladium (II) chloride in aqueous 1M hydrochloric acid solution and its subsequent separation into chloroform. The effects due to hydrochloric acid, alcohol and oxime concentrations are described. Cobalt (II) and copper (II) are not extracted in macroscopic amounts under the same recommended procedure.

A condensed version of this work has been published (35).

PART III
THE CHLOROFORM EXTRACTION OF THE
4-HEPTANONE OXIME COMPLEX OF
GOLD (III) CHLORIDE

CHAPTER I

INTRODUCTION

Gold separations from the platinum metals present no problem. A variety of reagents have been proposed, the greater percentage of which are reducing agents. Gold can readily be precipitated from extremely dilute, acid solutions by such reducing agents as stannous chloride, zinc and magnesium if a suitable collector is used (36). Mercury, mercurous chloride, lead and tellurium have been used successfully as collectors. Directions for the tellurium coprecipitation are given by Pollard (37) in connection with the rhodamine method for the determination of gold.

Maynard (38) has used tetraethylammonium chloride to separate gold from small amounts of palladium and platinum.

Gilchrist reported (39) a successful procedure using sodium nitrite to separate gold from the platinum metals.

Gold can be precipitated with various organic reducing agents such as p-phenylenediamine, and hydroquinone (40,41) from hot hydrochloric acid solution.

Lehner (42) gives a list of photographic developers which precipitate gold instantly from either acid or

alkaline solutions.

The use of ethyl ether and ethyl acetate as extractants of chlorauric acid from hydrochloric acid medium is well documented (43-47). Isopropyl ether has been found more satisfactory as a solvent for extracting gold than ethyl ether, ethyl acetate, or hexone.

Trioctylphosphine oxide was used by Holbrook and Rein (48) to produce a goldbromoaurate complex extractable by chloroform.

Ziegler describes several useful procedures (49-51) of solvent extraction of gold ~~from~~ some platinum and base metals using polyethylene glycol 400 and extracting into dichloromethane.

Ethyl violet has found some use (52) in an extractive photometric determination of gold.

Tarayan *et al.* (54) removed gold with ethyl acetate at pH 1.0 as the hydrochloric acid solution.

This work presents a study of the extraction of gold according to the recommended procedure for palladium (II). As well it will describe variations in different parameters to attempt a quantitative separation of gold (III) from hydrochloric acid solution.

CHAPTER II

EXPERIMENTAL

A. APPARATUS AND MATERIALS

1) Instruments

Spectrophotometric measurements were made with a Beckman DB spectrophotometer equipped with a Sargent Model-SRL recorder and 1.00 cm matched silica cells.

A Sargent Model-DR pH meter was used for pH measurements.

2) 4-Heptanone Oxime

The reagent is prepared by the reaction of hydroxylamine hydrochloride with 4-heptanone as previously described (27). The reagent was stable for at least one year.

3) Chloroauric Acid

Chloroauric acid was obtained from Fisher Scientific Company.

4) Standard Gold (III) Chloride Solution

A stock solution was prepared by dissolving 7 g of chloroauric acid in 82 ml of concentrated hydrochloric acid, diluting to 1 liter with distilled water and standardizing with hydroquinone according to the method of Beamish, Russel and Seath (40).

5) Miscellaneous Reagents

The chloroform and the hydrochloric acid were A.C.S. grade.

B. PROCEDURES

1) Extraction of Gold (III) According to the Recommended Procedure for Palladium

An aliquot containing 33.8 mg of gold (III) was transferred to a 250 ml separatory funnel. Upon dilution to the 100 ml mark the solution was made 1.0M in hydrochloric acid. The procedure outlined in Part II of the dissertation was adhered to. That is, a total volume of 0.6 ml of 4-heptanone oxime was used in a double extraction technique (2 X 0.3 ml). The twenty minute reaction time was observed and then the solution extracted as recommended. The water layer was analyzed as described below. The results are summarized in Table XII.

2) Analysis of Gold (III) in the Water Layer

The water layer was transferred to a 150 ml beaker and aqua regia added. The separatory funnel was then rinsed with concentrated nitric acid to dissolve any trace amounts of gold that may have adhered to the glassware. These rinsings were added to the 150 ml beaker and the solution was then evaporated to a small volume. Concentrated hydrochloric acid was repeatedly rinsed down the sides of the beakers during the evaporation step to avoid losses of gold and expell the oxides of

nitrogen which might reduce the gold. The gold (III) was then determined spectrophotometrically with di-2-pyridylketoxime (55).

3) Analysis of Gold in the Chloroform Layer

The chloroform extracts were collected in 250 ml beakers and evaporated to dryness. The residual organic matter was destroyed by digestion with aqua regia. Again, concentrated hydrochloric acid was repeatedly rinsed down the sides of the beakers during the evaporation step to avoid losses of gold and expel the oxides of nitrogen which might reduce the gold. The gold was then determined gravimetrically by the method of Beamish, Russell and Seath (40).

4) Studies to Determine a Recommended Procedure of Extraction for Gold (III)

Studies were undertaken to alter the recommended procedure of extraction that was previously developed (Part II) for palladium (II). The effects of varying the hydrochloric acid concentration, reaction time, total volume of 4-heptanone oxime used and the number of extractions performed were studied. The optimum conditions found in these studies then became part of the recommended procedure for the extraction of gold (III). The aqueous and organic layers involved in these studies were analyzed according to the procedures outlined above. The results of these studies are summarized in Tables IX, X, XI, and XIII.

5) Recommended Procedure for the Extraction of Gold (III)

Transfer a 10 ml aliquot of gold (III) chloride solution which is 1.0M in hydrochloric acid and contains approximately 34 mg of gold (III) into a 250 ml graduated separatory funnel. Dilute to the 100 ml mark with distilled water making the solution 0.1M in hydrochloric acid. Transfer 0.50 ml of 4-heptanone oxime into the separatory funnel and shake vigorously for thirty seconds. Extract with two 25 ml portions of chloroform (20 seconds shaking time each). Transfer the chloroform extracts to a suitable container. Repeat the above procedure twice with the residual water layer. Combine the chloroform extracts which contain greater than 99.0% of the gold (III) taken.

TABLE IX

Effect of Hydrochloric Acid Concentration

Gold taken 33.8 mg; Total volume of 4-heptanone oxime,
1.5 ml (3 X 0.5)

Run	Molarity of Hydrochloric Acid	Gold Found in Water Layer, mg	% Gold Found in Water Layer
1	5.0	17.5	51.8
	5.0	18.5	54.7
2	3.0	6.33	18.7
	3.0	6.21	18.4
3	1.0	0.527	1.6
	1.0	0.527	1.6
4	0.5	0.439	1.3
	0.5	0.386	1.1
5	0.2	0.095	0.3
	0.2	0.071	0.2
6	0.1	0.071	0.2
	0.1	0.064	0.2
	0.1	0.040	0.1
	0.1	0.048	0.1
7	0.05	0.192	0.6
	0.05	0.090	0.3
8	0.01	0.069	0.2
	0.01	0.046	0.1
9	0.001	0.110	0.3
	0.001	0.112	0.3

TABLE X
Effect of Total Volume of 4-Heptanone Oxime

Gold taken, 33.8 mg; Hydrochloric Acid Concentration, 0.1M; triple extraction.

