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MINUTES OF CONFERENCE ON THE CHEMISTRY
OF RUTHENIUM, DECEMBER 13 AND 14, 1948

By
H. Baxman, E. Turk, and L. Deutsch

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For The Atomic Energy Commission

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Dec. 16, 1955

Argonne National Lab.
Lemont, Ill.

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Chemistry-General, Chemistry
Separations Processes for Pu

ARGONNE NATIONAL LABORATORY

P. O. Box 5207
Chicago 80, Illinois

MINUTES OF CONFERENCE ON THE CHEMISTRY OF RUTHENIUM

December 13 and 14, 1948

Report Compiled by H. Bazman, E. Turk, and L. Deutch

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O. ABSTRACT

The conferees discussed gravimetric, colorimetric, and radiochemical techniques for ruthenium analysis. Acceptable procedures were reported using each of these techniques. The determination of valence states was in a less satisfactory state. Ruthenium tetroxide and ammonium hexachlororuthenate were suggested as primary standards.

The absorption spectrum of ruthenium in a wide variety of solutions has been investigated and some peaks identified as characteristic of a particular ruthenium structure in different solutions. The effects of complexing ions, acidity and valence states have all been studied by this technique.

Polarographic data of a preliminary nature was presented for various solutions.

The difficulty of analyzing typical solvent extraction data on the behavior of ruthenium was emphasized. The possibility of radiocolloid formation as an explanation was mentioned. It was pointed out that other platinum metals showed similar irreproducibility in extraction into hexone from dissimilar aqueous solutions.

The behavior of ruthenium tetroxide in solvent extraction was discussed as well as the production and volatilization of this form of the element. Its use as a special decontamination procedure was emphasized.

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I. ANALYTICAL METHODS FOR RUTHENIUM

A. Gravimetric

The three methods of gravimetric analyses principally investigated at the various sites were the magnesium precipitation⁽¹⁾, the thionalid method of Rogers and Beamish⁽²⁾, and the Gilchrist procedure⁽³⁾.

The magnesium precipitation method was standardized at Argonne by means of the standard ammonium hexachlororuthenate, $(\text{NH}_4)_2\text{RuCl}_6^*$. The precipitation, when carried out in 6 M hydrochloric acid, agreed within $\pm 1\%$ with the calculated value after adding a 6% empirical correction factor. In 3 M hydrochloric acid the results were erratic. When the acid concentrations were as low as 0.5 M, the results were 20 to 30% above the calculated value.

The thionalid procedure reported by Rogers and Beamish has been tested both at Argonne and Chalk River.

The method consists of a sodium bromate-sulfuric acid distillation of ruthenium tetroxide (sample should contain 8 - 10 mg. ruthenium) into a cold 3% hydrogen peroxide absorbing solution. This is followed by boiling to eliminate the hydrogen peroxide and to concentrate the solution. The acidity is then adjusted to 0.2 to 0.5 M hydrogen ion concentration with hydrochloric acid and the thionalid added. The precipitate is coagulated by boiling and collected on ashless filter paper. It is then ignited in air to oxidize off the organic material. The resulting residue is carried through a hydrogen ignition.

Several difficulties in procedure were encountered at Argonne when the above instructions were followed. Some form of ruthenium precipitated from the absorbing solution unless a small amount of acid was added. A more serious defect appeared to be the possible occlusion of foreign material on the bulky thionalid precipitate. A blank ran as high as 5% and known samples analyzed 5 - 8% high even after correcting for this blank.

-
- (1) L. E. Glendenin, CC-971 (September, 1943) and CN-1312 (May, 1945)
 - (2) Ind. Eng. Chem., Anal. Ed., 12, 561, (1940)
 - (3) Bureau of Standards, J. Res., 12, 283, (1934)

* This may be either $(\text{NH}_4)_2\text{RuCl}_6$ or $(\text{NH}_4)_2\text{Ru}(\text{OH})\text{Cl}_5$. See Preparation of Standards.

W. Hardwick of Chalk River reported that prolonged distillation in the presence of an excess of sulfuric acid added continuously throughout the distillation prevented solid formation in the absorbing solution. He also suggested that the high blank value would indicate an impure reagent and re-crystallization of the thionalid should be attempted.

Preliminary investigations of the Gilchrist procedure showed that the optimum amount of ruthenium is about 0.1 gram and that at lower quantities of ruthenium there was a tendency for colloid formation.

When proper precautions were taken the method as described below gave good results at Argonne:

The sample is converted to the sulfate by fuming down several times with concentrated sulfuric acid and then taken up in 100 milliliters of water. If the sample is in the form of a nitrate it should be taken to dryness several times with hydrochloric acid before being treated with sulfuric acid. The sample is then placed in the distilling flask, 100 milliliters of a 10% sodium bromate solution added and the solution distilled for 2 hours. The distillate is caught in a 1:1 hydrochloric acid solution saturated with sulfur dioxide. Three absorbing flasks are used, the first containing 150 milliliters of the absorbing solution and the other two containing 50 milliliters each. The delivery tubes should be washed with sulfurous acid from time to time during the distillation. The combined absorbing solutions are evaporated to a moist residue which is then dissolved in 10 milliliters of concentrated hydrochloric acid and digested for one-half hour. Fifty milliliters of water are added, the solution is heated to boiling, filtered to remove silica and the silica washed with a solution of 1:99 hydrochloric acid:water. The filtrate is diluted to 200 milliliters and heated to boiling. To the solution is added dropwise a 10% filtered solution of sodium bicarbonate to a pH of 6. The solution is then boiled to coagulate the precipitate, filtered and washed with a hot 1% solution of ammonium sulfate followed by several washings with a cold 2.5% ammonium sulfate solution. The precipitate is ignited strongly in air once, then in hydrogen, and cooled in hydrogen. The precipitate is washed thoroughly with hot water, reignited in air and in hydrogen and cooled in hydrogen. The ignition and cooling are repeated to constant weight of the precipitate as ruthenium metal.

In addition to the aforementioned methods, Hanford analyzed for ruthenium by evaporating a solution of commercial ruthenium chloride (Am. Pt. Wks.) to dryness and reducing the residue to the metal in hydrogen.

B. Colorimetric Methods

P. Wehner of Argonne reported a colorimetric method for determining total ruthenium in perchloric acid solutions. The method is as follows:

Ten cc. of a solution containing ruthenium in 1 M perchloric acid are treated with 50 - 100 mg. of solid ammonium persulfate and a small crystal of silver sulfate. The solution is heated in a closed flask at 80 - 100°C for 15 to 20 minutes and then cooled rapidly. The optical density at 385 mμ is determined. The ruthenium concentration is then read from a calibration curve of density versus ruthenium concentration as ruthenium tetroxide.

Very little gassing was observed during heating when the above method was used. Use of sodium bromate or silver oxide resulted in vigorous gas evolution with loss of ruthenium tetroxide.

The method was checked by a reduction-oxidation cycle on a stock solution of ruthenium tetroxide in 1 M perchloric acid. The ruthenium concentration was read off the calibration curve using the 385 mμ peak. The ruthenium was reduced with mercury and reoxidized by the above procedure. The following table gives the results:

Table I
Per Cent Error in Ruthenium Analysis

<u>Sample</u>	<u>Original Ruthenium</u>	<u>Ruthenium After Reduction-oxidation Cycle</u>	<u>Error</u>
1	1.84×10^{-3}	1.85×10^{-3}	+0.65%
2	1.84×10^{-3}	1.87×10^{-3}	+1.02%
3	0.765×10^{-3}	0.798×10^{-3}	+3.8%
4	1.42×10^{-3}	1.45×10^{-3}	+2.6%
5	0.773×10^{-3}	0.787×10^{-3}	+1.8%
			+2% Average

Since all errors were positive, it was at first thought that they were due to slight decomposition of the ruthenium tetroxide used in preparing the stock solution with which the calibration curve was established. To test this hypothesis, fresh ruthenium tetroxide stock was prepared and an attempt made to check the old curves. Immediately after the silver sulfate-ammonium persulfate treatment the readings were taken and the same +2%

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average error found. No satisfactory explanation for this discrepancy was advanced. Within the established limits, the method would presumably hold for sulfuric acid solutions.

In the method described above it was necessary to exclude chloride. A rough method for detection of chloride was devised.

