1972

The Separation of the Noble-Metals and the Determination of These Metals by Atomic Absorption Spectrophotometry.

Helen Stalcup Copeland
Louisiana State University and Agricultural & Mechanical College

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THE SEPARATION OF THE NOBLE METALS AND THE DETERMINATION OF THESE METALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Department of Chemistry

Helen Stalcup Copeland
B.S., University of Alabama, 1967
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ABSTRACT

Optimum operating variables for the atomic absorption determination of the chloro complexes of gold(III), palladium(II), platinum(IV), rhodium(III), iridium(IV), osmium(VIII), and ruthenium(III) were established. Interferences from the other noble metals in the atomic absorption determination of the chloro complexes of iridium and ruthenium were investigated in an air-acetylene flame and those of osmium in a nitrous oxide-acetylene flame. The interferences found in the determination of iridium, ruthenium, and osmium were eliminated by the addition of 3000 ppm, 2000 ppm, and 3000 ppm of copper as copper(II) sulfate, respectively. The effects of hydrochloric acid and copper concentration on the absorption of these metals were also determined.

Procedures for the atomic absorption determination of the bromo complexes of the noble metals were developed. The absorption of the bromo complexes relative to that of the chloro complexes was determined. Also, the effects of hydrobromic acid and copper concentration on the bromo complexes of the noble metals were determined.

Diantipyrylpropylmethane (DAPM) was studied as an extractant for the bromo complexes of gold(III), palladium(II), platinum(IV), rhodium(III), iridium(IV), osmium(IV),
and ruthenium(III) into 4-methyl-2-pentanone (MIBK) prior to the atomic absorption determination of these metals. The effects of hydrobromic acid and DAPM concentration on the extraction of these metals were observed, and methods for the extraction of all of the bromo complexes of the noble metals into MIBK were developed. Only gold, palladium, and rhodium yielded sensitive atomic absorption analyses after extraction into the MIBK solvent.

Distribution coefficients were calculated from batch extractions of the bromo complexes of the noble metals in the 4 N hydrobromic acid-MIBK solvent system using a 1:1 volume ratio of extractant to raffinate. These distribution coefficients were used in a computer program of the Craig equation which was modified to give a plot of the equation to predict possible separations and to determine the optimum conditions (number of stages and volume ratios) for extraction.

Various binary mixtures of gold(III) and iridium(IV), palladium(II), platinum(IV), rhodium(III), or ruthenium(III) were separated easily by counter-current extraction using a 1:1 volume ratio of extractant to raffinate in 10 stages of a Craig apparatus in the 4 N hydrobromic acid-4-methyl-2-pentanone solvent system. Rhodium(III), platinum(IV), and gold(III) were separated in 75 stages using a 1:1 volume
ratio of extractant to raffinate. Rhodium and platinum were quantitatively separated from gold while 92 percent of the platinum was separated from the rhodium. Rhodium(III), palladium(II), and gold(III) were separated in 100 stages with a 1:1 volume ratio of extractant to raffinate. Rhodium and palladium were quantitatively separated from gold and the palladium was 92 percent separated from rhodium. The separation of ruthenium(III), iridium(IV), and osmium(IV) was attempted. No separation of the iridium and ruthenium was obtained in 80 stages using a 1:1 volume ratio of extractant to raffinate, but the osmium was quantitatively separated from both the iridium and the ruthenium. The osmium results were determined spectrophotometrically due to the low sensitivity for the atomic absorption determination of osmium.
I. INTRODUCTION

Many attempts to separate the noble metals have been summarized by Beamish. Some of these separations have been time consuming or meticulous and others have met with only limited success, but those separations which have involved solvent extraction, particularly countercurrent or pseudocountercurrent extraction appear to offer a simple, rapid, and possibly economical means of separating the noble metals.

Berg and Senn were the first to report on the separation of the platinum group metals by countercurrent extraction. Platinum and palladium or platinum and rhodium mixtures were separated in 16 stages in a Craig apparatus with a 3 M hydrochloric acid-tributyl phosphate (TBP) solvent system. The extraction of iridium from rhodium was unsuccessful ostensibly due either to reduction of iridium (IV) to iridium (III) by the TBP or the existence of iridium in some form requiring drastic conditions to produce the extractable species. Berg and Senn did succeed in separating the chloro complexes of rhodium and iridium in the previously mentioned solvent system by using a nine stage multiple extraction procedure after the method of Bush and Densen. It was necessary, however, to oxidize
the iridium which remained in the raffinate after each extraction prior to the next extraction. Ninety-nine percent of the rhodium and 94 percent of the iridium were recovered free of the other element.

Berg and Lau\textsuperscript{5} utilized an acid thiocyanate-TBP solvent system and a 10 stage Craig apparatus to effect the separation of iridium from platinum, rhodium from palladium, and iridium from palladium. Optimum conditions for separations involved a thiocyanate:metal mole ratio of 10:1 and a pH of 1. Even more effective separations were predicted on the basis of distribution coefficients determined with a 200:1 mole ratio of thiocyanate:metal, but for unknown reasons the separations were not effective.

Berg and Sanders\textsuperscript{7} separated various binary and ternary mixtures of the bromo complexes of platinum (IV), palladium (II), rhodium (III), and iridium (IV) by countercurrent extraction on a Craig apparatus. The bromo complexes of the metals were extracted from 4.38 M hydrobromic acid solutions into various organic solvents. Rhodium-platinum and rhodium-palladium mixtures were quantitatively separated in 10 stages using a 90 percent TBP-10 percent benzene solvent. Rhodium and iridium were resolved by three consecutive batch extractions in the same solvent.
system. Palladium, rhodium, and iridium mixtures were separated in 90 stages using 4-methyl-2-pentanone (MIBK) as the extractant. Berg and Sanders employed a computer program of the Craig equation to predict from the measured distribution coefficients the number of stages required for good separations and the distribution of solutes after multiple equilibrations of the Craig apparatus. There was not a good agreement between the experimentally observed and theoretically calculated solute distributions in the Craig apparatus.

Casey, et al. separated rhodium, iridium, and platinum with a 20 stage Craig apparatus and a 3 M HCl-TBP solvent system. Again, anomalous behavior was noted for the extraction of iridium. The distribution coefficient for iridium measured in a batch extraction was 22 compared to a value of 2.8 calculated from the distribution of iridium in the Craig apparatus. A poor separation of platinum from osmium in 50 stages was obtained.

Berg and Mosely separated the bromo complexes of osmium and ruthenium in a single equilibration by means of a 6 M HBr-MIBK system and determined the degree of separation by employing radioactive isotopes of osmium and ruthenium as tracers.
All or most of these separation studies were hampered by methods of determination for the individual metals which are unselective and/or lacking in sensitivity. For example, the conventional spectrophotometric procedures for the noble metals provide good sensitivities, but they are notably unselective in that other noble metals usually interfere in the determination.

The purpose of this work was to investigate further the possibilities for separating mixtures of the platinum group metals by countercurrent extraction using the Craig apparatus. The large number of sample fractions inherent to this type of study required that a simple, rapid, sensitive, and selective analytical procedure be available to evaluate the separation efficiency of the chosen procedure. Of those tools available to this laboratory, only atomic absorption spectrophotometry appeared capable of satisfying the analytical requirements of the study, and it was unproven for the analysis of mixtures of platinum group metals. Thus, it was necessary to devise an atomic absorption method suitable for the determination of mixtures of the platinum group metals.

Atomic absorption spectroscopy has often been said to be free of interferences and to be a sensitive method of
analysis. Lockyer and Hames were the first to study the atomic absorption determination of the noble metals: gold, palladium, platinum, and rhodium. Using an air-town gas burner they determined gold with the 242.8 nm (nanometers) line, palladium at 247.6 nm, platinum at 265.9 nm, and rhodium at 343.5 nm and observed no interferences whatsoever. Menzies reported a sensitivity of 1, 2, 10, and 2 ppm (parts per million of metal giving 1 percent absorption in the flame) respectively for gold, palladium, platinum, and rhodium. They also found the analysis to be free of interferences from other noble metals. Ginzburg, et al. also studied the above four metals with an air-propane flame. They, however, suggested the use of a flame temperature higher than that of air-propane for the determination of platinum and rhodium due to observed interferences from many metal salts. No report on the interferences of the other noble metals with the determination of these two metals was presented. Strasheim and Wessels used a butane-propane gas flame in their study of the atomic absorption determination of these four metals. The same spectral lines recommended by Lockyer and Hames were used with the exception of palladium for which the 340.4 nm line was found to be superior to their recommended 247.6 nm line. Gold, palladium,
platinum, and rhodium were reported to have a sensitivity of 0.5, 1.2, 5.0, and 0.2 ppm respectively. Palladium and gold were found to be free of noble metal interferences in agreement with previous findings. Contrary to the results of Lockyer and Hames and Menzies, the absorption of platinum was seriously depressed by palladium, rhodium, iridium, ruthenium, and osmium, and very slightly depressed by gold. Twenty thousand ppm of copper as the sulfate effectively overcame these interferences in the determination of platinum. Also, the absorption of rhodium was subject to serious interferences which could not be overcome by the use of copper sulfate. The absorption for rhodium could be determined, however, by using an addition method since the absorption analysis curve was linear.

Zeeman and Brink also determined gold, palladium, platinum, and rhodium by atomic absorption spectroscopy using a propane-butane-air flame. They determined the metals simultaneously after extraction from base metals and dilution with acetone by using the nonabsorbing platinum line at 304.2 nm as the reference line and obtained a sensitivity of 0.01, 0.1, 0.5, and 0.1 ppm respectively for gold, palladium, platinum, and rhodium. A number of elements were found to interfere in the determination of rhodium.
Van Loon added a 1 percent lanthanum solution to eliminate interelement interferences in the determination of gold, palladium, and platinum in solutions containing mixtures of these metals. The limit of detection was 1, 1, and 5 ppm respectively for these metals in 6 M HCl at the spectral lines recommended by Lockyer and Hames.