Run	Total Volume of Oxime, ml	Gold Found in Water Layer, mg	% Gold Found in Water Layer
1	1.80 (3x0.6)	0.122	0.4
	1.80 (3x0.6)	0.118	0.3
2	1.65 (3x0.55)	0.110	0.3
	1.65 (3x0.55)	0.112	0.3
3	1.50 (3x0.5)	0.071	0.2
	1.50 (3x0.5)	0.064	0.2
	1.50 (3x0.5)	0.040	0.1
	1.50 (3x0.5)	0.048	0.1
4	1.35 (3x0.45)	0.154	0.5
	1.35 (3x0.45)	0.146	0.4
5	1.20 (3x0.4)	0.203	0.6
	1.20 (3x0.4)	0.195	0.6

TABLE XI

Effect of Multiple Extraction

Gold taken, 33.8 mg; Hydrochloric Acid Concentration, 0.1M; Total Volume of Oxime, 1.50 ml

Number of Extractions	Oxime Volume ml	Gold Found in Water Layer, mg	% Gold Found in Water Layer
One	1 x 1.50	1.44	4.3
	1 x 1.50	1.39	4.1
Two	2 x 0.75	0.312	0.92
	2 x 0.75	0.338	1.0
Three	3 x 0.50	0.047	0.13
	3 x 0.50	0.054	0.16
Four	4 x 0.375	0.091	0.27
	4 x 0.375	0.080	0.23

TABLE XII
Extraction of Gold (III) According to the
Procedure Recommended for Palladium

Gold taken, 33.8 mg; Hydrochloric Acid Concentration, 1.0M;
Total Volume Oxime, 0.6 ml; (2 x 0.3)

Gold Found in
Water Layer,
mg

% Gold Found
in Water Layer

10.9

32.2

9.7

28.7

TABLE XIII

Extraction of Gold (III) by Recommended
Procedure: Material Balance

Gold taken, 33.8 mg; Hydrochloric Acid Concentration 0.1M;
Total Volume of Oxime, 1.5 ml (3 x 0.5)

Run	Gold Found in Water Layer, mg	Gold Found in Chloroform Layer, mg	% Gold Found in Water Layer	% Gold Found in Chloroform Layer	% Recovery
1	0.3	33.5	0.9	99.1	100.0
2	0.3	33.5	0.9	99.1	100.0
3	0.3	33.5	0.9	99.1	100.0
4	0.3	33.5	0.9	99.1	100.0
5	0.2	33.5	0.6	99.1	99.7
6	0.2	33.6	0.6	99.4	100.0

CHAPTER III
RESULTS AND DISCUSSION

The development of a quantitative extraction procedure for palladium (II) in the previous work leads to further studies that should be initiated. In all separation procedures it must be determined to what extent associated metals will be coextracted. The study of the base metals copper (II), nickel (II), cobalt (II) and iron (III) was thus undertaken. The results of these studies were reported in Part II.

In the application of palladium, whether it be in jewellery, dentistry, metallurgy or chemical products on the commercial market, there quite often exists the presence of another precious metal, namely, gold. In any assaying procedure it is necessary usually to separate gold from palladium. It was then necessary to find the extent of coextraction of gold (III) according to the recommended procedure for palladium(II). The results of Table XII indicate that approximately 70% of the gold taken at the 34 mg level is extracted when the recommended procedure for the quantitative extraction of palladium (II) is followed. Gold (III) therefore constitutes a major interference for the quantitative separation procedure for palladium (II). It is evident that a great many

other procedures would far surpass the usefulness of 4-heptanone oxime in separating a synthetic system of gold (III) and palladium (II) chlorides.

Since gold (III) was 70% extracted under the recommended extraction procedure for the quantitative separation of palladium (II), it became evident that it might be possible to make this a quantitative procedure. A study was then conducted to investigate the effects of varying the hydrochloric acid concentration, reaction time, total volume of 4-heptanone oxime used and the number of extractions performed. A combination of changes in these conditions might conceivably result in a quantitative procedure for separating milligram amounts of gold (III).

The results of varying the hydrochloric acid concentration are given in Table IX. These results indicate that the concentration of the hydrochloric acid in the range 0.2M to 0.001M is not critical. Greater than 99.0% of the gold (III) taken at the 34 mg level is extracted over this range. In order to be at a safe point in this range, the value 0.1M was chosen to be a constant in future studies.

Thus, with the concentration of hydrochloric acid remaining constant at 0.1M, a study was made of varying the total volume of 4-heptanone oxime. The results are given in Table X and indicate that greater than 99.0% of the gold (III) taken, is extracted when a total of 1.20 ml to 1.80 ml of the oxime is used.

Again, holding the hydrochloric acid concentration

constant at 0.1M and holding the total volume of 4-heptanone oxime constant at 1.50 ml, a study of varying the multiplicity of the extraction techniques was made. The results are given in Table XI and these results indicate that at least a triple extraction procedure is necessary to recover greater than 99.0% of the gold (III) taken at the 34 mg level.

The results of a study dealing with the reaction time required indicate that there is essentially a complete reaction of the 4-heptanone oxime with gold (III) in acid solution after 30 seconds shaking. It is important in the case of gold that no ethanol is present since the oxidation of gold is very easily altered. In this case of palladium (II) which is more stable than gold, the ethanol could be tolerated at higher concentrations in order to solubilize the larger amounts of 4-heptanone oxime required for reaction. This would tend to indicate that a further study of gold (III) extracted at larger milligram quantities might be limited if ethanol were required for solubility purposes.

The overall result of these studies show that a completely quantitative (i.e. > 99.9%) extraction procedure is not possible at the 34 mg level. The recommended procedure for the extraction of gold (III) was thus developed from the cumulative optimum conditions of all the studies. This procedure is very acceptable for extracting greater than 99.9% of the gold(III) complex

of 4-heptanone oxime into chloroform. It should be noted that studies of palladium (even though they are not exactly comparable conditions) indicate that both palladium (II) and gold (III) would be nearly quantitatively extracted under the conditions for the recommended procedure for gold (III).