Four cc. of solution containing ruthenium in 1 - 6 M perchloric acid are treated with 2 drops of 1 M silver nitrate and 50 - 200 mgs. of solid ammonium persulfate and warmed gently to form ruthenium tetroxide. If chloride is present in a concentration greater than 10^{-4} m/l, the solution becomes hazy. A known solution containing chloride in a concentration of 10^{-4} M is compared with the test solution.

C. F. Callis of Hanford reported that DeFord's⁽⁴⁾ method was being used for total ruthenium analyses. His work was assumed to be accurate and a calibration curve was made up for their instrument using a sample analyzed by a hydrogen ignition.

An attempt was made by Hanford to determine valence by an iodide titration. Bromate ion was added to a nitric acid solution of ruthenium which was then heated at 90°C for 1 hour, a clear solution being obtained at the end of this time. Iodide ion was then added and the liberated iodine titrated with thiosulfate, using a starch indicator. Results were erratic.

A colorimetric procedure involving an alkaline fusion was found useful at K-25. A known weight of ruthenium metal, found to be greater than 99% pure by spectrographic analysis, was fused with a mixture of potassium nitrate and potassium hydroxide and dissolved and diluted to a known volume. Using various aliquots of this solution an absorption curve of density versus ruthenium concentration was obtained. The method was checked by analyzing pure ruthenium pentafluoride (Ruff's preparation). Determinations of ruthenium gave an average value of 51.2 $\pm$ 0.9% as compared with the calculated value of 51.3% ruthenium. Another group, working independently, reproduced the calibration curve within experimental error. The method is good for a maximum of 25 - 50 mg. of compound. Beer's Law is obeyed at low concentrations with optimum values obtained in the region of 15 - 20 δ Ru/ml. It is believed that potassium ruthenate is the absorbing material in the solution.

(4) Discussed by M. Silverman at first Ruthenium Conference.

Reported in ANI-SI-43, June 1948.

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Recent investigations at Argonne showed that the previously reported colorimetric method of Verhoek⁽⁵⁾ is not applicable to all solutions.

The method consists of adding 5 drops of 2.5% thiourea to the ruthenium sample and diluting to 5 mls. with 3 M hydrochloric acid. This is followed by heating on a steam bath for 2-1/2 to 3 minutes and then cooling rapidly in ice. The optical density at 635 ~~mμ~~ is then observed. To use a standard calibration curve the solution being investigated must be in equilibrium, i.e., in practice the optical density must be a maximum.

In order to determine the extinction coefficient for equilibrium solutions, two hydrochloric acid solutions were prepared by different methods and analyzed gravimetrically. The first was prepared by dissolving solid ruthenium chloride in 3 M hydrochloric acid; the second by distilling ruthenium tetroxide into concentrated hydrochloric acid and diluting to 3 M hydrochloric acid. Neither solution so obtained appeared to be satisfactory, but when both solutions were boiled, an identical maximum density reading was obtained. The required boiling time differed for the two solutions, but Solution I yielded a conversion factor, K, of 156.2 and Solution II gave a conversion factor of 156.6, where $K = \frac{\text{mg Ru/5 ml.}}{\text{optical density}}$ for a 1 cm. cell.

C. Valence State Analyses

Reports from all sites seemed to indicate that the valence state determination by reduction with iodide and subsequent titration of the liberated iodine with thiosulfate was not satisfactory.

P. Wehner of Argonne stated that with careful control of pH and iodide concentration the method was workable in perchloric acid solutions.

L. W. Niedrach of KAPL has obtained encouraging results in preliminary experiments using chromous ion in hydrochloric acid.

L. W. Niedrach attempted to reduce ruthenium (IV) in 0.1 N perchloric acid solutions with various 0.1% amalgams with the idea of titrating the reduced solutions. Lead, tin, and cadmium amalgams gave colorless solutions which were thought to be ruthenium (II). On standing in air, after the removal of the amalgam, the solutions became red-brown. With bismuth amalgam, a yellow solution thought to be ruthenium (III) resulted. Mercury gave a pink solution which was thought to be the result of incomplete reduction to ruthenium (III).

(5) Private Communication from Verhoek. Discussed by B. Kaplan at first Ruthenium Conference. Reported in ANL-SL-43, June, 1948.

P. Wehner reported that in an attempt to reduce ruthenium with hydrogen, ruthenium (III) apparently catalyzed the reduction of perchloric acid, resulting in the formation of chloride.

D. Radiochemical Methods of Analysis

Several aspects of radiochemical analysis were discussed. The methods of analyzing for radioactive ruthenium Redox process solutions, while routine at both Oak Ridge and Argonne, are not thoroughly established. Virtually all the conferees agreed that the source of the ruthenium activity was important. Variable behavior often appeared to be connected with the dissolving technique in preparing an irradiated uranium feed. Hardwick reported the use of ammonium hexanitrate cerate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, (50 mg/ml.) to oxidize the ruthenium to the tetroxide. The pH of the resulting solution was adjusted to 1.0 ± 0.2 and the ruthenium tetroxide extracted with tetrachlorethane. Normally the ruthenium was 96 - 98% extracted with a radiochemical purity of as much as 99.9%. When employed on feeds which had been kept in contact with metallic uranium until they were substantially acid deficient, this procedure failed to remove the ruthenium, presumably due to failure to oxidize it even under acid conditions after the basic dissolution.

R. Stoughton of Oak Ridge recommended the use of an absorber to screen out the weak betas when ruthenium activity is counted. It was generally agreed that counting of ruthenium samples should be done more carefully.

Some back-scattering work was attempted at Oak Ridge. It was found that addition of aluminum nitrate to ruthenium tracer might increase the count as much as 50 - 100%.

The use of perchloric acid distillation with added carrier for routine analyses at Argonne was reported as giving ~80% recovery of the ruthenium. Since it is not always possible to guarantee exchange, the usual correction for chemical yield offers no assurance of the reliability of this procedure for all cases. It is certainly satisfactory for most process solutions.

Runion reported that Gresky of Oak Ridge discounted his previous work on the separation of Ru^{103} and Ru^{106} tracer during some experiments.

E. Preparation of Standards

Ruthenium tetroxide as a standard has been widely employed. Nitric acid solutions of the tetroxide have been preferred at Hanford, but there is some doubt that these solutions were free from chloride. R. C. Vogel of the Illinois Institute of Technology has been using a sulfuric acid - sodium bromate distillation to prepare ruthenium tetroxide with good results. Before distillation the ruthenium sample was fumed down three times with concentrated sulfuric acid. No chloride could then be detected.

P. Wehner prepared ruthenium tetroxide by the following method:

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The tetroxide is distilled from a sulfuric acid - ammonium persulfate solution and dried by sweeping it with dry nitrogen through a tower filled with magnesium perchlorate. The tower is held at 50 - 60°C. The ruthenium tetroxide is then caught in a flask cooled in ice or dry-ice. Weighed amounts of this material can be used as standards.

Standard solutions of this ruthenium tetroxide were used routinely. Samples of dry ruthenium tetroxide were pipetted into a flask containing a weighed amount of perchloric acid. The flask was weighed again and the difference of the second and first weighings gave the weight of tetroxide to 0.5 - 1.0%. Two forms of ruthenium tetroxide have been observed, the usual bright yellow form and a brown form which appeared on long standing at 25°C in a closed tube. On heating, this form changed to the bright yellow form. Solutions of ruthenium tetroxide in water and 1 M perchloric acid are stable for relatively short periods of time. Solutions in concentrated perchloric acid and apparently in 2 N sulfuric and 2 N nitric acids are quite stable even when stored with no special precautions and exposed to air and light.

Ammonium chlororuthenate was prepared by B. Kaplan and L. Deutsch at Argonne. Ruthenium tetroxide was distilled from a sulfuric acid-sodium bromate solution into constant boiling hydrochloric acid. The solution was concentrated by boiling and then refluxed for one hour in order to insure complete conversion to chloro-ruthenic acid. The ammonium chlororuthenate was re-crystallized by rapid cooling in an ice bath. This was followed by successive washings with 95% ethyl alcohol until the washings were colorless. The crystals were then dried over phosphorous pentoxide.

Analysis of two samples gave the following results:

N:	7.6%	Volumetric
	7.5%	
Ru:	30.3%	Gravimetric
	30.3%	
Cl:	33.8%	Gravimetric
	37.4%	

The discrepancy in Cl analysis is unexplained.