Mulford extracted palladium and platinum with ammonium pyrrolidine dithiocarbamate into MIBK in order to enhance the sensitivity approximately five times that obtained with aqueous solutions of these metals by atomic absorption analysis. Schnepfe and Grimaldi employed a 0.5 percent solution of cadmium and copper to enhance the sensitivity of palladium and platinum as well as to overcome interferences from the other noble metals. A sensitivity of 0.8 ppm was obtained for palladium at the 340.5 nm line and 1.7 ppm for platinum. It was not demonstrated that interferences (notably rhodium at greater than 150 ppm and gold with its 1 percent depressive effect for each 100 ppm of gold present) were overcome in the case of platinum.

Scarborough determined palladium, rhodium, and ruthenium at the 247.6 nm, 343.5 nm, and 349.9 nm lines respectively in an air-unstated fuel flame. Addition of uranium effectively eliminated the depression of rhodium absorption
by ruthenium or palladium, the depression of palladium absorption by ruthenium or rhodium; and the enhancement of ruthenium absorption by palladium or rhodium. The interferences noted in the palladium determination were contrary to those reported in the previous studies.

Greaves observed the atomic absorption of gold in air-coal gas flames and obtained a sensitivity of 0.3 ppm. Extraction of the bromo complex of gold into MIBK appeared to be the most promising analysis medium due to the small effect of the MIBK on the combustion characteristics of the flame. Tindall and Strelow, et al. also determined gold by atomic absorption after extraction into MIBK. Many others have now determined gold by atomic absorption after extraction of the gold (III) chloro or bromo complex from aqueous solution into a pure organic solvent. Extractants were used in order to avoid rigid control of the pH. Beevers extracted the gold (III) complex into amyl acetate by means of p-dimethylamino benzyl rhodannine. Pollock and Anderson determined gold by the extraction of the iron (II) 1,10-phenanthroline tetrabromoaurate into chloroform prior to atomic absorption analysis. Groenwald used tertiary and quaternary amines for the extraction of gold (III) ions
and gold (I) cyanide ions into diisobutyl ketone. Zlatkis, et al. utilized an initial chelation on a chromatographic column to concentrate gold contained in natural waters which was then extracted into MIBK. By this means gold was determined with a sensitivity of 0.5 ppb (parts per billion) in the original sample by atomic absorption spectroscopy.

Mulford observed a sensitivity of 44 ppm for the 264.0 nm line of iridium and found that an air-acetylene flame could be successfully used rather than the higher temperature nitrous oxide-acetylene flame to obtain a suitable absorption. Manning and Fernandez also recommended the 264.0 nm line for analysis in an air-acetylene flame and obtained a sensitivity of 13 ppm. A sensitivity of 12 ppm was obtained by Makarov and Kukushkin in the presence of 1 mg (milligram) of copper (II) chloride in an air-propane flame. The addition of bromide ions to a solution of iridium containing the chloride produced a decrease in the sensitivity of the analysis. Van Loon reported an enhancement of the iridium absorption by platinum and gold and a depression by palladium and rhodium. These interferences were said to be eliminated by a combination of sodium
and copper ions. The effect of osmium and ruthenium on the iridium absorption was not studied.

The atomic absorption of the thiourea complex of osmium was investigated by Osolinski and Knight. The complex first was destroyed with hydrogen peroxide and then the osmium concentration determined at the 290.9 nm line using a nitrous oxide-acetylene flame with a sensitivity of 1 ppm. These solutions were stable only for a few days. Fernandez observed a sensitivity of 5.0 ppm for osmium contained in a solution of 0.1 M sulfuric acid with a nitrous oxide-acetylene flame also at the 290.9 nm line. An operating range of 500 to 1000 ppm for the analysis of osmium by atomic absorption was reported by Makarov, et al. Their sensitivity was 17 ppm for the 290.9 nm line using a flame mixture of propane-butane and air. No study has been made of the interferences which might occur in the atomic absorption determination of osmium.

Erinc and Magee observed a general increase in the absorption of palladium in organic solvents miscible with water and in the presence of nitric, sulfuric, hydrochloric, and acetic acids. Takeuchi, et al. studied the atomic absorption of the dithizonate and diethyldithiocarbamate complexes of palladium extracted into MIBK. No difference
in absorption was observed with these two complexes. A sensitivity three times that obtained with aqueous solutions was observed with the MIBK solutions of palladium.

Pitts, et al. studied the atomic absorption of platinum and the interferences in this determination by the other noble metals and by various acids and cations in an air-acetylene flame. The interferences were eliminated by the addition of lanthanum (III) chloride with the exception of those due to rhodium and iridium. Hydrobromic acid was found to interfere at all concentrations. No method was found to eliminate these latter interferences. A nitrous oxide-acetylene flame while producing a lower sensitivity did tend to minimize interferences. The interferences from the cations were suggested to be due to a condensed phase chemical interference in which a less volatile platinum salt was formed. The extent of the interference was said to be dependent upon the degree of formation of the salt and on its volatility in comparison to the chloro form of platinum.

The 343.5 nm line was recommended by Heneage for the atomic absorption determination of rhodium. A detection limit of 0.03 ppm was obtained with a very lean flame. An atomic absorption procedure for the trace determination of
rhodium was developed by Deily in which the sample and standards differed in solvent composition. The rhodium samples contained in either benzene-ethanol or cyclohexane-ethanol solution were diluted to volume with ethylene glycol monomethyl ether prior to analysis. It was determined that these solvents produced little effect on the absorption of rhodium as long as a lean fuel mixture was maintained. MIBK proved unsuitable for a solvent in the analysis of rhodium because the flame could not be made lean enough with that solvent. Ginzburg, et al. obtained a sensitivity of 2.5 ppm for the 343.5 nm line of rhodium using an air-propane flame. The sulfate, perchlorate, and nitrates of rhodium exhibited much less absorption than the chloride of rhodium. The addition of acetone, methanol, and ethanol produced an increase in the absorption while the reverse was observed with the addition of butanol and isoamyl alcohols. Hydrochloric and nitric acids up to 3-5 M did not affect the absorption. Gold, palladium, and platinum increased the absorption by rhodium while ruthenium and iridium decreased the absorption. Atwell and Hebert found that interferences from gold, iridium, palladium, platinum, and ruthenium and various acids on the rhodium absorption were less in a nitrous oxide-acetylene flame with only iridium and ruthenium
showing significant interference in the latter flame. They were unable to eliminate completely the interferences of ruthenium with copper but did succeed with a 0.5 percent zinc solution. A sensitivity of 0.7 ppm for the rhodium absorption in the nitrous oxide-acetylene flame was observed at the 343.5 nm line.

Ruthenium absorption in an air-propane flame was investigated by Makarov and Kukuskin\textsuperscript{31} who obtained a sensitivity of 2 ppm for the 349.9 nm line. They reported little interference from other noble metals and a doubling of the sensitivity of ruthenium by the addition of a few mg/ml of cupric salts. Montford and Cribbs\textsuperscript{35} studied the effects of forty ions other than the noble metals and the effects of a number of acids on the absorption of ruthenium in both air-acetylene and nitrous oxide-acetylene flames. All these ions exhibited interferences which with the exception of titanium were effectively eliminated by the addition of a 4 percent weight/volume (w/v) solution of uranyl nitrate as Scarborough\textsuperscript{44} did in his study of palladium, rhodium and ruthenium. In the case of titanium, ruthenium tetroxide was distilled from oxidizing acid media thus removing the ruthenium from the presence of titanium. The use of uranyl nitrate also allowed an enhanced sensitivity
for ruthenium of 0.88 ppm compared to 1.4 ppm in 3 M HCl at the 349.9 nm line. The absorption was suppressed as the molarity of HCl was increased. The addition of the uranyl nitrate eliminated the variation due to acidity.

Extraction of a metal into the organic phase prior to analysis by atomic absorption has been used in the determination of a number of the noble metals (namely gold, palladium, platinum and osmium)\(^{19,25-27,38,39,42,48-50,54}\) and has been discussed in the preceding pages. Generally when a metal is extracted into an organic solvent which is immiscible with water, an enhancement of the absorption signal up to seven times that in an aqueous media may be realized depending on the solvent used. This enhancement has been attributed by Allen\(^1\) to be primarily due to a greater introduction of solvent into the flame and to a temperature effect. When the organic solvent is introduced into the flame, the acetylene flow is reduced and a cooler flame results. The absorption then increases as a result of the temperature reduction which in turn reduces the Doppler width of the absorption line. The concentration of atoms in the flame is also increased due to a smaller volume of flame. A greater volume of solution reaches the flame because the organic solvent produces a finer spray with less condensation.
on the burner walls. Also the solvent evaporates more rapidly from the solute which results in a smaller droplet size with a greater chance of reaching the flame due to the lesser chance of condensation. Viscosity, surface tension, and vapor pressure of the solvent contribute to the enhanced sensitivity, with the organic solvents having the lowest viscosity, lowest surface tension, and highest vapor pressure exhibiting the greatest enhancement in absorption. Compounds other than esters and ketones are usually eliminated for use as solvents in atomic absorption work because of smoke formed by combustion or unstable flames. Esters and ketones exhibit the steady flames, complete combustion, and lack of absorption in the region of the element being determined that is required for atomic absorption analysis.

When an organic solvent has been selected for use in atomic absorption, it is sometimes necessary to use a complexing agent to extract the metal into the chosen organic solvent. Generally there is a chelating agent which will form a stable, neutral, and extractable complex with a particular metal although extractants do exist which alone will extract two or three of the noble metals but which generally require a close control of the pH for successful extraction. Usually it is desirable that only one metal be
extracted with the use of a particular extracting agent
under a particular set of conditions, but for the analysis
of the fractions from a Craig apparatus one complexing agent
is needed which will extract all of the noble metals under
the same conditions. From a study of the literature it
appeared that diantipyrylpropylmethane might extract all
of the noble metals from solution simultaneously.