In a private communication (30), Dunn described experiments with trace amounts of gold (III). It became evident that at this level the efficiency of extraction dropped off considerably. These studies lead to an explanation of why a truly quantitative procedure for the extraction of gold (III) at the 34 mg level is not possible. It appears that hydrolysis of the oxime, even at trace levels, yields the ketone and hydroxylamine hydrochloride. The hydroxylamine hydrochloride acts as a reducing agent and thus a 100% extraction becomes impossible as the gold may appear as gold (I) or even as elemental gold. The reduced acidity (0.1M) as opposed to the 1.0M condition for palladium may be the reason for a substantial increase in extraction from 70% to greater than 99.0%.

A material balance was made studying the percent recovery of a series of extractions according to the recommended procedure of extraction for gold (III). The results of this study are summarized in Table XIII and these results indicate that greater than 99.0% of the gold (III) is extracted. The reliability of the methods used in the analyses of the water and chloroform layers

is good since the percent recovered in the mass balance was almost always 100%.

In order to understand the reaction of gold (III) with 4-heptanone oxime, attempts were made to isolate the complex. The composition of the complex could not be determined as all attempts to isolate the gold complex from the water layer before extraction, or from the chloroform layer after extraction, failed due to decomposition with deposition of elemental gold.

CHAPTER IV
SUMMARY AND CONCLUSIONS

A procedure is outlined for the extraction of the gold (III) chloride complex of 4-heptanone oxime into chloroform. Using the recommended procedure, greater than 99.0% of the gold (III) taken at the 34 mg per 100 ml level is extracted. The effects due to hydrochloric acid concentration, oxime concentration and multiple extraction are described. The extent of interference of gold (III) according to the recommended procedure for palladium (II) is also given.

A condensed version of this work has been published (56).

PART IV
THE CHLOROFORM EXTRACTION OF THE OTHER
PLATINUM METALS AFTER REACTION
WITH 4-HEPTANONE OXIME

CHAPTER I
INTRODUCTION

In the previous work presented in this dissertation, a procedure was developed to effect the quantitative extraction into chloroform of palladium (II) from 1.0M hydrochloric acid solution as the 4-heptanone oxime complex. It was discovered that the base metals iron (III), nickel (II), cobalt (II), and copper (II) were not significantly extracted under the same conditions at the milligram level. Since gold is often associated with palladium, a study was conducted and it was shown that gold interferes severely in the quantitative procedure for separating palladium (II). But upon changing the conditions of extraction it was also shown that gold (III) could be extracted greater than 99.0% at the 34 milligram level. It was therefore possible to separate both palladium (quantitatively) and gold (near quantitatively) from a synthetic system of each.

A separational system for palladium would not be complete if a study of the other platinum metals were not included. The present work constitutes an investigation of the extent of extraction of platinum (IV), platinum (II), iridium (IV), iridium (III) and rhodium (III), after reaction with 4-heptanone oxime, into chloroform following

the recommended procedure for the quantitative extraction of palladium (II).

CHAPTER II
EXPERIMENTAL

A. APPARATUS AND MATERIALS

1) Instruments

Spectrophotometric measurements were made with a Beckman DB spectrophotometer equipped with a Sargent Model-SRL recorder and 1.00 cm matched silica cells.

A Sargent Model DR pH meter was used for all pH measurements.

2) Miscellaneous Reagents

The chloroform and hydrochloric acid were both A.C.S. grade.

3) Chloroplatinic Acid

The purified chloroplatinic acid was obtained from Johnson and Mathey Company.

4) Rhodium Trichloride

The analyzed rhodium trichloride trihydrate was obtained from the Mathey and Bishop Company.

5) Platinum and Iridium Chloride

Both the platinum dichloride and chloroiridic acid were supplied by the Alfa Inorganic Company.

6) 4-Heptanone Oxime

The reagent was prepared by reaction of 4-heptanone with hydroxylamine hydrochloride as previously described (27).

7) Standard Platinum (IV) Chloride Solution

A stock solution was prepared by dissolving 8.5 gm of chloroplatinic acid into a small amount of distilled water and 82 ml concentrated hydrochloric acid added.

The solution was then diluted to 1 litre with distilled deionized water. The solution was then standardized gravimetrically by the sodium formate method of Beamish, Russell, and Seath (40) to give a solution that contained 32.8 mg platinum (IV) per 10 ml aliquot.

8) Standard Rhodium (III) Chloride Solution

A stock solution was prepared by dissolving rhodium trichloride trihydrate in distilled water and concentrated hydrochloric acid added to make the solution 1.0M in hydrochloric acid when diluted to 1 litre. The solution was standardized gravimetrically by precipitation of the rhodium as the sulphide and igniting to the metal under a stream of hydrogen (57).

9) Standard Platinum (II) Chloride Solution

A stock solution was prepared by dissolving an analyzed lot of platinum dichloride and boiling it in 40 ml of concentrated hydrochloric acid for one hour. The solution was allowed to settle, decanted and filtered into a 1 litre flask. The residue was then dissolved in another 40 ml of concentrated hydrochloric acid by boiling it for one or two hours. The contents were then filtered into the volumetric flask and diluted to 1 litre with distilled, deionized water. The gravimetric

standardization by the method of Beamish, Russell and Seath (40) gave a stock solution which contained 30.5 mg of platinum (II) per 10 ml aliquot.

10) Standard Iridium (IV) Chloride Solution

A stock solution was prepared by dissolving 5.00 gm of chloroiridium acid in distilled deionized water.

Approximately 57 ml of concentrated hydrochloric acid were added, the solution filtered into a volumetric flask and diluted to the 700 ml mark with distilled deionized water. The solution was standardized gravimetrically by precipitating the iridium as the hydrated oxide and then igniting the oxide to iridium metal under a stream of hydrogen (57). Ten ml of the stock solution contained 26.3 mg of iridium (IV).

11) Standard Iridium (III) Chloride Solution

A stock solution was prepared by reduction of a known volume of the standard iridium (IV) stock solution with hydroxylamine hydrochloride. These solutions had to be freshly prepared before use to avoid any air oxidation when in a hydrochloric acid media.

B. PROCEDURES

1) Extraction Procedure

A 10 ml aliquot of one of the standard platinum metal solutions was transferred to a 250 ml graduated separatory funnel and sufficient standardized concentrated hydrochloric acid added so that on dilution to the 100 ml mark the solution was 1.0M in hydrochloric acid. The extraction procedure outlined for the quantitative extraction of palladium (II) from a 1.0M hydrochloric acid solution after reaction with 4-heptanone oxime was followed. The procedure was repeated with 10 ml aliquots of each of the standard platinum metal solutions.

2) Procedure to Determine Acid Concentrations of the Platinum Metal Stock Solutions

The hydrochloric acid concentrations of the standardized platinum (IV), platinum (II), rhodium (III) and iridium (IV) stock solutions were determined by withdrawing appropriate aliquots, adding 1 gm of sodium chloride and titrating to a pH of 5.00 with a standard sodium hydroxide solution.