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II. PURE COMPOUNDS

A. Ruthenium Pentafluoride

The preparation of ruthenium pentafluoride and possibly the ruthenium trifluoride were discussed by R. L. Farrar of K-25. The method of Ruff⁽⁶⁾ was used to prepare the pentafluoride. Some modifications in apparatus were made. Instead of a platinum apparatus, which was found to be attacked by fluorine at 300°C, nickel was used. The ruthenium pentafluoride was prepared by the action of fluorine on ruthenium metal at a high temperature in a dry evacuated nickel tube. The compound was extremely sensitive to moisture and reacted with mercury and glass after a period of time. It reacted with water to form large amounts of ruthenium dioxide, some hydrogen fluoride, small amounts of ruthenium tetroxide and possibly some higher fluorides of ruthenium.

The following physical constants were determined:

Boiling Point	313°C
Melting Point	106°C
Critical temperature	606°C
$\Delta H_{\text{vap.}}$	12.7 kcal/mole
$\Delta S_{\text{vap.}}$	2.16 cal/degree/mole
ΔH_f	10.4 kcal/mole
ΔS_f	27.7 cal/degree/mole

The high value of ΔS_f suggested that possibly a polymer forms in the solid phases whereas the normal value of $\Delta S_{\text{vap.}}$ indicated a monomer in the vapor phase. X-ray studies are in process. Further material on this compound may be found in report K-294, November 1, 1948. The preparation of ruthenium trifluoride has been attempted but no data is available at present.

(6) Ruff and Vidic, Z. Anorg. Allg. Chem., 143, 163, (1925)

III. SOLUTION CHEMISTRY

A. Spectrophotometric Data

P. Wehner reported on the action of various reducing agents on ruthenium tetroxide in perchloric acid solutions. On titrating the tetroxide in perchloric acid with mercurous ion, no additional change in the spectrum of ruthenium was observed after the addition of 3.81 equivalents of mercurous ion. The tetroxide peaks had disappeared and a broad shallow maximum was present at 490 $m\mu$. This peak was attributed to ruthenium (IV). The addition of 5 equivalents of chloride ion per mole of ruthenium tetroxide in a perchloric acid solution containing 5×10^{-3} M ruthenium gave no reduction. The addition of bromide ion resulted in the qualitative reduction of ruthenium (VIII) to ruthenium (IV) and the solution had a spectrum identical with that obtained from the solution reduced with mercurous ion. This brackets the ruthenium (VIII) - (IV) potential between -1.1 and -1.3 volts. The addition of 4 equivalents of stannous ion per mole of ruthenium tetroxide gave reduction to ruthenium (IV). Further addition of stannous ion up to 9 equivalents resulted in an amber colored solution which was unstable in air. The spectrum obtained from this solution exhibited no peaks. The original spectrum was observed after the solution stood in air for some time. Assuming that excess stannous ion resulted in the formation of ruthenium (III), the ruthenium (IV) - (III) potential may be bracketed between -0.2 and -0.8 volts. It was felt that the (IV) - (III) potential is close to the stannous-stannic potential. This would place the ruthenium (IV) - (III) potential in the region of -0.3 volts.

The addition of hydrogen peroxide and sodium nitrite gave only a slow reduction.

An attempt was made to obtain lower valence states of ruthenium using hydrogen reduction of ruthenium tetroxide in the presence of a platinum black electrode. With 6 M perchloric acid no ruthenium tetroxide peaks were present after 18 hours. The solution was now red and a 460 $m\mu$ peak was obtained. Chloride ion was detected in the solution. Analyses showed ruthenium to have a valence of 4.1. An aliquot was heated to 100°C for one hour and showed a plateau where the peak had been originally.

Another sample of ruthenium tetroxide was dissolved in concentrated perchloric acid, the ruthenium reduced with alcohol, the solution fumed down and the residue taken up in concentrated perchloric acid. A dark colored solution was obtained. The spectrum of this solution was very similar to that of the heated solution previously mentioned. There was no chloride ion present and the effective valence number of the ruthenium was 4.2. The solution was then subjected to a hydrogen reduction. After one hour a peak at 560 $m\mu$ appeared. On continued reduction this band rose and then disappeared while at the same time a peak at 460 $m\mu$ appeared. The reduction was carried out for eight hours and at the end of this time chloride ion could be detected.

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Reduction of ruthenium tetroxide in concentrated perchloric acid with hydrogen and a platinum black electrode for 22 hours resulted in a solution which had no tetroxide peaks. After 90 hours, a peak at 460 $m\mu$ appeared. No chloride ion could be detected at the end of 22 hours, but when the reduction was stopped at the end of 118 hours, chloride ion was present. The measured valence number of the ruthenium was 4.0.

Solutions of ruthenium tetroxide in 6 M perchloric acid decomposed quite rapidly, becoming colorless after 4 hours. A slight peak near 220 $m\mu$ was observed at this time. After 16 days the solution was red, the optical density had risen and a plateau had appeared in the visible region. After 55 days the optical density had again risen and the peak near 220 $m\mu$ had disappeared.

Niedrach of KAPL prepared a solution of ruthenium tetroxide in 1 M perchloric acid. The ruthenium was 0.005 M. The tetroxide was reduced with hydrogen peroxide and then boiled. A peak at 490 $m\mu$ was observed. The curve checked Wehner's curves for ruthenium reduced with mercurous ion in 1 M perchloric acid in every respect. Two dilutions of this stock solution were made up with a constant ionic strength of 1 M. A plot of the log of the optical density versus wavelength for these three solutions gave parallel curves except at low hydrogen ion concentration. Above a pH of 3 the color of the solution changed and at higher pH's precipitation resulted.

R. Vogel of I.I.T. has attempted to measure the ruthenium (III) - (IV) couple in the following cell:

Pt, Ru(III) - Ru(IV) (as perchlorates), $(\text{HClO}_4)_{(c_1)}$ // $\text{HClO}_4_{(c_1)}$, H_2 , Pt.

An attempt was made to prepare ruthenium perchlorate, presumably ruthenium (IV), by a hydrogen reduction of ruthenium tetroxide in perchloric acid. A sample of ammonium chlororuthenate was evaporated to sulfur trioxide fumes three times with concentrated sulfuric acid, the residue taken up in a sulfuric acid-sodium bismuthate mixture and distilled into 2 M perchloric acid. The ruthenium concentration was 0.001 M and the hydrogen used in the reduction was at about 1 atmosphere. Two experiments were run, one at 0°C and one at about 25°C. The spectra of these solutions showed a plateau at 460 $m\mu$ to 480 $m\mu$ and a shoulder at 300 $m\mu$. In both of the solutions the concentration of chloride ion was less than 10^{-4} M, the concentration of chlorate ion was less than 10^{-3} M and a qualitative test for ruthenium (IV) by the iodide method was positive.

The chlorate test was run as follows:

Two milliliters of the stock solution in 1 M perchloric acid are treated with 10 drops of saturated potassium nitrate and the potassium perchlorate formed is removed by centrifugation. To the supernatant is added 0.4 milliliter of concentrated nitric acid, 0.1 milliliter of 1 M silver nitrate and 0.2 milliliter of 0.25 M sodium sulfite, the latter to reduce chlorate ion to chloride. If chlorate ion is present a precipitate of silver chloride is obtained immediately. About 10^{-4} M chlorate ion can be detected.

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A second attempt to prepare a ruthenium (IV) perchlorate solution which was free of chloride was made using an electrolytic reduction of ruthenium (IV) to ruthenium (II), precipitation of ruthenium (II) as the hydroxide and dissolution of the hydroxide in perchloric acid. Ruthenium (II) hydroxide was used because it was felt it would be more soluble in acid than other hydroxides. The procedure was as follows:

One hundred milliliters of approximately 0.05 M ruthenium (IV) chloride was prepared by dissolving solid ruthenium chloride in 1.5 M hydrochloric acid and bubbling chlorine through the solution for two hours. The solution was then boiled to remove excess chlorine. Sixty milliliters of this solution were electrolyzed with 0.8 volts and 40 m.a. for 100 minutes. At the end of this time the solution was straw colored. It was then electrolyzed for 20 minutes longer and the solution became intensely blue. The amount of current used to produce the light colored solution checked with the amount needed to obtain ruthenium (III). A boiled solution of 1.5 M sodium hydroxide was used for the precipitation. The hydroxide obtained was dark brown and darkened further over night. The precipitate was treated with several 30 milliliter portions of 1 M perchloric acid. A dark solution was obtained but the precipitate did not appear to dissolve appreciably. Therefore, 5.6 M perchloric acid was used and the precipitate dissolved. The color of this solution was almost black. Oxygen was then bubbled through the solution.