Diantipyrylpropylmethane (DAPM) has the structure
\[
\begin{align*}
\text{H}_3\text{C-} & \text{C=} \text{C} \quad \text{C} = \text{C-CH}_3 \\
\text{H}_3\text{C-} & \text{N} \quad \text{C=O} \quad \text{H} \quad \text{O=}= \text{C} \quad \text{N-CH}_3 \\
\end{align*}
\]

and is a nonbenzenoid aromatic compound. Acido complexes
of metals form compounds with DAPM of the ion association
type. The ion-association complexes are generally less
selectively extracted than chelates. Busev and Akimov\footnote{12}
using a ten fold excess of DAPM in dichloroethane were able
to extract osmium from HCl and HBr solutions with an acidity
of from 0.5 to 5 M. Of the solvents considered dichloroethane
and chloroform were considered best for the extraction. MIBK
was not considered. Busev and Akimov\footnote{13} also found that quad­
rivalent ruthenium is readily extracted from HCl solutions
with DAPM in dichloroethane, but the extraction is dependent
on the acidity and excess of reagent used. The extraction of trivalent ruthenium is even less than that of the quadrivalent form but also increases with an increase in ruthenium or reagent (DAPM) concentration. Both forms were reported to be extracted from HBr solutions. The same researchers found that palladium and platinum were readily extracted from HCl and HBr solutions over the range 0.5 to 5 M acid with DAPM in dichloroethane. With a six fold excess of DAPM the extraction was greater than 99 percent. The extraction of the hexahaloiridates with DAPM in dichloroethane was reported to be dependent on the acidity of the aqueous phase and on the reagent concentration. The chloro complex of iridium was extracted over a range of 1 to 7 M HCl while the extraction of the bromo iridate decreased very rapidly beyond 1.5 M HBr ostensibly due to the instability of IrBr₆⁻ in solutions with a high concentration of HBr. Tervalent iridium did not form the DAPM compounds. The extraction of rhodium was dependent on acidity (almost no extraction from 8 M HCl solutions) and on the preliminary treatment of the solutions (rhodium is not extractable from solutions which have been boiled or allowed to stand). All of the platinum metals were said to be extractable from HBr solutions. Busev and Akimov separated the chloro complexes
of rhodium from those of platinum, palladium, and iridium respectively by extraction into dichloroethane with DAPM. The rhodium was obtained pure with respect to platinum, palladium, and iridium, but a large number of extractions were necessary to obtain pure platinum, palladium, or iridium with respect to rhodium. Shendrikar and Berg studied the extraction of the platinum metals from HCl solutions into chloroform by means of DAPM. A 1 percent solution of DAPM in chloroform was found to extract 97-98 percent of platinum, palladium, osmium, and iridium from 0.1 to 6 M HCl solutions. Ruthenium required a 5 percent DAPM solution for near complete extraction while no method attempted could enhance the poor extraction of rhodium into chloroform with DAPM. No study has been made of the extraction of the noble metals into MIBK using DAPM.

A careful evaluation of the work done by Berg and Sanders suggested that the ternary mixtures of ruthenium-osmium-palladium; ruthenium-osmium-platinum; and ruthenium-osmium-rhodium might be resolved in 15 stages in the Craig apparatus using a 4 M HBr-MIBK solvent system. Therefore it was proposed that this solvent system be investigated in detail as a possible medium for the separation of mixtures
of the platinum group metals and gold by pseudocountercurrent extraction in a Craig apparatus.

Atomic absorption spectrophotometry will be used for the analysis of the metals separated in the Craig apparatus. From the preceding review of the known interferences in the atomic absorption determination of the noble metals it is apparent that a further investigation of the extent to which the other noble metals interfere in the determination of osmium, ruthenium, and iridium is needed. A method for the prevention of these interferences is also needed. Since copper salts have proved successful in the elimination of certain noble metal interferences, copper sulfate is to be studied as an interference suppressant. The feasibility of extracting all of the noble metals into MIBK as DAPM complexes from each tube of the Craig apparatus after multiple equilibrations prior to analysis by atomic absorption spectrophotometry will be investigated.

A computerized form of the Craig equation will be used to assist in the interpretation of data and in the prediction of possible separations.
II. EXPERIMENTAL

A. Reagents

A gold (III) standard solution in 10 percent concentrated HCl by volume was prepared with a concentration of 1480 ppm.

A standard iridium solution (568 ppm) was prepared by dissolving 0.9863 g of iridium (IV) chloride in 100 ml of concentrated HCl and diluting to 1 liter with distilled water.

A standard solution of osmium (780 ppm) was prepared by dissolving 1.028 g of osmium tetroxide in 250 ml of 0.2 M sodium hydroxide and diluting to 1 liter with distilled water.

A standardized palladium solution (1592 ppm) was prepared by dissolving 1.592 g of palladium metal and diluting to 1 liter with 2 N HCl.

A standard solution of platinum (943 ppm) was prepared by dissolving 0.9427 g of platinum wire in aqua regia. The solution was taken to dryness 3 times with 1:1 HCl. The residue was then taken up with 10 ml of concentrated HCl and diluted to 1 liter with distilled water.

A rhodium (III) solution (314 ppm) was prepared by dissolving rhodium (III) chloride in 100 ml of concentrated
HCl and diluting to 1 liter with distilled water. The solution was standardized by the method of Gilchrist.  

Standard solutions of the bromo complexes were prepared from the corresponding chloro standard solutions. Equal volumes of the chloro standard solution and 48 percent HBr were taken almost to dryness twice. The residue was taken up with 4 M HBr and restored to its original volume so that the concentration of the bromo complex corresponded to that of the respective chloro complex of the noble metal.

Diantipyrylpropylmethane was prepared according to the method of Busev and Tiptsova. Five grams of antipyrine was dissolved in a small amount of water. Two ml of concentrated HCl then was added to 2 ml of freshly distilled butyraldehyde. The solution was heated on a steam bath for 30 minutes and then diluted to 200 ml with water. The DAPM then was precipitated in an ice bath with 1:10 ammonium hydroxide:water according to the modification of Shendrikar and Berg, filtered in a buchner funnel, and washed with a small amount of water. The product was recrystallized from 1:1 acetone:water. A yield of 5.22 g or 92 percent was obtained. The product was stored in darkness since it
slowly decomposes with exposure to light. All other reagents were Reagent Grade Chemicals.

Nitrous oxide suitable for atomic absorption was obtained from Matheson.

B. Apparatus

The atomic absorption analyses were carried out using a Beckman Atomic Absorption Assembly, Model 1301 consisting of the Lamp Power Supply, Gas Regulator Unit, Model DB-G Spectrophotometer, Ten-inch Laboratory Potentiometric Linear-Log Recorder, and two Preheated Laminar Flow Burners (air-acetylene burner and nitrous oxide-acetylene burner).

The gold, iridium, osmium, palladium, platinum, rhodium and ruthenium hollow cathodes were obtained from Westinghouse.

The analysis of osmium in the solvent separation studies was carried out using a Beckman Model DB spectrophotometer with matching silica cells.

The one hundred stage Craig Apparatus was manufactured by H.O. Post and Co. The twenty stage Craig apparatus was based on a design by Craig and Post and built in this laboratory.

The IBM 360/65 computer was used for the calculation and plot of the Craig equation.
C. Atomic Absorption Instrumental Parameters

Studies were carried out on the chosen system to establish the optimum operating variables for the atomic absorption determination of the noble metals. Figures I-VII show the effect of slit width, lamp current, burner height, support gas pressure, and fuel pressure on the atomic absorption of gold, iridium, osmium, palladium, platinum, rhodium, and ruthenium respectively. Table I summarizes the choice of wavelength and the optimum parameters as determined from the results illustrated in Figures I-VII. These same parameters were suitable for the analysis of all samples by atomic absorption with the exception of the fuel which was always adjusted for maximum absorption and in the analysis of rhodium where the burner height also was adjusted for maximum absorption.

D. Atomic Absorption Interference Study of Iridium, Osmium and Ruthenium

1. Procedures

The preparation of iridium and ruthenium samples was as follows. An appropriate sized aliquot of the stock solution of iridium or ruthenium as the chloride was transferred to a 25.00 ml volumetric flask and mixed with aliquots of the stock solution of the potentially interfering element.
Figure I

Optimum Parameters for the Determination of Gold with the 242.8 nm Line

+ Extreme noise in signal

- Lamp Current (mA)

- Support Pressure = 20
- Support Pressure = 18

- Fuel Pressure (lbs/in²)
Figure II

Optimum Parameters for the Determination of Iridium with the 264.0 nm Line

- Slit Width (mm) vs. Percent Absorption
- Lamp Current (mA) vs. Percent Absorption
- Burner Height (in) vs. Percent Absorption
- Fuel Pressure (lbs/in²) vs. Percent Absorption
Figure III

Optimum Parameters for the Determination of Osmium with the 290.3 nm Line

- Slit Width (mm)
  - Percent Absorption
  - Lamp Current (mA)
  - Burner Height (in)
Figure IV

Optimum Parameters for the Determination of Palladium with the 247.6 nm Line

- Slit Width (mm)
- Lamp Current (mA)
- Support Pressures
- Burner Height (in)
- Fuel Pressure (lbs/in²)
Figure V

Optimum Parameters for the Determination of Platinum with the 265.9 nm Line

- Percent Absorption vs. Slit Width (mm)
- Percent Absorption vs. Lamp Current (mA)
- Percent Absorption vs. Burner Height (in)
- Percent Absorption vs. Fuel Pressure (lbs/in²)
Figure VI

Optimum Parameters for the Determination of Rhodium with the 343.5 nm Line

- Slit Width (mm)
- Burner Height (in)
- Lamp Current (mA)
- Fuel Pressure (lbs/in²)
- Support Pressures
Figure VII

Optimum Parameters for the Determination of Ruthenium with the 372.8 nm Line

- **Slit Width (mm)** vs. Percent Absorption
- **Lamp Current (mA)** vs. Percent Absorption
- **Burner Height (in)** vs. Percent Absorption
- **Fuel Pressure (lbs/in²)** vs. Percent Absorption

Support Pressures:
- ○ 20
- △ 17.5
- □ 15
Table I
Optimum Operating Conditions for the Atomic Absorption Analysis of the Noble Metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Slit Width (mm)</th>
<th>Lamp Current (ma)</th>
<th>Burner Height (in.)</th>
<th>Support* Pressure (lbs./in.²)</th>
<th>Fuel* Pressure (lbs./in.²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>242.8</td>
<td>0.10</td>
<td>14</td>
<td>0.2</td>
<td>18</td>
<td>3.5</td>
</tr>
<tr>
<td>Iridium</td>
<td>264.0</td>
<td>0.07</td>
<td>17</td>
<td>0.3</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Osmium</td>
<td>290.9</td>
<td>0.10</td>
<td>15</td>
<td>0.3</td>
<td>20</td>
<td>Adjust**</td>
</tr>
<tr>
<td>Palladium</td>
<td>247.6</td>
<td>0.08</td>
<td>15</td>
<td>0.2</td>
<td>15</td>
<td>2.5</td>
</tr>
<tr>
<td>Platinum</td>
<td>265.9</td>
<td>0.075</td>
<td>15</td>
<td>0.2</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>Rhodium</td>
<td>343.5</td>
<td>0.10</td>
<td>10</td>
<td>***</td>
<td>15</td>
<td>2.5</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>372.8</td>
<td>0.08</td>
<td>17</td>
<td>0.2</td>
<td>15</td>
<td>4</td>
</tr>
</tbody>
</table>

*The fuel used for each metal was acetylene. The support gas was air except for the osmium determination which was nitrous oxide.