3) Purity Studies of the Platinum Metal Stock Solutions

All platinum metal stock solutions were checked for impurities or hydrolyzed products by visible spectrophotometric scans. The resultant spectra were analyzed

and compared to literature values of shapes and extinction coefficients given by Jorgensen (58,59) and discussions by Ballhausen (60).

4) Platinum (IV) Analysis of the Chloroform Layer

The combined chloroform extracts were collected in a 250 ml beaker and evaporated to a syrup on a steam bath. The syrup was transferred to a porcelain evaporating dish and taken to dryness on a hot plate. The dish was cooled and 10 ml of 1:9 sulphuric acid plus 15 ml of cold hydrogen peroxide were added and the solution warmed gently on a hot plate. The solution was heated to fumes and slowly brought to dryness. The residue was ignited in the full flame of a Meker burner for exactly four minutes. This was cooled for two minutes and 2 ml of aqua regia added cautiously to the hot evaporating dish. This was boiled down to approximately 0.5 ml and then transferred to a 50 ml beaker. Concentrated hydrochloric acid was added repeatedly until the solution was free of the oxides of nitrogen using moistened potassium-iodide-starch impregnated test paper. The solutions were then analyzed spectrophotometrically with p-nitrosodimethylaniline according to the method of Kirkland and Yoe (61). The results are presented in Table XIV.

5) Platinum (II) Analysis of the Water Layer

After the extraction procedure an appropriate aliquot of the residual water layer was transferred

to a 100 ml beaker and treated with 1.5 gm of sodium chlorate and 4 ml of concentrated hydrochloric acid. The solutions were evaporated with repeated additions of concentrated hydrochloric acid until the potassium-iodide-starch indicator paper showed the absence of any oxidant. The solutions were then transferred to a 25.0 ml volumetric flask, diluted to the mark and the platinum determined spectrophotometrically at 455 nm. The absorbance readings were compared to those obtained with standard platinum (IV) solutions treated in the same manner. The results are presented in Table XIV.

6) Rhodium (III) Analysis of the Chloroform Layer

The combined chloroform extracts were evaporated to a syrup on the steam bath and the organic matter was destroyed by careful digestion with sulphuric acid and hydrogen peroxide. The rhodium content was determined spectrophotometrically with tin (II) bromide according to the procedure of Berman and Ironside (62). The results are summarized in Table XIV.

7) Iridium (IV) Analysis of the Water Layer

After the extraction procedure, an appropriate aliquot of the water layer was transferred to a 100 ml beaker. To this was added 0.5 gm sodium chlorate as well as 4 ml of concentrated hydrochloric acid. The hydrochloric acid treatment was repeated until the solution was free of oxidant. The moistened potassium-iodide-starch impregnated test paper was used for this test. To the hot solution was added 2.25 gm of sodium chloride

in order to stabilize the chloroiridate anion. The solution was then cooled, transferred to 50 ml volumetric flasks and diluted to the mark. The iridium (IV) content was then determined spectrophotometrically at 490 nm; the absorbance readings being compared to those obtained with standard iridium (IV) solutions treated in the same manner. The results are summarized in Table XIV.

8) Iridium (III) Analysis of the Water Layer

After the extraction procedure an appropriate aliquot of the water layer was transferred to a 100 ml beaker and treated with concentrated hydrochloric acid and sodium chlorate as was done in the Ir (IV) analysis. After repeated evaporations with hydrochloric acid the iridium content was determined spectrophotometrically at 490 nm. The absorbance readings were then compared to those obtained with standard iridium (IV) solutions that had been treated in the same manner. The results are summarized in Table XIV.

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TABLE XIV

% Extraction into Chloroform after Reaction with 4-Heptanone Oxime

Metal	Taken, mg	Found, mg	Range, mg	Number of Determinations	Average % Extraction
Pt (IV)	32.8	0.031**	0.018 - 0.044	10	0.09
Pt (II)	30.5	29.2 *	28.7 - 30.5	16	4.26
Rh (III)	28.3	0.009**	0.007 - 0.013	8	0.03
Ir (IV)	26.3	26.1 *	25.5 - 26.3	22	0.76
Ir (III)	26.3	26.0 *	25.4 - 26.3	18	1.15

* average mg found in water layer

** average mg found in chloroform layer

CHAPTER III
RESULTS AND DISCUSSION

In order that the procedure for the quantitative extraction of palladium (II) be complete, it was necessary to initiate a study to investigate the extent to which the other platinum metals might co-extract under the same conditions. It can be noted at this point that many studies of methods of separation of palladium (II) that are reported in the literature do not attempt the study of the associated base metals or the remaining platinum metals. It is true that each analyst should try the reported methods as applied specifically to his own matrix but a great deal of work could be avoided if the original authors could give some indication of interfering substances in a given procedure. It is also true, that one cannot study every possible substance that may be encountered, so it is the purpose of Part IV of this dissertation to give some insight into the relative extent of co-extraction of the other platinum metals (platinum, iridium and rhodium) that might be present in a given system with palladium (II).

It should be noted first of all, that osmium and ruthenium were not studied as they are almost always readily separated by efficient distillation steps prior

to any analysis of the other four platinum metals.

The results of this study are summarized in Table XIV. In the cases of platinum (IV) and rhodium (III) the analyses were performed on the chloroform layers as opposed to the cases of iridium (IV), platinum (II) and iridium (III) in which the analyses were performed on the aqueous phases. The results indicate that platinum (IV) does not constitute an interference since less than 0.1% of the platinum taken at the 33 mg level was extracted under the conditions given. The p-nitrosodimethylaniline was chosen as it was very sensitive and very applicable to the amounts that were present in the chloroform layer. A purely wet digestion procedure failed to destroy the complex that was formed and extracted into the chloroform. An ignition step alleviated this problem but introduced another. When using porcelain crucibles, ignition at temperatures which were required to decompose the organic matter, caused traces of platinum (IV) to be adsorbed into the unpolished finish of the crucible. All attempts to recover the adsorbed (or baked) platinum were unsuccessful, even a boiling aqua regia treatment (for days). This was alleviated by using porcelain evaporating dishes that were highly polished. The step in the procedure given, i.e. to heat under the full heat of a meker burner for exactly four minutes gave metallic platinum that was readily recovered with 2 ml of boiling aqua regia. This problem could not have been solved by merely digesting

the platinum solution to a small volume of fuming sulphuric acid since the spectrophotometric procedure to follow was sensitive to sulphate at levels greater than 300 ppm.