Two solutions were obtained, one in 1 M perchloric acid containing ruthenium at 0.003 M, the other in 5.6 M perchloric acid containing ruthenium at 0.007 M. In both solutions the coordinated chloride ion concentration was less than 10^{-4} M, the chlorate ion concentration was less than 10^{-3} M, and a qualitative test for ruthenium (IV) was positive. Spectra of solution I (1 M perchloric acid) and solution II (5.6 M perchloric acid) diluted to 1 M acid showed a peak at 258 m μ .

A portion of solution I after being heated for three hours on a water bath showed no appreciable change in color and no increase in chloride ion. No spectrum of this solution was taken.

A third attempt to prepare chloride free ruthenium (IV) perchlorate was based on the oxidation of ruthenium chloride with chlorine followed by conversion to sulfate and metathesis with barium perchlorate. A solution of 0.05 M ruthenium chloride in hydrochloric acid was treated with chlorine gas. The solution was boiled down three times with concentrated sulfuric acid and the residue taken up in 1 M perchloric acid. The ruthenium concentration was 0.0037 M and the chloride concentration was less than 10^{-4} M. An excess of barium perchlorate was added and the precipitated barium sulfate filtered off. The spectrum obtained was the same as that obtained in the first preparation, a plateau at 460 - 480 m μ and a shoulder at 300 m μ . The test for ruthenium (IV) was positive and a test for coordinated sulfate ion gave less than 5×10^{-4} M.

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The sulfate ion test consists of the following:

Ten milliliters of concentrated nitric acid are added to 2 milliliters of solution and the solution is then evaporated to dryness to remove ruthenium as the tetroxide. A white solid is left. If this is soluble in water no sulfate is present. If sulfate were present, a precipitate of barium sulfate would be expected. The test is good to about 5×10^{-4} M.

H. Baxman of Argonne has done spectrophotometric work on ruthenium solutions in hydrochloric, nitric, and sulfuric acids. Most of the work has been done in the hydrochloric acid system.

Solutions of ruthenium in hydrochloric acid have been prepared: (1) by dissolving solid ruthenium chloride in hydrochloric acid, and (2) by distilling ruthenium tetroxide into hydrochloric acid. Method (1) gives a solution containing a mixture of ruthenium (III) and ruthenium (IV) whereas method (2) gives an original solution containing ruthenium in an unknown valence state, possibly (VIII). On standing at room temperature the ruthenium is reduced to (IV) by the hydrochloric acid with the formation of chlorine.

Using method (1) and chlorinating the resulting solution to oxidize all the ruthenium to the (IV) state, a stock solution, (I) in Table II and Figure 1, was prepared and various dilutions with water, acid, or base were made up. These solutions were labeled aI, bI, cI, etc., as shown in the Table. It was found that except for three cases, dI, fI, and lI, three peaks were exhibited in common by all the solutions. These peaks occurred at 695, 460 - 466, and 386 - 388 m μ (see Figures 1 - 4, 7 - 10, and 12 - 14). In the case of the three exceptions, all had an acid concentration no greater than 0.3 M and in two cases, dI and fI, had stood for at least six days after being prepared before they were examined. The third solution, lI, had the lowest acidity, 0.1 M (see Figures 5, 6, and 11).

Using method (2) and reducing the ruthenium either with hydrogen peroxide and heat, or with hydrochloric acid itself followed by nitrogen sparging to remove chlorine, it was again found that the 695, 460 - 466, and 388 m μ peaks were present. This would seem to indicate that the solutions prepared by these three different methods, oxidation with chlorine, reduction with hydrogen peroxide or with hydrochloric acid, contain the same species, presumably a ruthenium (IV) complex ion.

Table II has several things worth mentioning. First, with regard to the position of the peaks on the wavelength scale, high acid concentration favored the higher wavelength. Thus, in the series mI, nI, and oI, where the ruthenium concentration was constant, the acid varied from 2 M for mI to 0.3 M for oI, and at the same time the values of the peaks for mI were 695, 462, and 385 to 389 m μ ; the same peaks in nI were at 690, 456, and 383 m μ , and in oI were at 685 to 690, 454, and 376 to 381 m μ . This same shift can be observed in other places in the table and in every case the peaks at 388 and 460 m μ appeared to be affected to a larger degree.

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Table II

The Absorption Spectra of Ruthenium (IV) in Hydrochloric Acid Solutions

Sol'n No.	Method Of Prep.	Days Between Prep. and Run	Ru in mols/l. $\times 10^{-3}$	Acidity in mols/l.	Light Path in cm.	M A X I M A			Molar Extinction Coefficient	R e m a r k s
						Wave Length in $m\mu$	Optical Density			
I	a	116	6.8	2.75	0.02	695	0.095		74.2	
aI	b	0	6.8	0.275	1.002	695	0.450		66.0	Color became darker on standing. Peak at 680 $m\mu$ after standing very shallow.
		27			1.002	680	0.780		114	
bI	b	0	6.8	3.14	1.002	695	0.429		63.0	
		22			1.002	700	0.406		59.6	
		56			1.002	695-700	0.409		60.0	
					0.02	468	0.670		4930	
					0.02	388	0.805		5920	
cI	c	0	0.68	0.275	1.002	690-695	0.057		83.7	Solution became darker on standing. After standing no trace of peaks at 695 $m\mu$ and 452 $m\mu$ except for slight shoulders.
					0.497	452	1.681		4970	
					0.497	380	1.152		3410	
		28			0.497	375	1.448		4270	
dI	d	6	0.068	0.275	1.002	495	0.066		969	Both peaks well defined.
						375	0.333		4890	
fI	b	62	0.068	0.312	5.008	496	0.265		778	Peak at 375 $m\mu$ quite strong and fairly sharp.
						375	1.370		4020	
gI	b	9	0.068	3.00	10.014	695	0.032		52.4	Similar in all respects to bI.
					1.002	464-466	0.265		4340	
					1.002	388	0.3395		5550	

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Table II (cont'd)

Table II (cont'd)

Sol'n No.	Method of Prep.	Days Between Prep. And Run	Ru in mols/l. $\times 10^{-3}$	Acidity in mols/l.	Light Path in cm.	M A X I M A			Remarks
						Wave Length in $m\mu$	Optical Density	Molar Extinction Coefficient	
hI	b	1	6.4	1.975	1.002	695	0.454	70.8	
					0.02	464	0.729	5700	
					0.02	388	0.757	5910	
		7			1.002	695	0.482	75.2	
					0.02	462	0.797	6230	
					0.02	386	0.718	5610	
		24			1.002	690-695	0.490	76.4	
					0.02	462	0.772	6030	
					0.02	388	0.700	5470	
jI	b	2	6.4	0.996	1.002	690	0.536	83.6	
					0.02	458	0.771	6020	
					0.002	387	0.559	4370	
		8			1.002	690	0.580	90.4	
					0.02	456	0.789	6160	
					0.02	385	0.514	4020	
		23			1.002	690-695	0.588	91.7	
					0.02	457	0.801	6260	
					0.02	386	0.5435	4250	
kI	b	2	6.4	0.492	1.002	690	0.556	86.7	Peak at 380 - 385 $m\mu$ becoming very shallow with time. Other peaks unaffected or slightly strengthened.
					0.02	458	0.761	5940	
					0.02	385	0.570	4450	
		8			1.002	690	0.677	106	
					0.02	454	0.802	6270	
					0.02	382	0.481	3760	
		16			1.002	690	0.693	108	
					0.02	454	0.807	6310	
					0.02	380	0.481	3760	
lI	b	2	6.4	0.1071	0.02	450	0.525	4100	Solution very dark. Peak at 390 $m\mu$ very shallow. Peak at 444 - 450 $m\mu$ becoming shallow with time. Slight shoulder in region of 695 $m\mu$
						390	0.420	3280	
		8			0.02	445	0.328	2562	
		16			0.02	444	0.2315	1810	

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Table II (cont'd)