**The fuel is adjusted so that the pink portion of the flame is approximately 0.5 inches in height.

***The burner height was adjusted to 0.6 in. for aqueous samples and 0.2 in. for organic samples.
and interference suppressant (copper sulfate). The 25.00 ml of standard sample solution then was transferred to a 25 ml sampling vial and aspirated directly into the flame of the atomic absorption spectrophotometer. Note that all the standard stock solutions were acidified with HCl with the exception of the osmium solutions which were slightly alkaline. Generally upon dilution the HCl concentration of the iridium samples was between 2 and 4 percent by volume with the exception of the samples containing 200 ppm ruthenium and 200 ppm rhodium which were 8 and 14 percent respectively. The hydrochloric acid concentration of the ruthenium samples was between 3 and 10 percent. In order to determine the effect of the acidity upon the determination, iridium and ruthenium samples with a composition of 10, 20, 30, 40, and 50 percent concentrated HCl by volume were analyzed. The analysis with potentially interfering elements present was then repeated at a constant acidity of 10 percent concentrated HCl by volume to remove any possible variations in absorption which may have been due to differences in the acid concentration.

The effect of the amount of copper sulfate on the absorption was also studied in an attempt to optimize
conditions for absorption as well as the suppression of the interferences.

A modification of the procedure was necessary to accommodate the determination of osmium. There was a tendency for the copper to precipitate as the hydrous oxide when copper sulfate was added to the stock osmium solution. To avoid the precipitation of copper, 2 or 3 drops of concentrated sulfuric acid were added to the 25.00 ml volumetric flask before diluting the sample to volume.

Finally samples containing aliquots of all 7 of the noble metals were analyzed for the concentration of iridium, osmium, and ruthenium using copper sulfate as the interference suppressant.

2. Results and Discussion

a. Iridium

In the atomic absorption analysis of iridium where there was some variation in acidity, the other platinum metals interfered when present in concentrations as low as 5 to 200 ppm with the exception of 5 and 75 ppm palladium. The extent of interference by the individual metals in the determination of 100 ppm iridium is illustrated in Figure VIII. Both positive and negative deviations from the normal percent absorption observed for 100 ppm iridium are recorded.
Figure VIII

Percent Absorption of Iridium (100 ppm) as a Function of Interfering Element With and Without Copper Sulfate Suppressant

Ir plus

- © ■

20

- a

10

{0

5 ppm Interferent △ 200 ppm Interferent

□ 75 ppm Interferent ○ 200 ppm Interferent and 20000 ppm Cu

Percent Absorption

None Pt Rh Pd Ru Au Os

Interfering Element
Note that each metal, platinum, rhodium, palladium (at concentrations greater than 75 ppm), ruthenium, gold, and osmium interferes significantly, particularly at concentrations as high as 200 ppm.

A study of the effect of acidity on the absorption of iridium revealed that the variation in absorption between samples containing 1.8 and 10 percent concentrated HCl by volume was important as can be seen in Figure IX. Beyond 20 percent HCl the absorption of iridium was constant. Whether the change in absorption was due to a change in the physical properties of the solution or is a result of chemical interferences in not known.

Figure X (bottom line of data) shows the results of the analysis of iridium solutions each containing 200 ppm of potentially interfering metal and each at a constant 10 percent concentrated HCl by volume. In the absence of an interference suppressant, with the exception of gold, all of the platinum metals cause a deviation in absorption greater than twice the standard deviation of the absorption of the 100 ppm iridium solution containing no interfering metal. The interference of palladium is seen to be very slight.
Figure IX

Percent Absorption of Iridium (100 ppm) as a Function of Hydrochloric Acid Concentration
Figure X

Percent Absorption of Iridium (100 ppm) as a Function of Interfering Element and Copper Concentration at Constant Acidity (10 percent HCl by volume)

- ▲ no copper
- □ 1000 ppm copper
- ○ 2000 ppm copper
- ○ 3000 ppm copper

Interfering Element (200 ppm)
Strasheim and Wessel\textsuperscript{47} were successful in eliminating similar interferences in the absorption of platinum by introducing 20,000 ppm of copper as copper sulfate in each sample. Therefore, copper sulfate was used in an attempt to suppress the noble metal interferences in the determination of iridium. The addition of 20,000 ppm of copper not only eliminated the interferences due to 200 ppm of each of the other metals and to acid differences but also increased the sensitivity of the analysis. The effect of 20,000 ppm of copper on the iridium analysis is shown in Figure VIII. Problems arose, however, with samples containing such a high salt content. Only a limited number of samples could be run before the burner had to be shut down so that the burner assembly could be cleaned of the accumulated salts. In an attempt to avoid this problem, a study was made to determine if a smaller concentration of copper would be an effective interference suppressant. The study began with the determination of samples containing 100 ppm iridium, 200 ppm potential interfering metal, 10 percent concentrated HCl by volume, and 1000 ppm copper. The results are shown in Figure X. Note that 3000 ppm copper effectively eliminated the interference of the other platinum group metals in the determination of iridium.
The sensitivity of the iridium determination was observed to be dependent on the copper concentration. The percent absorption recorded for the 264.0 nm iridium line as a function of the copper concentration is given in Figure XI. The maximum absorption for iridium was observed with 250 ppm copper, but there is only a minor loss in sensitivity if the optimum concentration for elimination of interferences is accepted as 3000 ppm copper. A standard curve for the analysis of iridium solutions containing 3000 ppm copper, and 10 percent HCl is shown in Figure XII. The sensitivity, ppm of metal yielding 1 percent absorption, is 2.5 ppm and the analysis range is 37 to 223 ppm iridium.

b. Ruthenium

Each of the noble metals except rhodium at 200 ppm interferred with the determination of 50 ppm ruthenium but it was found that 20,000 ppm copper as the sulfate would effectively suppress these interferences. These data are summarized in Figure XIII. A study of the variation in the ruthenium absorption with acidity showed a considerable depressant effect on the absorption of ruthenium as the acidity was increased from 10 to 40 percent concentrated HCl by volume. Figure XIV demonstrates the relationship between the absorption of ruthenium and the acidity.
Figure XI

Percent Absorption of Iridium (100 ppm) as a Function of the Copper Concentration

Percent Absorption

ppm Copper x 10^4
Figure XII

Iridium Standard Curve

Absorbance

Iridium Concentration (ppm)
Figure XIII

Ruthenium (50 ppm) Absorption as a Function of Interfering Element With and Without Copper Sulfate Suppressant

- ○ no copper
- △ 20,000 ppm copper

Percent Absorption

Interfering Element (200 ppm)
Figure XIV

Percent Absorption of Ruthenium (25 ppm) as a Function of Hydrochloric Acid Concentration

HCl Concentration (percent by volume)
At a constant 10 percent HCl each of the noble metals greatly depressed or enhanced the absorption of 25 ppm ruthenium as is seen in Figure XV.

In the case of ruthenium it was considered doubly desirable to find a lower level of copper concentration that would suppress the noble metal interferences. Besides the problem of burner clogging, the copper sulfate also lowers the sensitivity of the ruthenium determination contrary to the results obtained by Makarov and Kukuskin.31 The effect of the copper concentration on the percent absorption of ruthenium is given in Figure XVI. Figure XV shows the results which the addition of copper sulfate had on the percent absorption of ruthenium solutions containing the other noble metals. It was found that a copper concentration of 2000 ppm would adequately suppress the interferences due to the other noble metals at a constant 10 percent HCl concentration.