In the platinum (II) study it was found that platinum (II) constituted a major interference in the quantitative procedure for extraction of palladium (II). Analyses were performed on the water layer and good results could be obtained by oxidizing platinum (II) to platinum (IV) and comparing absorbances at 455 nm to those obtained by standard platinum (IV) solutions containing equal amounts as those taken in the extraction procedure. The results were limited in accuracy to that of the spectrophotometer, but these were sufficient in indicating the degree of interference that platinum (II) might present.

Rhodium (III) provided a system that was simple and could be analyzed quite easily spectrophotometrically with the tin (II) bromide complex. The results show that rhodium (III) does not constitute an interference according to the recommended procedure for palladium (II).

The results for the iridium analyses show that both iridium (III) and iridium (IV) constitute minor interferences to the recommended procedure for palladium (II).

The analyses of iridium (IV) and iridium (III) were done identically by comparing the visible spectra of the unknown extracted solutions to known quantities that were treated in a similar manner. The lower oxidation state (+3) of iridium could be quantitatively converted to the higher

(+4) state by treatment with hydrochloric acid and sodium chlorate.

The interferences from iridium (III) and platinum (II) therefore can be overcome before extraction by oxidation to the higher oxidation state. In most applications a digestion procedure involving aqua regia would be used thus resulting with the platinum metals being in their highest oxidation state that is stable in solution.

In the case of the 4.26 percent extraction of platinum (II) at the 30 mg level, a preliminary investigation indicates that platinum (II) may be quantitatively extracted after reaction with 4-heptanone oxime into chloroform by reducing the chloride ion concentration and allowing a longer standing time before extraction (63).

The visible spectrophotometric studies on the purity of the platinum metal stock solutions provided a very useful method of checking hydrolysis or any oxidation that may have occurred while the stock solutions were standing. This was especially helpful in the monitoring of the iridium (III) solution which was prepared by reduction of the stock iridium (IV) solution.

The concentrations of hydrochloric acid in the stock solutions were successfully determined by titration of the acid solutions against a standard sodium hydroxide solution.

7

CHAPTER IV
SUMMARY AND CONCLUSIONS

A study of the chloroform extraction of the platinum (IV), rhodium (III), iridium (IV), iridium (III) and platinum (II) chlorides after reaction with 4-heptanone oxime in 1.0M hydrochloric acid solution indicates that platinum (II) constitutes a major interference in the quantitative extraction of the palladium (II) chloride-4-heptanone oxime complex. Trace amounts of platinum (IV) and rhodium (III) are extracted. Iridium (IV) and iridium (III) constitute a minor interference.

A condensed version of this work is in press.

PART V
THE QUANTITATIVE SEPARATION OF TRACE AMOUNTS
OF PALLADIUM FROM PLATINUM

CHAPTER I
INTRODUCTION

In the previous section (Part IV), it was discovered that the noble metals platinum (IV), iridium (IV), and rhodium (III) constituted at the most, a minor interference to the recommended procedure for the quantitative extraction of palladium (II). The small amount that platinum (IV) was extracted is to some extent quite surprising! A large percent of the solvent extraction methods of separation include platinum as an interference. In some of the methods though, both palladium and platinum will be separated completely and simultaneously. This then would lead to a problem of separating the palladium from the platinum.

The most generally useful method for separating palladium from platinum was described by Ziegler and Bucholz (22). This method allows for separation from 1000-fold quantities of platinum with a large excess of iron, cobalt, nickel, copper and chromium. Palladium is extracted from pH 1-4 in hydrochloric acid solutions by phenylacetylene or isopropenylacetylene into dichloromethane as $(RC\equiv C)_2.Pd$. The major stipulation is that the 1000-fold ratio of separation is true only for solutions containing less than twenty mg of platinum. This procedure

is probably the most favourable published in the literature to date.

Reinecke's salt was used to separate palladium from gold and platinum with reasonable accuracy when present in equal amounts.

Egli (64) used 2-chloropyridine to separate and determine palladium and platinum. The technique has the drawback that the extraction must be applied with exact precision. Variations in time, after the addition of the chloropyridine will alter the distribution of the platinum in the two phases because of the dissociation of the platinum-chloropyridine complex.

Lystova (65) used thiooxime (8-quinolinethiol) to separate palladium and platinum using a masking procedure which involved thiourea.

Mezharaups et al. (66,67) used thiooximate in a solution of both platinum and palladium, to separate and determine each. The method is applicable to samples containing 20-200 μg of platinum and 20-150 μg of palladium, but the sum of the metals must be less than 200 μg .

Miyamoto (68) separated platinum and palladium from high purity gold. After adding hydrogen bromide the gold was extracted with isopropyl ether. The palladium was then separated as the dimethylglyoximate in chloroform. Finally the trace platinum was separated by extraction with dithizone into carbon tetrachloride and then determined with tin (II) chloride.

In determining platinum and palladium in rocks, the conventional method of tellurium precipitation was used by Grimaldi and Schnepfe (69). The palladium is eventually separated by the selective extraction of palladium as the α -furildioxime in chloroform. The platinum again is determined by the tin (II) chloride procedure. The recovery of 94% of the two metals leaves something to be desired.

The purpose of the present work is to test the efficiency of separation of trace amounts of palladium (II) from mg amounts of platinum in hydrochloric acid, as well as from mg amounts of platinum containing microgram amounts of rhodium (III) and iridium (IV).

CHAPTER II

EXPERIMENTAL

A. APPARATUS AND MATERIALS

1) Instruments

Spectrophotometric measurements were made with a Beckman DB spectrophotometer equipped with a Sargent Model-SRL recorder and 1.00 cm matched silica cells. A Sargent Model-DR pH meter was used for all pH measurements.

2) Miscellaneous Reagents

The chloroform, hydrochloric acid, hydroxylamine hydrochloride and sodium chlorate were A.C.S. grade.

3) 4-Heptanone Oxime

The reagent is prepared by the reaction of hydroxylamine hydrochloride with 4-heptanone as previously described (27). The reagent was stable for at least one year.

4) Rhodium Trichloride Trihydrate

The rhodium trichloride trihydrate was obtained from an analyzed lot from Mathey and Bishop Company.

5) Chloroiridic Acid

The chloroiridic acid was packed under argon and was obtained from Alfa Inorganic Company.

6) Platinum Sponge

The platinum sponge obtained from Johnson Mathey Company was ultrapure. The spectrographic analysis of this sponge was also obtained.

7) Palladium Chloride

Purified anhydrous palladium chloride was obtained from Fisher Scientific Company.

8) Standard Rhodium (III) Chloride Solution

A stock solution was prepared by dissolving rhodium trichloride trihydrate in hydrochloric acid and diluting to 1 litre with distilled, deionized water. The solution was standardized gravimetrically by precipitation of the rhodium as the sulphide and igniting this to the metal under a stream of hydrogen (57).