Sol'n No.	Method of Prep.	Days Between Prep. and Run	Ru in mols/l. x 10 ⁻³	Acidity in mols/l.	M A X I M A				R e m a r k s
					Light Path in cm.	Wave Length in mμ	Optical Density	Molar Extinction Coefficient	
mI	b	1	0.64	2.055	1.002	695	0.049	76.4	
					0.02	462	0.077	6020	
					0.02	385	0.072	5630	
		15			10.014	695	0.481	75.1	
					0.104	462	0.378	5680	
					0.104	389	0.356	5350	
nI	b	4	0.64	0.8836	1.002	690-695	0.062	96.7	Peak at 383 - 384 mμ rather shallow.
					0.104	456	0.401	6030	
					0.104	384	0.274	4120	
		15			10.014	690	0.603	94.1	
					0.104	456	0.404	6070	
					0.104	383	0.272	4090	
oI	b	5	0.64	0.298	1.002	690	0.067	104	Peak at 380 mμ shallow and becoming shallower with time.
					0.104	454	0.398	5980	
					0.104	381	0.260	3910	
		14			1.002	685-690	0.078	122	
					0.104	451	0.397	5960	
					0.104	376	0.251	3770	
IX	e	0		1.89	1.002	690-695	0.062		Similar to bI and gI.
						462	0.403		
						388	0.362		
Xa	e	0		2.012	1.002	695	0.121		Similar to IX
					0.104	462	0.882		
					0.104	388-390	0.900		

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Table II (cont'd)

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Sol'n No.	Method of Prep.	Days Between Prep. and Run	Ru in mols/l. x 10 ⁻³	Acidity in mols/l.	Light Path in cm.	Wave Length in mμ	Optical Density	Molar Extinction Coefficient	Remarks
XV	f	4		2	1.002 0.104 0.104	695 460 359	0.099 0.742 0.674		Cl ₂ odor very noticeable
XVa	g	0		2	1.002 0.104 0.104	695 460 388	0.126 0.880 0.669		No change in color from XV. Cl ₂ odor gone.

- (a) Stock solution. Solid Ru chloride dissolved in 3 N HCl. Cl₂ gas bubbled through. Boiled to remove Cl₂.
- (b) Dilution of stock solution with H₂O, acid or base..
- (c) Dilution of aI
- (d) Dilution of cI
- (e) Distill RuO₄ from HClO₄ into 2 N HCl + H₂O₂. Reflux
- (f) Distill RuO₄ from HClO₄ into 2 N HCl. Let stand until red-brown color develops.
- (g) Sparge solution from preparation (f) with N₂ to remove Cl₂.

Range in mμ for I, aI, and bI is 500 - 1100 and for all others 300 - 1100.

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In varying hydrochloric acid concentrations at least three different factors have been changed at the same time. These are acidity, chloride ion concentration and ionic strength and it should be remembered that the effects noted may really be due to any one or any combination of these three factors. Further experiments have been planned to separate the effects of these variables.

Returning to the wavelengths of the three peaks, the concentration of ruthenium appeared to be without effect on the position. This can be observed in bI and gI, Figures 3 and 7, where the ruthenium concentration differed by a factor of 100. At a sufficiently high acidity, somewhere around 1.0 to 1.5 M, there was no shift in the absorption bands with time. Thus, bI showed no variation over a period of 56 days. Others such as hI, mI, and jI also showed no variation outside experimental error.

The effect of variations in hydrochloric acid concentration, ruthenium concentration, and time of standing on the molar extinction coefficient, E , were also observed. Decreased acid concentration as well as time of standing appeared to raise E for the 695 $m\mu$ peak, lower it for the 388 $m\mu$ peak and have little if any effect on E at the 460 $m\mu$ peak. This latter peak had an E of around 6000 except for bI and cI where the value was about 1000 lower. Since these solutions were prepared from the stock solution much earlier than those following in the Table, slow alteration of the stock solution may be responsible.

The ruthenium concentration had no systematic effect on E for any of the peaks and Beer's Law was obeyed quite well. The small variations noted may have been due to differences in acidity between the solutions and/or the solution and blank since these variables were not controlled rigorously.

In cases where the acidity was rather low, about 0.3 M, the absorption spectrum obtained when the solution was run shortly after being prepared was identical with those already mentioned, showing the peaks at 695, 460, and 388 $m\mu$. On standing, however, the shape of the curve changed markedly, some of the peaks disappearing completely and new peaks appearing. This is seen in aI and cI, Figures 2 and 4. At still lower acidities, 0.1 M, the original curve lI, Figure 11, obtained was vastly different from any of the others. This curve also changed on standing.

One more thing should be mentioned. Solution XV contained chlorine formed by the reduction of ruthenium (VIII) to ruthenium (IV) by hydrochloric acid. The presence of this chlorine appeared to have no effect on the 695 $m\mu$ or 462 $m\mu$ peaks. However, the 388 $m\mu$ peak was shifted to 359 $m\mu$, presumably due to the broad adsorption of molecular chlorine in this region (see Figure 15).

Table III shows the results obtained with some hydrochloric acid solutions whose absorption spectra are quite different from anything obtained previously. Solution XVc appeared at first glance to be ruthenium tetroxide. Only the 310 $m\mu$ peak was present, however, and it possessed none of the structure exhibited in the spectra of the tetroxide in perchloric, sulfuric or nitric acids (see Figure 16).

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Table III

The Absorption Spectra of Unknown Forms of Ruthenium in Hydrochloric Acid

<u>Sol'n No.</u>	<u>Method of Prep.</u>	<u>Days Between Prep. and Run</u>	<u>Probable Valence of Ru</u>	<u>Acidity in mols/l.</u>	<u>Light Path in cm.</u>	<u>Wave Length in mμ</u>	<u>Optical Density</u>	<u>Remarks</u>
X	a	0	?	2.012	1.002	450 330	0.721 2.69	
XVb	b	0	+ 3 (?)	2	0.10	326 284	0.305 0.577	Color very light.
XVc	c	0	+ 8 (?)	2	0.10	310	0.762	Bright yellow color. Changes to red-brown characteristic of Ru (IV) rapidly at R.T. and very slowly (2 - 3 weeks) at -10°C .

- (a) Distill RuO_4 from HClO_4 into $\text{HCl} + \text{H}_2\text{O}_2$
- (b) Distill RuO_4 from HClO_4 into HCl . Treat with H_2SO_3 and reflux.
- (c) Distill RuO_4 from HClO_4 into HCl . Keep cold and examine immediately.

Range in $m\mu$ for X 300 - 1100 and in others 220 - 1100.

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All the ruthenium nitrate solutions worked with so far have been prepared by distilling ruthenium tetroxide into nitric acid of varying strength. The resulting solutions were then treated in various ways and their absorption spectra studied. No tests were made for chloride ion concentration, for total ruthenium, or for the valence of the ruthenium. Table IV summarizes the data obtained from these solutions.

It is interesting to note that ruthenium tetroxide is apparently quite stable in 2 N nitric acid*, showing no signs of decomposition even on refluxing (see Figure 16). It should also be noted that reduction of the original solution with either sulfurous acid and boiling or hydrogen peroxide and boiling resulted in solutions with almost identical spectra as shown in Figure 17. This fact coupled with the color of the solution, red-brown, and the mode of preparation would indicate the species present here was ruthenium (IV). Additional evidence for this conclusion that might be cited are: (1) electrolysis of a red-brown solution prepared by hydrogen peroxide reduction gave a light yellow solution which had a peak at 330 m μ , (2) reduction with sulfurous acid in the cold gave a light yellow solution with a peak at 322 m μ , (this solution became red-brown again on boiling), and (3) a peak at 490 m μ was observed for ruthenium (IV) in perchloric acid and at 460 m μ for ruthenium (IV) in hydrochloric acid. It is likely that these two peaks and the 480 m μ peak in nitric acid are due to a characteristic, ruthenium (IV) structure, with the shift in wavelength being caused by the different anions present.

The sulfuric acid solutions were prepared similarly to the nitric acid solutions, by distilling ruthenium tetroxide into sulfuric acid. Table V summarizes the data from these solutions.

The tetroxide appeared to be quite stable in 2 N sulfuric acid even in the presence of hydrogen peroxide in the cold. It was not readily apparent what occurred when a solution of ruthenium tetroxide containing hydrogen peroxide was boiled however. Also, little if anything, can as yet be said about the solutions which were treated with hot sulfurous acid or hot formic acid. The presence of the peak at 477 m μ in the solution treated with sulfurous acid in the cold might indicate the presence of ruthenium (IV) by analogy with the peaks in this region in nitric, hydrochloric and perchloric acids. The evidence is rather sketchy at the present time however.