Under the conditions decided upon for analysis of ruthenium (10 percent concentrated HCl by volume and 2000 ppm copper) a sensitivity of 0.25 ppm and an analysis range of 8 to 56 ppm was obtained. Figure XVII represents a typical analysis curve for the determination of ruthenium.
Figure XV

Percent Absorption of Ruthenium (25 ppm) as a Function of Interfering Element and Copper Concentration at Constant Acidity

- △ no copper
- □ 1000 ppm copper
- ○ 2000 ppm copper

Interfering Element (200 ppm)
Figure XVI

Percent Absorption of Ruthenium (25 ppm) as a Function of the Copper Concentration
Figure XVII

Ruthenium Standard Curve

Absorbance

Ruthenium Concentration (ppm)
c. Osmium

The initial work with osmium was disappointing in that no osmium absorption was observed. In fact, it was not until copper sulfate was introduced in the osmium samples that osmium absorption occurred. Figure XVIII illustrates the effect that varying copper concentrations had on the osmium absorption. The other platinum metals interfered with the determination of osmium absorption, but the data in Figure XIX show that 3000 ppm copper in the samples is an effective interference suppressant.

d. Mixtures

Table II indicates that solutions containing all of the noble metals can be analyzed successfully for iridium, ruthenium, and osmium when copper sulfate has been added to the solution. Each of the samples contained 3000 ppm of copper and were 10 percent concentrated hydrochloric acid by volume.
Figure XVIII

Percent Absorption of Osmium (100 ppm) as a Function of the Copper Concentration

Percent Absorption

ppm Copper x 10^4
Figure XIX

Percent Absorption of Osmium as a Function of Interfering Element and Copper Concentration

- □ 1000 ppm copper
- △ 2000 ppm copper
- ○ 3000 ppm copper

Interfering Element (200 ppm)
### Table II

Analysis of Noble Metal Mixtures for Iridium, Ruthenium, and Osmium

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (ppm)</th>
<th>Sample Composition (ppm of Metal)</th>
<th>( \Delta A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>100</td>
<td>100-Os, 75-Pd, 100-Rh, 25-Pt, 200-Au, and 25-Rw</td>
<td>36.5</td>
</tr>
<tr>
<td>Ir</td>
<td>100</td>
<td>200-Os, 25-Pd, 50-Rh, 200-Pt, 50-Au, and 25-Ru</td>
<td>35.7</td>
</tr>
<tr>
<td>Ru</td>
<td>25</td>
<td>100-Os, 75-Pd, 100-Rh, 25-Pt, 200-Au, and 100-Ir</td>
<td>36.9</td>
</tr>
<tr>
<td>Ru</td>
<td>25</td>
<td>200-Os, 25-Pd, 50-Rh, 200-Pt, 50-Au, and 100-Ir</td>
<td>36.0</td>
</tr>
<tr>
<td>Os</td>
<td>100</td>
<td>75-Pd, 100-Rh, 25-Pt, 200-Au, 100-Ir, and 25-Ru</td>
<td>35.9</td>
</tr>
<tr>
<td>Os</td>
<td>200</td>
<td>25-Pd, 50-Rh, 200-Pt, 50-Au, 100-Ir, and 25-Ru</td>
<td>6.8</td>
</tr>
<tr>
<td>Os</td>
<td>200</td>
<td>25-Pd, 50-Rh, 200-Pt, 50-Au, 100-Ir, and 25-Ru</td>
<td>6.5</td>
</tr>
<tr>
<td>Os</td>
<td>200</td>
<td>25-Pd, 50-Rh, 200-Pt, 50-Au, 100-Ir, and 25-Ru</td>
<td>10.7</td>
</tr>
<tr>
<td>Os</td>
<td>200</td>
<td>25-Pd, 50-Rh, 200-Pt, 50-Au, 100-Ir, and 25-Ru</td>
<td>10.2</td>
</tr>
</tbody>
</table>
E. Atomic absorption Analysis of the Bromo Complexes of the Noble Metals

1. Procedures

A brief study of the effect which converting the chloro complexes of the noble metals to the corresponding bromo complexes had on the atomic absorption of these metals was made. An identical aliquot of standard chloro complex and bromo complex of each noble metal was added to 10.0 ml volumetric flasks and diluted to volume with distilled water. Another aliquot of the bromo complex of each noble metal (the same concentration as the preceding samples) was diluted to volume in a 10.0 ml volumetric flask such that the final concentration of HBr was 4.4 M. A third aliquot of the bromo complex of each metal was diluted to volume with distilled water after the addition of 3000 ppm of copper was added to the sample. The samples were then aspirated directly into the flame of the atomic absorption spectrophotometer and the percent absorption recorded at the wavelength of analysis for each noble metal. Standard curves were then constructed for each element under the conditions decided upon for analysis.
2. Results and discussion.

The results are summarized in Table III. With the exception of gold and palladium, aqueous solutions of the bromo complexes of the noble metals exhibited a significantly lower percent absorption than the corresponding aqueous solution of the chloro complex. The same can also be said of the bromo complexes which had a 4 M HBr concentration with the exception of gold which showed a considerable enhancement in the percent absorption. The 4 M HBr concentration besides generally lowering the sensitivity of the noble metal bromo solution also had a rather destructive effect on the atomizer assembly and the insides of the burner as well as producing unstable and sometimes erratic signals. The addition of 3000 ppm Cu as copper sulfate to the aqueous iridium bromo sample produced a signal where none had been obtained for the iridium bromo solutions without copper. The absorption of platinum, rhodium, and ruthenium was also enhanced by the addition of copper to the bromo solutions of these metals. The absorption of gold and palladium was cut to about half that of the aqueous bromo solutions by the addition of copper.

Due to the unfavorable effect on the burner and the reduction in sensitivity by high concentrations of HBr, it
### Table III

Comparison of the Percent Absorption of the Bromo Complexes with that of the Chloro Complexes of the Noble Metals

<table>
<thead>
<tr>
<th>Metal (ppm)</th>
<th>Chloro Complex in Aqueous %A Solution</th>
<th>Bromo Complex in Aqueous %A Solution</th>
<th>Bromo Complex in 4 N HBr %A Solution</th>
<th>Bromo Complex in Aqueous Solution plus %A 3000 ppm Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>4</td>
<td>45.5</td>
<td>44.5 (0.18% HBr)</td>
<td>*80</td>
</tr>
<tr>
<td>Pd</td>
<td>4</td>
<td>40.0</td>
<td>40.0 (0.17% HBr)</td>
<td>27.0</td>
</tr>
<tr>
<td>Pt</td>
<td>30</td>
<td>24.0</td>
<td>5.0 (2.18% HBr)</td>
<td>5.0</td>
</tr>
<tr>
<td>Ir</td>
<td>100</td>
<td>16.0</td>
<td>0 (7.4% HBr)</td>
<td>0</td>
</tr>
<tr>
<td>Rh</td>
<td>10</td>
<td>49.5</td>
<td>23.0 (2.16% HBr)</td>
<td>12</td>
</tr>
<tr>
<td>Ru</td>
<td>15</td>
<td>25.0</td>
<td>7 (2.1% HBr)</td>
<td>4</td>
</tr>
</tbody>
</table>

*average figure, very erratic signal*
was considered desirable to analyze bromo solutions of the noble metals at as low a concentration of HBr as possible. Since the aqueous samples from the Craig separations to be performed would be 4 N HBr, some method was required which would reduce this high level of acidity. Neutralization was rejected because this would result in the production of large amounts of salts which would in turn clog the burner atomizer system as well as possibly producing interferences in the determination of the noble metals. The removal of the noble metal from the acid media by total extraction into the organic phase is explored in the next section. A third method, that of evaporation finally proved to be the most favorable method for the reduction of the acidity prior to analysis even though it was somewhat time consuming. It was also decided to add copper to the solution to reduce interferences and in some cases enhance the absorption. The absorption was enhanced for all the metals except gold and palladium which while exhibiting a depressed absorption still could be analyzed at lower concentrations than any of the other noble metals.

Figures XX-XXV are the typical curves of absorbance versus concentration obtained in the atomic absorption analysis of the noble metal solutions which were 1 percent
Figure XX

Gold Standard Curve (Bromo Aqueous Complex)
Figure XXI

Iridium Standard Curve (Bromo Aqueous Complex)
Figure XXII

Palladium Standard Curve (Bromo Aqueous Complex)
Figure XXIII

Platinum Standard Curve (Bromo Aqueous Complex)

Percent Absorption

Platinum Concentration (ppm)
Figure XXIV

Rhodium Standard Curve (Bromo Aqueous Complex)
Figure XXV

Ruthenium Standard Curve (Bromo Aqueous Complex)
HBr and contained 3000 ppm copper. Table IV gives the sensitivity of the metal and the range of concentration which could be analyzed by atomic absorption under the conditions of analysis stated above.
### Table IV

Sensitivity and Analysis Range in the Determination of the Bromo Complexes of the Noble Metals by Atomic Absorption

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sensitivity (ppm)</th>
<th>Analysis Range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>0.17</td>
<td>2.6 → 16.8</td>
</tr>
<tr>
<td>Ir</td>
<td>2.5</td>
<td>43 → 284</td>
</tr>
<tr>
<td>Pd</td>
<td>0.09</td>
<td>1.5 → 10.1</td>
</tr>
<tr>
<td>Pt</td>
<td>9.28</td>
<td>152 → 870</td>
</tr>
<tr>
<td>Rh</td>
<td>0.10</td>
<td>1.8 → 27.0</td>
</tr>
<tr>
<td>Ru</td>
<td>0.78</td>
<td>13.5 → 126</td>
</tr>
</tbody>
</table>
F. Extraction of the Noble Metals Into 4-Methyl-2 Pentanone Utilizing Diantipyrylpropylmethane as an Extractant

1. Procedure

An attempt was made to develop a method by which the noble metals in the organic and raffinate phases after a Craig separation could be readily extracted into the organic phase prior to atomic absorption analysis by introduction of a non selective extracting agent such as the basic dye diantipyrylpropylmethane (DAPM).

The same initial procedure was used for the study of the extraction of each of the noble metals into MIBK by means of DAPM. To 0.5 ml of the bromo complex of metal (4 N HBr) in a 15 ml separatory funnel 4.5 ml of 4 N HBr was added to form a total volume of 5.0 ml. Then 5.0 ml of MIBK containing 1 percent (w/v) DAPM was added to the separatory funnel. The separatory funnel was shaken and the phases allowed to separate. The colors of the two phases were observed before and after the attempted extraction.

In a second study of the extraction feasibility, 5.0 ml of 100 ppm bromo complex (made by diluting an appropriate aliquot of metal to volume with distilled water) was added to a separatory funnel. To this solution was added 5.0 ml
of MIBK containing 1 percent DAPM solution in MIBK. The colors of the phases before and after extraction were observed.

Additional studies were necessary in the extraction study of ruthenium, iridium, and rhodium by the use of DAPM. Following the general procedures listed previously, the extraction of ruthenium from a 1 percent HBr solution was attempted using a 1 percent DAPM solution. Then the effect of increasing the concentration of DAPM was observed. The additional DAPM was added in ethanol to prevent the precipitation of the DAPM in the MIBK. Finally a few drops of bromine in carbon tetrachloride were added to the solution. A similar procedure was also applied to rhodium. For the study of iridium, DAPM in ethanol was added to the iridium solutions together with a few drops of bromine in carbon tetrachloride. Blank solutions containing no metal were similarly treated.