9) Standard Iridium (IV) Chloride Solution

A stock solution was prepared by dissolving chloroiridic acid in hydrochloric acid and diluting to approximately 700 ml with distilled, deionized water. The solution was standardized gravimetrically by precipitating the iridium as the hydrated oxide and igniting to the metal under a stream of hydrogen (57).

10) Standard Palladium (II) Chloride Solution

A stock solution was prepared by dissolving anhydrous palladium (II) chloride in hot concentrated hydrochloric acid and diluting to 1 litre with distilled, deionized water. The solution was standardized gravimetrically with di-2-pyridyl ketoxime (28).

11) Standard Platinum (IV) Chloride Solution

A stock solution was prepared by dissolving an accurately weighed amount of the ultra pure platinum sponge in aqua regia, evaporating repeatedly with hydrochloric acid and diluting to an exact volume with distilled deionized water.

Appropriate diluted stock solutions were made from the above standard stock solutions.

B. PROCEDURES

1) Extraction Procedure

An aliquot of the standard palladium (II) chloride solution containing 50 μ g of palladium was transferred to a 250 ml graduated separatory funnel and sufficient standardized hydrochloric acid added so that on dilution to the 100 ml mark the solution was 1.0M in hydrochloric acid. The extraction procedure outlined for the quantitative extraction of palladium (II) from a 1.0M hydrochloric acid solution after reaction with 4-heptanone oxime was followed. The procedure was repeated with added known amounts of platinum (IV), rhodium (III) and iridium (IV).

2) Palladium Analysis of the Chloroform Extract

The combined chloroform extracts were evaporated to dryness on the steam bath. The residual organic matter was destroyed by treatment with 0.5 gm of sodium chlorate and 4 ml of concentrated hydrochloric acid. The solutions were evaporated with repeated additions of concentrated hydrochloric acid until the potassium-iodide-starch indicator paper showed the absence of any oxidant. The palladium content was then determined spectrophotometrically with di-2-pyridyl ketoxime (32).

The results are summarized in Table XV.

3) Determination of Acid Concentrations of Stock Solutions

The hydrochloric acid concentrations of the platinum (IV), rhodium (III), iridium (IV) and palladium (II) stock solutions were determined by withdrawing appropriate aliquots, adding 1 gm of sodium chloride and titrating with a standard sodium hydroxide solution to a pH of 5.00.

TABLE XV

% Recovery of Palladium (II) after Reaction with 4-Heptanone Oxime and Extraction into Chloroform; Total Volume of Oxime, 0.4 ml (2 x 0.2)

Pd (II) taken μg	Average Pd (II) found μg	Pt (IV) taken mg	Iridium (IV) taken μg	Rhodium (III) taken μg	Number of Runs	Average % Recovery	Standard deviation μg
101	100	0	0	0	12	99.0	0.21
50.3	51.0	0	0	0	12	101	2.0
50.3	50.7	50.0	0	0	9	101	1.1
50.3	50.0	50.0	52.6	56.6	9	99.4	0.18
50.3	50.2	100	52.6	56.6	9	99.8	0.71
50.3	50.2	500	52.6	56.6	5	99.8	0.26

CHAPTER III
RESULTS AND DISCUSSION

The results of previous work described in this dissertation have shown that palladium (II) could be separated from hydrochloric acid solutions both at the 45 mg and 18 mg level. It has been shown in Table XV that palladium (II) can also be separated at levels down to 100 and even 50 μg from a hydrochloric acid solution.

The somewhat surprising evidence that was discovered in Part IV showed that platinum (IV) did not interfere greatly in the separation procedure for palladium (II). Table XV showed that when 50 μg of palladium are extracted in the presence of 50 mg (1000-fold quantities) of platinum (IV) a successful separation is achieved (i.e., 101%) with a standard deviation of only 1.1 μg . This also was the case in an identical extraction of 1000-fold quantities of platinum (IV) when rhodium (III) and iridium (IV) were present in quantities roughly equal to that of palladium (II). This same system containing 50 μg of palladium (II), rhodium (III) and iridium (IV) was studied while increasing the platinum (IV) to 10,000-fold. The recovery was very good since 99.8% of the palladium (II) taken was recovered with a standard deviation of 0.26 μg .

The best procedure yet reported for the same system

was that by Ziegler and Bucholz (22) in 1965. They state that the separation of palladium from 1000-fold quantities of platinum can be achieved using acetylene derivatives. Separations are made from a pH range of 1-4. This may well lead to trace amounts of hydrolysis. In this respect the present method is superior. Zeigler and Bucholz have a definite limitation in the fact that the upper limit to which their method is applicable is 20 μ g palladium and 20 mg platinum. The present method far surpasses these limits. Quantities as high as 500 mg of platinum were studied in the presence of 50 μ g of palladium.

It is this author's opinion that this method could quite conceivably be just as effective at the 100,000-fold level of platinum with no appreciable losses in recovery.

The study of palladium from 10,000-fold quantities of platinum can be thought of in a different manner. For an application type study this would show that palladium could be separated from pure platinum metal even at levels down to 0.01% impurity (as palladium) even in the presence of trace amounts of iridium and rhodium.

This method of separation could then lead to a procedure for the determination of microgram amounts of palladium in platinum sponge or platinum chlorides and for the preparation of chloroplatinic acid or.

platinum metal free of palladium.

CHAPTER IV
SUMMARY AND CONCLUSIONS

A procedure is outlined for the quantitative separation of microgram amounts of palladium from hydrochloric acid solution. This procedure is effective also from hydrochloric acid solutions containing milligram amounts of platinum (IV) and microgram amounts of rhodium (III) and iridium (IV).

A condensed version of this work is presently in press.

PART-VI

THE SEPARATION OF TRACE AMOUNTS OF
PALLADIUM (II) FROM MACRO AMOUNTS
OF COPPER, IRON AND NICKEL

CHAPTER I

INTRODUCTION

In previous sections (Part I and II) it was shown that mg quantities of the base metals iron, nickel and copper did not interfere in the recommended procedure for palladium (II). The possibility of increasing these base metal levels to a macro scale then became evident.

The present work constitutes an investigation into a study of extraction of the base metals at gram levels. The recovery of μg levels of palladium (II) from the base metals at this gram level is studied. The base metals are introduced both as the chlorides and sulphates. A synthetic mixture of these base metals is made and a recovery of μg quantities of palladium (II) from this and a known analyzed matrix is given.

In most work reported in the literature to date, either the separation of palladium (II) from large quantities of nickel, copper and iron is not reported or one of the three base metals causes an interference. In the cases where these three base metals do not interfere, the co-extraction of platinum, rhodium or iridium usually exists. The application of Reinecke's salt to the separation of palladium from gold and platinum yields

reasonable accuracy. The data indicated a significant lack of precision for separations from high proportions of copper, iron, cobalt and nickel (23).