From all of the above data certain conclusions and some guesses may be made:

1. Oxidation of hydrochloric acid solutions of solid ruthenium chloride with chlorine and reduction of hydrochloric acid solutions of ruthenium tetroxide with hydrogen peroxide or hydrochloric acid resulted in ruthenium (IV).

* It has since been found that the tetroxide slowly decomposes on standing at room temperature over a period of about 45 days, depositing a black solid, probably the dioxide.

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Table IV

The Absorption Spectra of Ruthenium in Nitric Acid Solutions

(Range in $m\mu$ for I-Ru-1, 300 - 1100 and for all others 251 - 1100)

Sol'n No.	Method of Prep.	Days Between Prep. and Run	Probable Valence of Ru	Acidity in mols/l.	Light Path in cm.	Wave Length in $m\mu$	Optical Density	Remarks
I-Ru-1	d	30	+ 3(?)	1.045	1.002	330	1.506	Peak very sharp. Slight shoulder at 400 $m\mu$ to 460 $m\mu$. Density falls rapidly on either side of peak.
VIa	c	10	+ 4	0.523	1.002	900	0.1345	Peak at 900 $m\mu$ very broad and shallow. Peak at 478 $m\mu$ shallow. Peak at 253 $m\mu$ questionable because of high absorption of HNO_3 here.
					1.002	478	0.920	
					0.10	320	0.247	
					0.10	253	0.457	
XIV	a	3	+ 8	2	0.10	310	0.423	Very similar to curve for RuO_4 in $HClO_4$. Definite structure connected with both peaks. Peak at 310 $m\mu$ stronger.
					1.002	385	1.701	
XIVa	b	3	+ 8	2	0.10	310	0.245	Similar to XIV except density lower due to some loss of RuO_4 .
					0.104	385	0.096	
XIVb	e	1	+ 3(?)	2	0.10	322	0.247	Peak very small and shallow.
XIVc	f	0	+ 4	2	1.002	860	0.1395	Very similar to VIa. Peaks at 860 and 480 $m\mu$ broad and shallow.
					1.002	480	0.920	
					1.002	329	2.08	
					0.10	253	0.462	
XIVd	g	1 -	+ 3(?)	2	0.10	328	0.0405	Peak narrow. Plateau from 440 to 500 $m\mu$.
XIVe	c	0	+ 4	2	0.104	321	0.252	Peak at 485 $m\mu$ shallow. Peak at 321 $m\mu$ questionable.
					1.002	485	1.020	

(a) Distill RuO_4 from $HClO_4$ into HNO_3
 (b) Reflux (a)
 (c) Treat (a) with H_2O_2 and reflux
 (d) Electrolyze (c)

(e) Treat (a) with H_2SO_3
 (f) Reflux (e)
 (g) Treat (a) with $HCOOH$ and reflux

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Table V

The Absorption Spectra of Ruthenium in Sulfuric Acid Solutions

Sol'n No.	Method of Prep.	Days Between Prep. and Run	Probable Valence of Ru	Acidity in mols/l.	Light Path in cm.	M A X I M A		Remarks
						Wave Length in m μ	Optical Density	
XVI	a	0	+ 8	1	0.10 0.10 0.104	234 310 385	0.346	Similar to RuO ₄ in HClO ₄ and HNO ₃ . Structure with both peaks. Peak at 234 m μ questionable. Near limit of instrument here.
XI	b	0	+ 8	1	1.002	315 385	2.16 0.683	Structure appears to be masked or distorted.
XIa	c	0	?	1	1.002	310	1.097	Plateau from 370 - 400 m μ . No structure with 310 m μ peak.
XIc	d	0	?	1	1.002	440	0.567	Color darkened.
XII	e	0	+ 4 (?)	1	1.002	477	1.336	Peak well defined.
XIIa	f	0	?	1	1.002	None		Color very light
XIIa	g	0	?	1	1.002	None		Color very light

- (a) Distill RuO₄ from HClO₄ into H₂SO₄
 (b) Treat (a) with H₂O₂
 (c) Reflux (b)
 (d) Sparge (c) with N₂

- (e) Treat (a) with H₂SO₃
 (f) Reflux (e)
 (g) Treat (a) with HCOOH and reflux.

Range in m μ for XVI 220 - 1100; for all others 300 - 1100

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2. Reduction of nitric acid solutions of ruthenium tetroxide with hydrogen peroxide or sulfurous acid and boiling resulted in ruthenium (IV).

3. Ruthenium tetroxide is quite stable in 2 N nitric or sulfuric acids, the former even after boiling and the latter even in the presence of hydrogen peroxide.

4. Ruthenium tetroxide is not stable in hydrochloric acid, being reduced by the acid rapidly at room temperature and more slowly at about 10°C.

5. The presence of a peak in the region from 450 m μ to 490 m μ in all four of the acids used would indicate that the same species, probably a ruthenium (IV) ion, was responsible for this peak and that the shift in wavelength was due to the change in acid.

B. Polarography

Polarography as a method of investigation of oxidation and reduction potentials was successfully exploited in alkaline solutions by M. D. Silverman (CNL-37, 107-113) and discussed at the first Ruthenium Conference.

M. D. Silverman employed the solid platinum electrode. E. Turk of Argonne has made some preliminary studies extending this work to acid solutions.

All the results were obtained using a solid platinum electrode sealed in soft glass as the cathode. The dropping mercury cathode was tried but the mercury appeared to react with some of the solutions tried so the inert platinum electrode was chosen to eliminate this difficulty. As a reference electrode the saturated calomel electrode was chosen. The platinum electrode was placed in the ruthenium solution and an agar-saturated potassium chloride bridge was used to make electrical connection from the ruthenium solution to the reference electrode. The voltage-current curve was measured using the Sargent Polarograph Model XXI. The values reported for the voltage positions of the half-waves were read directly from the charts and are only approximate. These voltages have not been referred to the hydrogen electrode. A table of results follows (see Table VI).

L. W. Niedrach of KAPL ran a polarographic curve on ruthenium (IV) in perchloric acid. A saturated mercurous sulfate reference cell was used against a dropping mercury electrode. Three inflection points were obtained. The first, at +0.65 volts, was assumed to be a reduction of ruthenium (IV) to (III); a second, at +0.45 volts was assumed to be reduction of (III) to (II); and a third, at -0.11 volts was assumed to be reduction of ruthenium (II) to the metal. The voltages were referred to the hydrogen electrode as zero. The currents obtained were about one-half the values which were expected for the reduction. The stock solution was tested for chloride and its concentration found to be less than 10⁻⁴ M, i.e., less than 2 molar per cent.

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Table VI

Summary of Polarographic Data on Various Ruthenium Solutions

Sol'n No.	Method of Solution Preparation	Voltage Reading* at Appearance of Half-wave
1	Ru chloride solid dissolved in 1 N HClO_4 , and Cl_2 saturated.	+0.3
2	Ru chloride solid dissolved in 1 N HClO_4	+0.9, +0.6, +0.3, +0.2
3	RuO_4 distilled into 0.5 N HNO_3 with H_2O_2 added, refluxed to destroy excess H_2O_2	+0.9, +0.6, +0.4, +0.2
4	RuO_4 distilled into 0.55 M HClO_4 with H_2O_2 added, refluxed to destroy excess H_2O_2	+0.9, +0.6, +0.3
5	RuO_4 distilled into 2 N HCl with H_2O_2 added and refluxed to destroy excess H_2O_2	+0.5

*Directly read from chart versus saturated calomel electrode.

In later work, controlled potential electrolyses were performed at -0.075, -0.50, and -0.85 volts which corresponded to the three plateaus. Integration of the current time curves indicated reduction of 0.5 electron on each of the first two waves. On this basis, the magnitude of the third polarographic wave indicated a further reduction of 1 electron. However, in the macro reduction on this wave the current never did decrease although a total number of coulombs equivalent to 3 electrons were consumed. Apparently there was a rather rapid reaction with the perchloric acid. After this final electrolysis, a positive test for chloride was obtained.

The product of the electrolysis on the first wave was a pink-violet solution whose absorption spectrum changed rapidly with time despite exclusion of air. A yellow solution was obtained from the second wave and this again was unstable. A decrease in the intensity of the yellow color was all that was attained by electrolysis in the third wave. Polarograms were recorded at each stage of the reduction and these confirmed the fact that none of the original waves are reversible.