The effect which the DAPM extraction of the noble metals into MIBK had on the atomic absorption determination of the noble metals was studied. The same procedure was followed for the extraction of gold, platinum, palladium, and osmium. To a suitable aliquot of standard noble metal bromo solution (4 N HBr) in a 15 ml separatory funnel was added 1.0 ml of
ethanol (containing 0.15 g DAPM) and 5.0 ml of MIBK pre-
quilibrated with 4 N HBr. The phases were equilibrated by
shaking and allowed to separate. The layers were separated
and the lower (aqueous) phase returned to the separatory
funnel. Five additional ml of preequilibrated MIBK were
added to the separatory funnel. After equilibration the
aqueous phase was withdrawn and the two organic phases
were combined to form a MIBK solution of noble metal.
Aliquots of this solution were diluted to form standards
of a concentration suitable for analysis by atomic absorp-
tion. The standards were aspirated into the flame of the
atomic absorption spectrophotometer and the percent absorp-
tion recorded. A slight modification of the above procedure
was followed for the extraction of rhodium, iridium, and
ruthenium prior to analysis by atomic absorption. After
the addition of ethanol solution of DAPM, a few drops of
bromine in carbon tetrachloride were added before the first
addition of MIBK.

2. Results and Discussion

The extraction of the noble metals from 4 N HBr solu-
tion with 1 percent DAPM in MIBK met with only limited
success. Gold, osmium, and platinum appeared to be almost
totally extracted into the organic phase leaving only a
faint trace of color in the aqueous phase. These solutions were highly colored so that an estimate of the extraction could be visually obtained. Palladium appeared to be only about half extracted into the organic layer as the two phases were about equal in color. The degree of extraction of iridium and rhodium was impossible to estimate accurately by visual observation due to the very pale green and lavender of these complexes respectively. The ruthenium solution was apparently composed of two different species, one the blue which is extractable into organic media and a brownish orange one which is not extracted. The blue species in not present in freshly prepared solutions of the ruthenium bromo complex but forms after the solution has aged for a few weeks. Extraction of the noble metals from very dilute HBr solutions (1-2 percent HBr) with 1 percent DAPM solutions in MIBK was more successful. A cloudy suspension formed in the aqueous phase but cleared up with the addition of a few drops of ethanol. Palladium was almost totally extracted into the organic phase so its extraction is certainly dependent upon the acidity of the solution with extraction being favored by low acidity. The aqueous phase of gold, osmium, and platinum were colorless after the metals were extracted into MIBK. The ruthenium complex was only slightly
extracted from a freshly prepared ruthenium bromo solution. Again the degree of extraction of rhodium and iridium was difficult to ascertain visually due to the pale color of these two complexes.

The extraction of ruthenium from 1 percent HBr solution with DAPM into MIBK was nearly complete leaving only a trace of color in the aqueous phase. The extraction of ruthenium from 4 N HBr solutions was much less complete. The addition of 0.4 g of DAPM (in ethanol) resulted in a better but still incomplete extraction. The addition of a few drops of bromine in carbon tetrachloride caused the color of the organic phase to go from a dirty green color to a dark blue color which was stable. The extraction appeared to be complete. The extraction of ruthenium is thus favored by low acidities and an excess of DAPM. A blank solution containing no ruthenium which was treated in a similar manner yielded no color in the organic phase.

Extraction of rhodium with DAPM in ethanol followed by the addition of MIBK and a few drops of bromine in carbon tetrachloride seemed visually to be complete. The extracted species formed a yellowish brown organic layer. A blank solution containing no rhodium exhibited no color in either phase after a few minutes.
The iridium bromo complex appeared to be completely extracted by the addition of bromine in carbon tetrachloride to the 1 percent solution of DAPM in MIBK. The initial extracted species was yellowish brown but after a few minutes became a highly noticeable purple. After a few weeks all color was gone from the organic phase and a precipitate was observed at the interface of the two phases. Again a blank solution containing no metal was colorless after being treated in the same manner.

It is evident from the preceding results that the extraction of the noble metals using the extracting agent DAPM can be achieved with varying degrees of difficulty and success. An attempt was then made to determine the sensitivity with which the noble metals could be determined in the DAPM-MIBK solutions by atomic absorption spectroscopy. Figures XXVI-XXIX show the standard curves obtained for the analysis of gold, palladium, platinum, and rhodium. Sensitivities of 0.65, 0.060 and 0.10 ppm respectively for gold, palladium, and rhodium show that these three metals can be determined at quite small concentrations by this method. These data are contrary to that of Deily who was unable to produce a lean enough flame using MIBK as a solvent in the analysis of rhodium. The standard curve for platinum, on
Figure XXVI

Gold Standard Curve (Organic Solution)
Figure XXVII

Palladium Standard Curve (Organic Solution)
Figure XXVIII

Platinum Standard Curve (Organic Solution)
Figure XXIX

Rhodium Standard Curve (Organic Solution)
the other hand, shows that this analysis is not sensitive and that the curve shows a negative deviation from Beer's Law. Unfortunately no signal was obtained for the 100 ppm ruthenium, 100 ppm iridium, or 200 ppm osmium solutions which would have yielded a detectable signal in the aqueous phase. It is quite possible that the organic solution produced a flame too cool for the atomization of these three metals since they are known to require a hotter flame than the other four metals when analyzed in the aqueous phase.

Therefore, due to the lack of sensitivity in the analysis of ruthenium, iridium, osmium, and platinum this extraction-analysis method for the determination of the noble metals was abandoned in favor of the evaporation method for lowering the acidity prior to atomic absorption analysis as described in the preceding section.
G. Determination of the Distribution Coefficients of the Noble Metals in the 4 N Hydrobromic Acid-(4-Methyl-2-Pentanone) System

1. Procedures

The same procedure was followed for the determination of the distribution coefficients of each of the noble metals. To a 60 ml separatory funnel, a suitable aliquot of metal was added together with sufficient 4 N HBr (previously equilibrated with MIBK) so that the total volume of raffinate was 25.0 ml. Then 25.0 ml of MIBK (previously equilibrated with 4 N HBr) was added to the separatory funnel. The separatory funnel then was shaken so that the two phases were thoroughly equilibrated. The phases were allowed to separate and the raffinate removed for analysis of the metal concentration. The raffinate was evaporated almost to dryness for all metals except osmium and then taken up with 1 percent HBr. The solution was restored to its original volume after addition of 3000 ppm of copper as the sulfate. Analysis of this solution was then carried out by aspirating the sample directly into the flame of an atomic absorption spectrophotometer. The percent absorption was recorded for the sample and the concentration of the metal determined using a standard curve of the absorbance
versus concentration for each metal. The osmium solution was analyzed directly by absorption spectrophotometry without prior treatment at the 450 nm line. The concentration in the organic phase was determined by difference. The distribution coefficient for each metal was then calculated using the equation

$$K_d = \frac{\text{concentration of metal in organic phase}}{\text{concentration of metal in raffinate}}$$

2. Results and Discussion.

Table V summarizes the data obtained for the distribution coefficients of the noble metals for the system 4 N HBr-MIBK. It is apparent that the distribution coefficient is dependent on the concentration of the metal in the solution in this system. With the exception of palladium there is a marked difference in the distribution coefficients obtained here and those of Berg and Sanders. Part of this difference may be due to the fact that no salt was added to aid the extraction in this study because of the problems this salt would cause in the operation of the burner in the atomic absorption analysis of these metals. Osmium and gold are extracted to a large degree into the organic phase while iridium, ruthenium, and palladium are only slightly extracted into the organic phase. Rhodium is
<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal Concentration in Raffinate Before Equilibration (µg/ml)</th>
<th>Metal Concentration in Raffinate After Equilibration (µg/ml)</th>
<th>Kd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>296</td>
<td>0.62</td>
<td>477</td>
</tr>
<tr>
<td></td>
<td>118</td>
<td>0.51</td>
<td>230</td>
</tr>
<tr>
<td>Pd</td>
<td>25</td>
<td>23.56</td>
<td>0.061</td>
</tr>
<tr>
<td></td>
<td>66.7</td>
<td>59.0</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>127</td>
<td>95.0</td>
<td>0.34</td>
</tr>
<tr>
<td>Ru</td>
<td>64.5</td>
<td>46.0</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>18.37</td>
<td>0.089</td>
</tr>
<tr>
<td>Pt</td>
<td>56.6</td>
<td>51.7</td>
<td>0.094</td>
</tr>
<tr>
<td></td>
<td>85.0</td>
<td>72.1</td>
<td>0.178</td>
</tr>
<tr>
<td></td>
<td>113.2</td>
<td>93.5</td>
<td>0.211</td>
</tr>
<tr>
<td></td>
<td>141.4</td>
<td>103.4</td>
<td>0.368</td>
</tr>
<tr>
<td>Rh</td>
<td>25.1</td>
<td>24.0</td>
<td>0.046</td>
</tr>
<tr>
<td>Ir</td>
<td>149</td>
<td>123.6</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>92.7</td>
<td>84.7</td>
<td>0.094</td>
</tr>
<tr>
<td>Os</td>
<td>20.0</td>
<td>6.67</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table V

Distribution Coefficients of the Bromo Complexes of the Noble Metals Between 4 N Hydrobromic Acid and 4-Methyl-2-Pentanone
hardly extracted at all and platinum is only moderately extracted.

On the basis of these distribution coefficients it would appear that the quaternary mixtures palladium-platinum-osmium-gold; ruthenium-platinum-osmium-gold; and iridium-platinum-osmium-gold can be separated using a Craig apparatus. It should also be possible to separate rather simply on a ten or fifteen stage Craig apparatus binary mixtures of gold or osmium and each of the remaining noble metals.
H. Computerized Form of the Craig Equation

In order to determine which metals could be separated and what volume ratio of organic phase to aqueous would produce the best separation, a computerized version of the Craig equation was utilized. Initially written by Sanders and modified by Mosely, the computer program was further rewritten so that a plot of the output was produced and up to a 100 stage prediction could be calculated. A reproduction of the program is given in Table VI. For operation, all that is necessary is for a data card containing the distribution coefficient, volume ratio, and number of stages to be inserted in the program.
Table VI

Computer Program for the Calculation and Plotting of the Craig Equation

Craig equation calculations of fraction of solute expected after n transfers in countercurrent extraction.