Ziegler and Pape (21) extract microgram amounts of palladium in the presence of large quantities of nickel and cobalt but interferences from platinum, copper and iron required a prior separation to obtain reasonable results.

CHAPTER II

A. APPARATUS AND MATERIALS

1) Instruments

Spectrophotometric measurements were made with a Beckman DB spectrophotometer, using 1.00 cm matched silica cells. A Sargent Model-DR pH meter was used for all pH measurements.

2) 4-Heptanone Oxime

The 4-heptanone oxime was prepared by reaction of 4-heptanone with hydroxylamine hydrochloride as previously described (27).

3) Miscellaneous Reagents

The chloroform, hydrochloric acid, sodium chlorate and sulphuric acid were all A.C.S. grade.

4) Base Metal Salts

The ferric chloride hexhydrate, cupric chloride dihydrate and nickel (II) chloride hexahydrate were A.C.S. grade.

5) Palladium Chloride

Purified, anhydrous palladium chloride was obtained from the Fisher Scientific Company.

6) Standard Palladium (II) Chloride

A stock solution was prepared by dissolving anhydrous palladium (II) chloride in hot concentrated hydrochloric

acid and diluting to 1 litre with distilled deionized water after filtering. The solution was standardized gravimetrically with di-2-pyridyl ketoxime (28). An appropriate diluted stock solution was made from the above standardized stock solution, to contain approximately 10 µg per ml.

7) Standard Copper (II) Chloride Solution

A stock solution was prepared by dissolving 175 gm of cupric chloride dihydrate in about a litre of distilled deionized water. Concentrated hydrochloric acid was added so that the solution would be 1M in hydrochloric acid upon dilution to the 2 litre mark. An appropriate aliquot was withdrawn and standardized against a standard sodium thiosulphate solution.

8) Standard Copper (II) Sulphate Solution

A stock solution was prepared by dissolving 175 gm of cupric chloride dihydrate in about 1 litre of distilled deionized water. Concentrated sulphuric acid was added so that the solution would be 1N in sulphuric acid upon dilution to the 2 litre mark. The copper solution was standardized as described above.

9) Standard Nickel (II) Chloride Solution

A stock solution was prepared by dissolving 396 gm of nickel(II)chloride hexahydrate in about 1 litre of deionized distilled water and enough concentrated hydrochloric acid added so that the solution would be 1M in hydrochloric acid upon dilution to the 2 litre mark.

The solution was standardized gravimetrically with dimethyl glyoxime.

10) Standard Nickel (II) Sulphate Solution

A stock solution was prepared by dissolving 396 gm of nickel(II)chloride hexahydrate in about 1 litre of deionized distilled water and enough concentrated sulphuric acid added so that the solution would be 1N in sulphuric acid upon dilution to the 2 litre mark. The nickel solution was standardized as described above.

11) Standard Iron (III) Chloride Solution

A stock solution was prepared by dissolving 316 gm of ferric chloride hexahydrate in 1 litre of distilled water. Enough concentrated hydrochloric acid was added so that the solution would be 1M in hydrochloric acid upon dilution to the 2 litre mark. An appropriate aliquot was withdrawn and standardized titrimetrically with potassium dichromate.

B. PROCEDURES

1) Procedure for Determining Acid Concentrations of the Stock Solutions

The acid concentration of copper, nickel and palladium stock solutions were determined by withdrawing appropriate aliquots, adding 1 gm of sodium chloride and rapidly titrating with a standard sodium hydroxide solution to a pH of 5. The acid concentration of the ferric chloride stock solution was estimated from the apparent pH reading of the solution.

2) Extraction Procedure

An aliquot of the standard palladium (II) chloride solution containing 80 μ g of palladium was transferred to a 250 ml graduated separatory funnel. Known amounts of the base metals copper (II), nickel (II) and iron (III) were added separately in gram quantities. Sufficient acid is added so that on dilution to the 100 ml mark the solution is 1N in acid. The extraction procedure outlined (Part II) for the quantitative extraction of palladium (II) was followed except that the total amount of 4-heptanone oxime was reduced to 0.4 ml (i.e. 2 x 0.2 ml).

3) Palladium Analysis of the Chloroform Layer

The combined chloroform extracts were evaporated to dryness on the steam bath. The residual organic

matter was destroyed by treatment with sodium chlorate and hydrochloric acid. After repeated evaporations with hydrochloric acid the palladium content was determined spectrophotometrically with di-2-pyridyl ketoxime (32).

The results are summarized in Table XVI.

4) Study of the Extent of Extraction of Gram Quantities of Copper, Nickel and Iron

Aliquots of copper, nickel and iron as chlorides and sulphates were added (separately) to a 250 ml graduated separatory funnel. The appropriate concentrated acid was added so that the solution would be 1N in acid when diluted to the 100 ml mark. The recommended extraction procedure outlined above was followed and the chloroform extracts were collected.

5) Copper Analysis of the Chloroform Layer

The combined extracts of the copper extraction were collected and evaporated to dryness on the steam bath. The residual organic matter was destroyed by repeated additions of aqua regia and finally brought to fumes with 25 ml of 1:5 sulphuric acid. The solutions were then treated appropriately and titrated with previously standardized sodium thiosulphate.

Similar analyses were performed on the chloroform extracts of the copper system in which the copper had been introduced as the sulphate.

The results are summarized in Table XVII.

6) Nickel Analysis of the Chloroform Extract

The combined chloroform extracts were evaporated to dryness on a steam bath and the residual organic matter destroyed by the addition of sodium chlorate and hydrochloric acid. After repeated hydrochloric acid treatment, the nickel content was determined gravimetrically with dimethyl glyoxime.

Similar analyses were performed on the chloroform extracts of the nickel system in which the nickel had been introduced as the sulphate.

The results are summarized in Table XVII.

7) Iron Analysis of the Chloroform Extract

The combined chloroform extracts were evaporated to dryness on a steam bath and the residual organic matter was destroyed by the addition of aqua regia. The solution was repeatedly evaporated to a small volume with concentrated hydrochloric acid until all oxides of nitrogen were expelled. The iron was then determined titrimetrically with potassium dichromate after the appropriate treatment.

The results are summarized in Table XVII.

8) Extraction of Palladium (II) from a Complex Matrix

Transfer by pipette 80 µg of palladium (II) chloride into a 250 ml separatory funnel. Add to the separatory funnel, approximately 160 mg of iron (III), 3.0 gm of copper (II) and 4.5 gm of nickel (II) as the chlorides. Appropriate amounts of hydrochloric acid are added to ensure that the final solution is 1M in acid when diluted

to the 100 ml mark. The 'extraction procedure' (section 2) outlined above is followed and the chloroform layers are treated with sodium chlorate and hydrochloric acid as previously described. After this treatment, the solutions are made approximately 1M in hydrochloric acid and the recommended 'extraction procedure' repeated again.