A table of the results follows:

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Table VII

Polarographic Reduction of Ruthenium (IV)in 1 N Perchloric AcidWave I

E 1/2 = merges with dissolution wave for mercury

C	i	$m^{2/3}t^{1/6}$	$I = \frac{i}{m^{2/3}t^{1/6}}$
m mol	a		
1.10	1.37	1.310	0.938
2.19	2.58		0.883

Wave IIE 1/2 = 0.20 volts versus saturated Hg_2SO_4 elec.

1.10	2.37	1.375	1.55
2.19	4.64		1.51

Wave IIIE 1/2 = 0.74 volts versus saturated Hg_2SO_4 elec.

1.10	4.53	1.390	2.92
2.19	8.99		2.90

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IV. RUTHENIUM IN SOLVENT EXTRACTION

T. C. Runion of Oak Ridge discussed solvent extraction distribution ratios in general process work. For most of the systems employed, on extraction the distribution ratios, (organic/aqueous) varied from 0.007 to 0.05 with 0.2 being obtained under special conditions. On scrubbing, the distribution ratios varied from 0.2 to 6.0, the latter value being observed frequently at the top of the scrub column. On stripping, the distribution ratios varied from 0.01 to 1. The aqueous to solvent volume ratios were from about 4 to 1 to about 1 to 2. It is believed that the material causing the greatest trouble was colloidal ruthenium, either the metal or the oxide or a mixture of both. Very stable macro sols of ruthenium in hexone have been prepared.

A sol of ruthenium metal and oxide was prepared on a micro scale by adjustment of the acidity and reducing conditions. It was found that the ruthenium in this sol could be dissolved in alkaline media by sodium hypochlorite and in acid media by periodic acid. The latter converted ruthenium to the tetroxide which is highly solvent soluble. It was found that strong oxidizing agents gave increased hexone soluble forms. Some Tygon tubing was added to a solution after the periodic acid treatment and it was found that the ruthenium was absorbed on the Tygon.

Ruthenium metal was treated with periodic acid and the solution extracted with hexone. The amount of periodic acid used appeared to control the stability of the hexone solution. Using a Tyndall beam the color of the solution could be seen to change from pure yellow to amber-brown and then black. The material coagulated on stirring and particles could be observed. The colloid tended to collect at the hexone-aqueous interface. Addition of acid caused the colloid to favor the organic phase and addition of base caused the colloid to favor the aqueous phase. Once the material had passed through a solvent phase it was indifferent to hydrogen ion. All of these experiments were carried out at room temperature. It was felt that on treatment with periodic acid ruthenium (VIII) went to a hexone soluble form and then, with a half-life in the order of minutes, it became colloidal; ruthenium (III) went to a hexone soluble form and then, with a half-life in the order of days, became colloidal; ruthenium (IV) was hexone insoluble.

A nitrite of doubtful composition was isolated. This was obtained by treatment of a nitric acid solution with excess sodium nitrite. The nitrite was extremely insoluble, being attacked by periodic acid only slowly. Treatment with sulfanilic acid followed by periodic acid resulted in solution.

O. F. Hill of Hanford reported on some extractions of ruthenium tracer with hexone. The validity of the results is questionable because of the variation in the tracer. Experiments with the old tracer gave extraction values around 0.1 to 0.5. A new batch of presumably identical tracer gave an extraction result of around 0.01 or slightly greater. It was found that if the ruthenium carrier and the ruthenium tracer were interchanged by distillation together into nitric acid and hydrogen peroxide, the distribution ratio (hexone/aqueous) was 0.1. On scrubbing the activity was

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removed. Table VIII presents these results.

Table VIII
Extraction and Scrub of Ruthenium Tracer
With and Without Interchange

Distribution Ratios (Organic/Aqueous)										
Conditions	1st Ext'n	S C R U B				2nd Ext'n	S C R U B			
		1	2	3	4		1	2	3	4
$\frac{1}{2}$ mg Ru inter- changed with carrier	0.13	0.0016				0.097				
Fresh tracer	0.16	0.16	0.7	4	4	0.14	0.12	0.2	2	3
With carrier, not interchanged	0.41	0.6	1.9	2.2	2.2	0.21	0.37	1.3	2.3	1.6
0.1 M Ce^{IV} + H_2O_2 to reduce Ce , $\frac{1}{2}$ 0.1 M $\text{Na}_2\text{Cr}_2\text{O}_7$	0.46	0.49	1.4	1.3		0.24	0.49	1.1	1.1	
0.1 M Ce^{IV}	0.73	0.72	1.0	1.5	2.5	0.22	1.6	2.0	1.9	2.3
New tracer, no carrier	0.03	0.08	(1.7)	(2.2)		0.008	(0.2)	(2)	(3)	

Solution - 1.3 M $\text{Al}(\text{NO}_3)_3$, 0.3 M HNO_3 , 0.1 M $\text{Cr}_2\text{O}_7^{2-}$

Scrub - 1.3 M $\text{Al}(\text{NO}_3)_3$

Strip - 0.1 M HNO_3

To a portion of the new tracer, some silver ion was added to precipitate silver chloride. The supernatant was used to make a new tracer supply by distilling ruthenium tetroxide into nitric acid and peroxide. After distillation no chloride ion could be found in the distillate or the residue. A solution was made up as follows: 1.3 N aluminum nitrate, 0.3 N nitric acid, 0.1 M sodium dichromate, and hydrochloric acid added to give various concentrations. Six different solutions were made up. Table IX showing the results appears on the following page.

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Table IX

The Effect of Hydrochloric Acid on the Extraction
and Scrubbing of Ruthenium Tracer

Expt. No.	HCl N	Extraction	Distribution Ratios (Hexane/Aqueous)		
			S C R U B		
			1	2	3
1	0.0	0.19	0.20	8.6	5.8
2	0.000012	0.18	0.21	4.7	6.0
3	0.00012	0.19	0.25	4.7	5.8
4	0.0012	0.16	0.24	4.4	5.0
5	0.012	0.21	0.46	3.5	2.0
6	0.12	(0.9)	0.78	0.10	2.1

H. M. Feder of Argonne summarized a paper from the Analytical Chemistry Journal, page 1094, November 1948, on the extraction of the platinum metals in hydrobromic and hydrochloric acids with isopropyl ether, ethyl acetate, and hexone. Results are shown in Table X.

W. Hardwick of Chalk River reported on a solvent extraction process for preparing ruthenium tracer from dissolver solutions. The pH of the solution was adjusted to 1.0 ± 0.2 and the ruthenium and fission products oxidized with 0.05 grams of ammonium hexanitrate cerate per milliliter. The ruthenium was then extracted with tetrachlorethane yielding a tracer of 99.9% purity. Using tracer, 96 - 98% of the ruthenium was found to extract. On back-washing with pure solvent about 95% was obtained. No uranium or fission products were detected in the solvent. The valence of the ruthenium in the tetrachlorethane was apparently lower than (VIII). Hardwick thought it was in the (IV) state but had no real evidence for this hypothesis. The method worked for ruthenium solutions prepared by dissolving either irradiated uranium metal or oxide in strong nitric acid. When the material was dissolved in a weak acid solution, only about 10% of the ruthenium was extracted as compared with those solutions in which there was strong acid and greater than 90% of the ruthenium was extracted. On mixing Ru^{106} from acid solution with Ru^{103} from the basic solutions and extracting, no change in the percentage of either extracted was observed.

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Table X

Per Cent Extraction of Platinum Metals

(1 mg/ml)

<u>Solvent</u>	<u>Acid</u>	<u>Pd^{II}</u>	<u>Pt^{IV}</u>	<u>Rh^{III}</u>	<u>Ir^{IV}</u>	<u>Ru^{III} + IV</u>	<u>Os^{VI}</u>
Isopropyl Ether	2.9 M HBr	0.16	0.10	0.07	0.03	0.00	25
	2.0 M HBr	0.22	0.21	0.15	0.03	0.00	43
Ethyl Acetate	2.9 M HBr	1.7	2.9	0.16	0.08	0.43	13
	2.0 M HBr	1.7	2.6	0.12	0.15	0.43	8
	2.8 M HCl	0.31	13.5	—	—	0.62	—
Hexone	2.9 M HBr	20.5	—	—	—	—	56
	2.0 M HBr	—	—	0.05	1.0	—	54
	4.0 M HCl	1.0	—	—	—	—	—
	2.8 M HCl	—	2.0	1.2	1.0	1.3	12

Au extracted 100% in all cases.