I is the total number of tubes.

Plotting of data is also done.

FACT(I) is the log of the factorial of I-1.

Dimension BUFFER(10000), TNR(101), PERCNT(101), TU(101), FACT(101), AB(13), ORD(5), ACT(78), BCT(23), HEAD(5)

Equivalence (FACT(1), ACT(1)), (FACT(79), BCT(1))

Data ACT/0., 0., 6.93147E-01, 1.79176, 3.17805, 4.78749, 6.57925, 1 8.52516, 1.06046E 01, 1.280183E 01, 1.510441E 01, 1.75023E 01, 2 1.99872E 01, 2.25521E 01, 2.51912E 01, 2.78992E 01, 3.06718E 01, 3 3.35050E 01, 3.63954E 01, 3.93398E 01, 4.23355E 01, 4.53801E 01, 4 4.84711E 01, 5.16066E 01, 5.47846E 01, 5.80035E 01, 6.12616E 01, 5 6.45574E 01, 6.78896E 01, 7.12569E 01, 7.46581E 01, 7.80920E 01, 6 8.15578E 01, 8.50543E 01, 8.85806E 01, 9.21360E 01, 9.57197E 01, 7 9.933060E 01, 1.029682E 02, 1.066317E 02, 1.103206E 02, 8 1.140342E 02, 1.17718E 02, 1.215330E 02, 1.253172E 02, 9 1.291239E 02, 1.329525E 02, 1.368026E 02, 1.406738E 02, A 1.445657E 02, 1.484777E 02, 1.524095E 02, 1.563607E 02, B 1.603310E 02, 1.643200E 02, 1.683272E 02, 1.723526E 02, C 1.763957E 02, 1.804562E 02, 1.845336E 02, 1.886280E 02, D 1.927389E 02, 1.968699E 02, 2.010091E 02, 2.051680E 02, E 2.093422E 02, 2.135320E 02, 2.177366E 02, 2.219562E 02, F 2.261902E 02, 2.304387E 02, 2.347014E 02, 2.389781E 02, G 2.432685E 02, 2.475726E 02, 2.5189E 02, 2.5622E 02, 2.6056E 02/

Data BCT/ 2.6492E 02,
H 2.6929E 02, 2.7367E 02, 2.7807E 02, 2.8247E 02, 2.8689E 02,  
I 2.9132E 02, 2.9576E 02, 3.00226 02, 3.0469E 02, 3.0916E 02,  
J 3.1365E 02, 3.1815E 02, 3.2266E 02, 3.2718E 02, 3.3172E 02,  
K 3.3626E 02, 3.4081E 02, 3.4538E 02, 3.4995E 02, 3.5454E 02,  
L 3.5913E 02, 3.6374E 02 /  
DATA AB/12H TUBE NUMBER/,0R0/18HFRACTION OF SOLUTE/  
DATA HEAD/20HTNR VERSUS TUBE R /  
REAL K,KD  
CALL PLOTS (BUFFER,10000)  
CALL PLOT (0.,0.,-3)  
CALL AXIS (0.,0.,AB,-12,40.,0.,0.,2.)  
CALL AXIS (0.,0.,ORD,+18,8.,90.,0.,0.125)  
CALL SYMBOL (.5,8.5,.14,HEAD,0.,18)  
18 CONTINUE  
PRINT700  
700 FORMAT ( 1H1 )  
READ I,N,KD,RATIO  
1 FORMAT (I3,2F10.5)  
IF (N.GE.101) GO TO 500  
2 K=KD*RATIO  
PRINT3,KD,RATIO  
3 FORMAT (1H0, 1X, 9TRANSFERS , 10X, 6HTUBE R , 10X,  
1 18HFRACTION OF SOLUTE , 5X , 7HPERCENT , 10X ,  
2 15HDIST. COEFF. = , F10.4 , 10X , 8HRATIO = , F8.3 / )  
IM1=N-1  
DO 4 I=1,N  
TU(I)=I  
IM1MT=N-I
TNR(I) = EXP(FACT(IM1+1) - FACT(I) - FACT(IM1MT+1)
1 - FLOAT(IM1) * ALOG(K+1.) + FLOAT(I-1) * ALOG(K))
PERCNT(I) = TNR(I) * 100.

4 PRINT 5, IM1, I, TNR(I), PERCNT(I)
5 FORMAT (1H ' ', 1X, 16, 10X, 16, 12X, 'F15.8', 5X, 'F10.1')
   KX = N
   TU(N+1) = 0.
   TU(N+2) = 2.
   TNR(N+1) = 0.
   TNR(N+2) = 0.125
   CALL FLINE (TU, TNR, -KX, 1, 1, 4)
   CALL PLOT (0., 0., 0., 1, 1, 4)
   GO TO 18
500 CALL PLOT (0., 0., 999)
STOP
END
I. Craig Separations of the Noble Metals

1. Procedures

The same procedure was followed for all separations. Figure XXX shows a single stage of the Craig apparatus. Equal volumes of 4 N HBr (preequilibrated twice with MIBK) were added to each stage of the Craig apparatus except the first such that when vertical the liquid was level with the connecting tube A. Aliquots of the stock chloro complexes of the noble metals to be separated were taken almost to dryness on a steam bath with an equal volume of concentrated HBr twice. The residue was taken up with 25.0 ml (20 stage Craig apparatus) or 10.0 ml (100 stage Craig apparatus) of 4 N HBr (preequilibrated with MIBK) and transferred to tube 1 of the Craig apparatus. Depending on which Craig apparatus was used, 25.0 or 10.0 ml of MIBK (preequilibrated twice with 4 N HBr) was added to the first tube containing the aqueous solution of metals to be separated. The two phases then were equilibrated by rocking the Craig extractor 50 times after which the phases were allowed time to separate. The Craig apparatus then was rotated 90 degrees and the organic phase transferred to the transfer tube B so that when the Craig apparatus was returned to its initial position the organic phase was transferred
Figure XXX

Single Stage of a Craig Apparatus

B Transfer Tube

A Connecting Tube

25.0 ml volume
into tube 2. A fresh aliquot of MIBK was added to tube 1 and the equilibration repeated as before. This procedure was repeated until the desired number of stages was attained. After the separation was complete both phases of each tube were simultaneously transferred to a 100 ml beaker (20 stage apparatus) or a 50 ml beaker (100 stage apparatus). The contents of each tube then was evaporated almost to dryness on a steam bath and the residue taken up with 1 percent HBr. The sample was restored to its original volume in a volumetric flask after the addition of 3000 ppm of copper and transferred to a 15 ml or 25 ml sampling vial. The sample was then aspirated directly into the flame of the atomic absorption spectrophotometer and the percent absorption recorded. By means of a standard curve such as those in section E of absorbance versus concentration, the concentration of each metal in each tube was determined and the fraction of each metal plotted versus the tube number. The osmium concentration was determined by absorption spectrophotometry. The sample was transferred to a 1 cm cuvette and inserted into the beam of the spectrophotometer and the percent transmittance determined at the 450 nm line. By comparison with a standard curve of absorbance versus
concentration such as Figure XXXI, the osmium concentration was determined.

The binary mixtures of gold with iridium, palladium, platinum, ruthenium, and rhodium were separated using 10 stages of the Craig apparatus. This allowed a comparison of the experimentally determined distribution coefficients of section G with those obtained using the equation:

\[ K_d = \frac{r_{\text{max}}}{n - r_{\text{max}}} \]

\( r_{\text{max}} \) is the tube containing the maximum amount of solute and \( n \) is the number of transfers.

A 75 stage separation of rhodium, platinum, and gold; a 100 stage separation of rhodium, palladium, and gold; and an 80 stage separation of ruthenium, iridium, and osmium was attempted. The organic phase was simply removed and not further equilibrated after the 60th stage because the separation of gold or osmium from the other metals was observed to be completed at this stage.

2. Results and Discussion

Figures XXXII-XXXVI show the results obtained in the Craig separation of gold from palladium, platinum, iridium, rhodium, and ruthenium. A good separation for each of these binary systems was obtained. Palladium, iridium,
Figure XXXI

Osmium Standard Curve (Spectrophotometric Determination)
Figure XXXII

Distribution Curves for the Separation of Iridium and Gold

- Experimental
- Theoretical

Percent of Metal Present

Tube Number
Figure XXXIII

Distribution Curves for the Separation of Palladium and Gold

- Experimental
- Theoretical

Percent of Metal Present

Tube Number

Pd

Au
Figure XXXIV
Distribution Curves for the Separation of Platinum and Gold

- Experimental
- Theoretical

Percent of Metal Present

Tube Number

Pt

Au
Figure XXXV

Distribution Curves for the Separation of Rhodium and Gold

Experimental

Theoretical

Percent of Metal Present

Rh

Au

Tube Number
Figure XXXVI

Distribution Curves for the Separation of Ruthenium and Gold

- Experimental
- Theoretical
rhodium, and ruthenium all had their maximum amount of solute in the first tube indicating from the application of the equation on the preceding page that their distribution coefficients lie somewhere between 0.0 and 0.059. Rhodium had all of its solute in the first tube with only a trace of solute in the second tube showing that it is particularly insoluble in the organic phase. Platinum exhibited its maximum in the second tube therefore, its distribution coefficient should lie between 0.06 and 0.19. Gold in every separation showed its maximum amount of solute in tube 10 so that by application of the same equation as above, the distribution coefficient is somewhere between 17 and infinity. Good agreement is obtained for the distribution coefficients calculated from the separation data and the experimentally determined coefficients listed in Table V for gold, rhodium, palladium, and platinum solutions of low metal concentrations. The calculated distribution coefficients from the actual separations involving ruthenium are smaller than the coefficients determined experimentally which are listed in Table V. These observations were made by a comparison of the experimental distribution data with the theoretical data plotted in Figures XXXII-XXXVI which was calculated by computer using
the distribution coefficients for low metal concentrations in Table V. Table VII shows the recovery data for these binary separations.