The collected chloroform extracts are evaporated and treated once more with the sodium chlorate-hydrochloric acid treatment. The palladium content is then determined spectrophotometrically with di-2-pyridyl ketoxime.

The results are summarized in Table XVI.

9) Separation of Palladium from a Standard Reference Matte

A standard reference nickel-copper matte certified by the Canadian Mines Branch in Ottawa, Ontario was used as a check to compare the ability of 4-heptanone oxime to separate trace amounts of palladium (II) from a complex matrix.

Accurately weigh out approximately 10 gm of the certified copper-nickel matte and leach it in a 600 ml beaker with 60 ml of concentrated hydrochloric acid. At this point the hydrogen sulphide should cease to be expelled. Add 5 ml of concentrated nitric acid and boil the solution until yellow sulphur is precipitated in a solid mass on the surface. Cool, and add 1-2 ml of A.C.S. bromine dropwise to dissolve the sulphur. Warm gently until the excess bromine has been boiled off. Filter the solution through a medium porosity, sintered

glass crucible to separate any undissolved matter. Add concentrated hydrochloric acid repeatedly until the solution is free of the oxides of nitrogen. Adjust the volume to 100 ml and approximately 1M in hydrochloric acid, then rinse the solution into a 250 ml separatory funnel with 15-20 ml of 1M hydrochloric acid. The solution is then extracted according to the recommended 'extraction procedure' as described in section (8). The extracts are worked up with a sodium chlorate-hydrochloric acid treatment and the 'extraction procedure' repeated again. After working up the chloroform extracts again with a sodium chlorate-hydrochloric acid treatment, the palladium was analyzed spectrophotometrically with di-2-pyridyl ketoxime.

The results are summarized in Table XVIII.

TABLE XVI

Separation of Trace Quantities of Pd (II) from Macro
Quantities of Base Metals *

Base Metal(s)	Metal Taken (gm)	Pd (II) added (ug)	Pd (II) found (ug)	Standard Deviation (ug)								
CuCl ₂ (in HCl)	2.94	80.4	80.4	1.1								
CuCl ₂ (in H ₂ SO ₄)	2.95	80.4	80.4	0.9								
NiCl ₂ (in HCl)	4.54	80.4	80.0	1.2								
NiCl ₂ (in H ₂ SO ₄)	3.48	80.4	80.0	0.7								
FeCl ₃ (in HCl)	3.06	80.4	80.6	0.6								
<table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>FeCl₃</td> <td>0.17</td> </tr> <tr> <td>NiCl₂</td> <td>4.43</td> </tr> <tr> <td>CuCl₂</td> <td>2.87</td> </tr> <tr> <td>(in HCl)</td> <td></td> </tr> </table> **	FeCl ₃	0.17	NiCl ₂	4.43	CuCl ₂	2.87	(in HCl)			80.4	80.0	1.8
FeCl ₃	0.17											
NiCl ₂	4.43											
CuCl ₂	2.87											
(in HCl)												

* Each result is the average of 12 determinations

** This matrix required a double extraction technique to produce consistent blanks.

TABLE XVII

Extraction of Base Metals Under the Recommended Procedure
for Palladium (II)

Base Metal	Metal Taken (gm)	Found in CHCl_3 (mg)	% Extracted
CuCl_2 (in HCl)	2.94	3.5	0.12
CuCl_2 (in H_2SO_4)	2.95	7.0	0.24
NiCl_2 (in HCl)	4.54	2.8	0.06
NiCl_2 (in H_2SO_4)	3.48	1.9	0.06
FeCl_3 (in HCl)	3.06	1.4	0.05

TABLE XVIII

Separation of Palladium from a Standard Reference Matte

The recommended value, certified by the Canadian Mines
Branch is 0.24 oz/ton

Run	Taken (gm)	Pd Found oz/ton
1	10.0	0.262
2	10.0	0.262
3	10.0	0.257
4	10.0	0.256
5	9.98	0.256
6	10.0	0.263
7	10.0	0.262
8	10.0	0.259
9	10.0	0.253
10	10.0	0.263
11	10.0	0.259
12	10.0	0.258

average 0.259

standard deviation 0.003

CHAPTER III

RESULTS AND DISCUSSION

The 'extraction procedure' used in studying the extraction of palladium (II) at the 80 μg level was the same as the recommended procedure for the quantitative extraction of palladium given in part (II) except for the reduced volume of reagent. The total volume of reagent was reduced to 0.4 ml (2 x 0.2 ml) because of the small amounts of palladium to be recovered.

The results of Table XVI indicate that trace amounts of palladium (II) can be separated quantitatively from gram amounts of each of the associated base metals copper (II), nickel (II) and iron (III). The results also indicate that either the chloride or the sulphate system can be used to achieve quantitative separations.

A study of the effect of each base metal according to the recommended procedure for palladium (II) is given in Table XVII. These results show that the co-extraction, of gram amounts of the base metals studied, do not constitute a major interference. The small milligram amounts that are extracted give some problems in later work in which a proper blank must be used for a spectrophotometric determinative step of an unknown mixture. The interferences that these base metals have on subsequent

spectrophotometric blanking procedures can be eliminated by employing a double work up procedure as was done in the analysis of the synthetic matte and the standard reference matte.

In order to attempt to verify a separational procedure, it should show tested performance in a complex matrix. The certified copper-nickel matte was chosen for a complex matrix containing trace amounts of palladium. Thus, a synthetic matte was made up and the results are given in Table XVI. The results indicate that very good recoveries of palladium can be achieved provided a double work-up procedure is employed. Even when results of a synthetic system are studied, there must be a set of results compiled for a known analyzed matte.

The certified standard copper-nickel matte was obtained from the Canadian Mines Branch in Ottawa for a comparison. The results of Table XVIII indicate that the efficiency of using 4-heptanone oxime in a separation of palladium (II) from a complex matrix, is comparable to results obtained for the standard matte. Thus, this method of separation gives results that can compare to those results obtained by fire assay followed by atomic absorption or spectrographic analysis. The certified matte was given a recommended value of 0.24 oz/ton of palladium. The present method gave 0.259 oz/ton with a standard deviation of 0.003 oz/ton.

The possibility of this separation procedure leading

to a method of separation and determination is quite conceivable. Further studies should be initiated in order to prove this and to extend the use of 4-heptanone oxime into areas of further applications.

CHAPTER IV

SUMMARY AND CONCLUSIONS

A procedure is outlined for the separation of microgram amounts of palladium (II) from hydrochloric or sulphuric acid solutions containing gram amounts of the base metals copper (II), nickel (II) and iron (III). This procedure is satisfactory for each system separately or a synthetic mixture. Results are given for the efficiency of the separation procedure as applied to a certified, standard reference matte.

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