Figure XXXVII gives the results obtained in the 75 stage separation of rhodium, platinum, and gold. The gold was readily separated from the rhodium and platinum while the platinum was 92 percent separated from the rhodium. Calculation of the distribution coefficients from the separation data yielded coefficients of 0.0068, 0.104, and 36 respectively for rhodium, platinum, and gold. The μg of each metal taken, the μg recovered and the percent recovery for each metal are recorded in Table VIII. The theoretically expected separation calculated using the distribution coefficients of Table V is also plotted in Figure XXXVII.

A plot of the percent of each metal in each tube for the 100 stage separation of rhodium, palladium, and gold is given in Figure XXXVIII. The separation was good with 97 percent of the palladium separated from the rhodium within the limits of detection and a quantitative separation of both of these metals from gold. Distribution coefficients calculated from the Craig separation data yield 0.0056, 0.076 and 48.5 for rhodium, palladium, and gold respectively. The data for the μg of each metal in the
Table VII

Recovery Data for the Binary Separations of Gold from Palladium, Platinum, Iridium, Rhodium, and Ruthenium

<table>
<thead>
<tr>
<th>Binary Mixture</th>
<th>ug Taken</th>
<th>ug Recovered</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1480</td>
<td>1334</td>
<td>90</td>
</tr>
<tr>
<td>Pd</td>
<td>1592</td>
<td>1527</td>
<td>96</td>
</tr>
<tr>
<td>Au</td>
<td>2220</td>
<td>1930</td>
<td>87</td>
</tr>
<tr>
<td>Pt</td>
<td>17,900</td>
<td>15444</td>
<td>86</td>
</tr>
<tr>
<td>Au</td>
<td>7400</td>
<td>7336</td>
<td>99</td>
</tr>
<tr>
<td>Ir</td>
<td>2781</td>
<td>2416</td>
<td>87</td>
</tr>
<tr>
<td>Au</td>
<td>7400</td>
<td>7100</td>
<td>96</td>
</tr>
<tr>
<td>Rh</td>
<td>4362</td>
<td>4120</td>
<td>94</td>
</tr>
<tr>
<td>Au</td>
<td>740</td>
<td>724</td>
<td>98</td>
</tr>
<tr>
<td>Ru</td>
<td>1616</td>
<td>1315</td>
<td>82</td>
</tr>
</tbody>
</table>
Figure XXXVII

Distribution Curves for the Separation of Rhodium, Platinum, and Gold

- Experimental
- Theoretical

Percent of Metal Present

Tube Number

Rh
Pt
Au
Table VIII

Recovery Data for the Separation of Rhodium, Platinum, and Gold

<table>
<thead>
<tr>
<th>Metal</th>
<th>µg Taken</th>
<th>µg Recovered</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>2124</td>
<td>2001</td>
<td>94</td>
</tr>
<tr>
<td>Pt</td>
<td>6601</td>
<td>6410</td>
<td>97</td>
</tr>
<tr>
<td>Au</td>
<td>1480</td>
<td>1078</td>
<td>73</td>
</tr>
</tbody>
</table>
Figure XXXVIII

Distribution Curves for the Separation of Rhodium, Palladium, and Gold
separation mixture, the µg recovered, and the percent recovery are listed in Table IX. Figure XXXVIII also contains the theoretically expected separation based on the distribution coefficients in Table V. A much better separation was obtained than had been expected.

The data for the attempted 80 stage separation of iridium, ruthenium, and osmium is plotted in Figure XXXIX. No separation was obtained for iridium and ruthenium, but both were completely separated from osmium. Calculation of the distribution coefficients from these data gives 0.0064 for both iridium and ruthenium and 2.9 for osmium. Table X contains the recovery data for each metal in the separation. The theoretically expected distribution of these metals in Figure XXXIX also indicates that no separation was expected. However a better indication of the true distribution coefficient was obtained for each of these metals.

The multistage separations were not entirely quantitative. It was possible to use only equal volumes of the two phases in the separation due to the size of the separation apparatus. Had it been possible to double or triple the volume of the organic phase, better separations would have resulted. Also the separation of more than three
Table IX

Recovery Data for the Separation of Rhodium, Palladium, and Gold

<table>
<thead>
<tr>
<th>Metal</th>
<th>μg Taken</th>
<th>μg Recovered</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>1593</td>
<td>1374</td>
<td>87</td>
</tr>
<tr>
<td>Pd</td>
<td>4776</td>
<td>3866</td>
<td>82</td>
</tr>
<tr>
<td>Au</td>
<td>740</td>
<td>538</td>
<td>73</td>
</tr>
</tbody>
</table>
Figure XXXIX

Distribution Curves for the Separation of Ruthenium, Iridium, and Osmium

- Experimental
- Theoretical

<table>
<thead>
<tr>
<th>Tube Number</th>
<th>Percent of Metal Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>IR and Ru</td>
</tr>
<tr>
<td>10-30</td>
<td>Os</td>
</tr>
</tbody>
</table>

- IR
- Ru
- Os
Table X

Recovery Data for the Separation of Iridium, Ruthenium and Osmium

<table>
<thead>
<tr>
<th>Metal</th>
<th>μg Taken</th>
<th>μg Recovered</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>4645</td>
<td>3960</td>
<td>85.2</td>
</tr>
<tr>
<td>Ru</td>
<td>1616</td>
<td>1610</td>
<td>99.6</td>
</tr>
<tr>
<td>Os</td>
<td>8547</td>
<td>8009</td>
<td>94.0</td>
</tr>
</tbody>
</table>
metals could have been attempted. Calculations of possible separations in the 4 N HBr - MIBK system using the distribution coefficients observed in the use of the Craig apparatus are presented in Figures XL and XLI. These predictions were obtained using the computer program described in the preceding section and represent the possible separation of six quaternary noble metal mixtures: rhodium-palladium-osmium-gold, rhodium-platinum-osmium-gold, ruthenium-platinum-osmium-gold, ruthenium-palladium-osmium-gold, iridium-palladium-osmium-gold, and iridium-platinum-osmium-gold using a 2:1 volume ratio and 100 stages. Only two figures are needed to represent these predictions due to the similarity of the distribution coefficients of rhodium, iridium and ruthenium whose distribution curves overlap very closely. Thus Figure XL shows the expected distribution for (rhodium or iridium or ruthenium)-platinum-osmium-gold and Figure XLI shows the distribution for (rhodium or iridium or ruthenium)-palladium-osmium-gold.
Figure XL

Theoretical Data for the Separation of Rhodium or Ruthenium or Iridium, Platinum, Osmium, and Gold

Percent of Metal Present

Rh, Ru or Ir

Pt

Os

Au

Tube Number
Figure XLI

Theoretical Data for the Separation of Rhodium or Ruthenium or Iridium, Palladium, Osmium, and Gold

Percent of Metal Present

Tube Number
III. Conclusions and Suggestions for Future Work

The interferences in the atomic absorption determination of the chloro complexes of iridium, ruthenium, and osmium have been investigated and effectively eliminated. The procedure described here for the analysis of iridium and ruthenium provides for a fairly sensitive analysis of iridium and ruthenium. Unfortunately the sensitivity of the osmium analysis does not indicate that atomic absorption will be a suitable means of analysis for this element contrary to the work of Osolinski and Knight. The procedures for the analysis of the bromo complexes of the noble metals in aqueous solutions give good sensitivities for all of the noble metals except platinum and osmium. Further study of the atomic absorption of platinum and osmium may yield a means to a more sensitive analysis for these two elements. It is quite probable that the interferences in the atomic absorption determination of the bromo complexes of the noble metals may not be the same as those of the chloro complexes studied here based on the findings of Pitts, et al. in their study of the absorption of platinum. Thus a study should be made of the interelement interferences in the determination of the bromo complexes of the noble metals by atomic absorption. The extraction of the
noble metals into 4-methyl-2-pentanone by means of the extracting agent diantipyrypropylmethane presents a good method for the removal of gold, palladium, and rhodium from high acidities prior to atomic absorption determination but is not recommended for the determination of iridium, osmium, or platinum.

It is disappointing that better results were not obtained when the Craig Countercurrent separation of more than two metals was attempted. This technique appears to offer a workable method for the separation of the noble metals, but limitations were imposed by the construction of the 100 stage apparatus so that the volume ratio could not be varied. Better separations would have resulted if this had been possible. An automated Craig apparatus would provide a much more convenient separation as well as saving the researcher's time.

The distribution coefficients calculated from data observed in the multistage separations are probably more accurate than those experimentally determined with only one equilibration. Variation in the coefficient which might be due to the concentration of the metal, absorption in the apparatus, or the presence of other metals are implicitly taken into account. The computerized program
of the Craig equation using the coefficients calculated from multistage separation data should bring about a good prediction of possible separations. On the basis of the data calculated from the Craig multistage separations, the computer output indicates that it should be possible to separate the quaternary mixtures rhodium-palladium-osmium-gold; rhodium-platinum-osmium-gold; ruthenium-palladium-osmium-gold; ruthenium-platinum-osmium-gold; iridium-palladium-osmium-gold; and iridium-platinum-osmium-gold with the volume ratio of 2:1 and 100 stages in the system 4 N hydrobromic acid-(MIBK). An alternate approach for a better prediction of separations would be to determine the variation of the distribution coefficient with its own concentration and with the concentration of other metals present and allow the distribution coefficient in the computer equation to behave as a variable rather than as a constant. The latter suggestion would be complicated and impractical.
BIBLIOGRAPHY


VITA

Helen Stalcup Copeland was born in Mobile, Alabama, on February 16, 1946. She attended Semmes High School, Semmes, Alabama, and graduated in May, 1964. She received her B.S. in Chemistry from the University of Alabama in August, 1967. She entered the Graduate School of Louisiana State University in September, 1967, where she is presently a candidate for the Doctor of Philosophy Degree.

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EXAMINATION AND THESIS REPORT

Candidate: Helen Stalcup Copeland

Major Field: Chemistry

Title of Thesis: The Separation of the Noble Metals and the Determination of These Metals By Atomic Absorption Spectrophotometry.

Approved:

[Signatures]

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: May 4, 1972