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V. SPECIAL PROBLEMS AND TECHNIQUES

A. Decontamination by Volatilization

C. F. Callis at Hanford attempted to remove ruthenium from dissolver solutions by volatilization. A solution was prepared containing 2 M uranyl nitrate hexahydrate, 0.3 M nitric acid, and ruthenium tracer at a concentration of about 1.5 to 2×10^6 counts per minute. This solution was oxidized with sodium bismuthate, cobaltic oxide, ozone, potassium permanganate, lead dioxide, ammonium hexanitrate cerate, mixtures of sodium dichromate and sodium bismuthate, and sodium dichromate and cobaltic oxide. In all cases oxygen was blown through the solution to carry off the ruthenium tetroxide produced.

On oxidation with ammonium hexanitrate cerate it was found that the ruthenium tended to stick to the glass and 25 to 90% was found on the walls after the experiment. When potassium permanganate was used 0.1 to 8% of the activity was on the walls. With ozone 0.1 to 3% was found on the walls. It was observed that the ruthenium was removed more rapidly at higher temperatures than at low temperatures. It was also observed that the flow rate and total flow of the air or gas was important.

In a series of experiments carried out at 75°C using 0.1 M potassium permanganate the following results were observed. With a flow rate of 38 cc. per minute for 2 hours, .02 to 0.3% of the ruthenium was left in the residue. Using a flow rate of 5 cc. per minute for 1/2 hour, 36.3% remained behind. After 11-1/2 hours no ruthenium could be detected in the residue.

In another series of experiments carried out at 75°C using ozone and 0.01 M silver nitrate the following results were observed. With a flow rate of 38 cc. per minute for 1 hour 0.02% of the ruthenium was left in the residue. At the same flow rate for 2 hours only 0.003% stayed behind. In one experiment a stainless steel coupon was inserted in the apparatus. It was found that about 3% of the activity collected on the coupon.

In experiments using ammonium hexanitrate cerate in which ruthenium was left on the walls after the oxidation subsequent treatment with ozone at elevated temperatures removed most of the activity. Ozone at room temperature did not work as well.

At Argonne the ruthenium has been oxidized to the tetroxide and then swept out with ozone by M. Beederman. Preliminary experiments in the absence of any catalyst had indicated that little or no removal of the ruthenium with ozone occurred at varying acid conditions at room temperature.

Up to the present the experiments using ozone to volatilize the ruthenium as the tetroxide were divided essentially into three groups. First, aqueous solutions containing only ruthenium tracer and in some cases, macro ruthenium; second, uranyl nitrate solutions containing ruthenium tracer, and third, dissolver solutions. The first set of results indicated

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that the ruthenium could be eliminated with volatilization using ozone and a catalyst at room temperature. Of the catalysts tested, potassium permanganate appeared to be most effective. However, silver ion and ceric ion also appeared to be suitable.

With 2 M uranyl nitrate hexahydrate solutions it was found necessary to use elevated temperatures to volatilize the ruthenium. At temperatures up to 75°C, the removal of ruthenium was not sufficient. When the temperature was raised to between 85 to 90°C, removal of ruthenium was essentially complete. These results were obtained with both silver and ceric ions as catalysts.

Finally, dissolver solution was used as a source of ruthenium. Ten milliliters of dissolver solution were used and made up to 50 milliliters with 2 M uranyl nitrate hexahydrate. After approximately 4 to 6 hours of ozonization at a temperature of about 85°C only about 75% of the ruthenium had distilled over. However, continued ozonization up to 13 hours produced results indicating that 98.3% of the ruthenium had distilled over. The data are summarized in Tables XI, XII, and XIII.

The poor correlation between actual dissolver solutions and synthetic solutions of the same macro composition is not encouraging, but it certainly is possible to remove the ruthenium by this procedure.

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Conc. H^+	Conc. Metal Ion	Ruthenium		Rate of O_3	Time	% Ru Distilled	Remarks
		Macro	Tracer				
$\sim 5 M$	---	+	+	60 cc/min	6 hrs.	8%	
"	.01 M Ag^+	+	+	"	30 hrs.	61%	
"	.025 M Ag^+	+	+	1400 cc/min	2 hrs.	94%	
"	.001 M MnO_4^-	+	+	"	2 hrs.	99%	
"	.001 M Ce^{IV}	+	+	"	6 hrs.	70%	
"	.001 M Pu	+	+	"	5 hrs.	59%	
.1 M	.025 M Ag^+	+	+	"	2½ hrs.	99.7%	
.1 M	.01 M Ag^+	+	+	"	3½ hrs.	99.1%	Further O_3 : additional 330 min = 99.7%
.1 M	.025 M Ag^+	+	+	840 cc/min	4 hrs.	99.2%	
.8 M	.025 M Ag^+	+	+	1400 cc/min	525 min.	99.7%	
.3 M	.025 M Ag^+	-	+	"	1½ hrs.	99.7%	
.3 M	.025 M Ce^{IV}	-	+	"	1½ hrs.	99%	
.3 M	.025 M Ni^{++}	-	+	"	8 hrs.	80%	
.3 M	.025 M Ni^{++}	-	+	"	8 hrs.	80%	

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Table XII

Ozonization from UNH Solutions

Conc. UNH	Conc. H^+	Conc. Ag^+	Add'n of Macro Ru	Add'n of Tracer Ru	Rate of O_3	Bath Temp.	Time	% Ru Distilled
2 M	2 M	—	present	present	.05 cu ft/min	50°C	150 min.	55
1 M	0.3 M	0.025 M	"	"	" "	—	360 min.	94
2 M (1)	0.3 M	0.01 M	—	"	.02 cu ft/min	75°C	600 min.	96
0.1 M (2)	0.3 M	0.01 M	—	"	.05 cu ft/min	—	150 min.	99.4
2 M (3)	0.3 M	0.025 M	—	"	" "	90°C	780 min.	99.98
2 M	0.3 M	0.025 M (4)	—	"	1400 cc/min	85°C	13 hrs.	99.1

- (1) O_3 first passed through HNO_3
- (2) 99.2% had distilled over within 2 hours.
- (3) 97% had distilled over within 5 hours.
- (4) In this case Co^{IV} was used in place of Ag^+ .

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Table XIII

Ozonization from Dissolver Solutions

<u>Conc. UNH</u>	<u>Conc. H⁺</u>	<u>Conc. Ag⁺</u>	<u>Add'n of Macro Ru</u>	<u>Add'n of Tracer Ru</u>	<u>Rate of O₃</u>	<u>Bath Temp.</u>	<u>Time</u>	<u>% Ru Distilled</u>
(2 M) 10 ml	--	0.025 M	--	--	.03 cu ft/min	50°C	240 min.	77%
" " (1)	0.3 M	"	--	--	" " "	"	" "	75%
10 ml dissolver (2) made up to 50 ml 2 M UNH.	0.3 M	"	--	--	.05 cu ft/min	90°C	772 min.	98.3%
" " " (3)	0.3 M	"	--	--	" " "	"	540 min.	16%

(1) O₃ first passed through 0.3 M HNO₃

(2) 72% in 372 minutes.

(3) O₃ first passed through 0.3 M HNO₃

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Absorption Curve of Ruthenium (IV) Chloride

Figure 2

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Absorption Curve of Ruthenium (IV) Chloride

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Absorption Curve of Ruthenium (IV) Chloride

Absorption Curve of Ruthenium (IV) Chloride

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Absorption Curve of Ruthenium (IV) Chloride

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Absorption Curve of Ruthenium (IV) Chloride

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Absorption Curve of Ruthenium (IV) Chloride

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Figure 8 47

Absorption Curve of Ruthenium (IV) Chloride

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Absorption Curve of Ruthenium (IV) Chloride

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Figure 10 49

Absorption Curve of Ruthenium (IV) Chloride

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Absorption Curve of Ruthenium (IV) Chloride

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Absorption Curve of Ruthenium (IV) Chloride

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Absorption Curve of Ruthenium (IV) Chloride

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Figure 14 53

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Figure 16
The Absorption Spectra of Ruthenium Tetroxide
in 2 N Nitric and 2 N Hydrochloric Acid Solutions

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Figure 17
The Absorption Spectra of Two Ruthenium Tetroxide - Nitric Acid Solutions
Reduced with (1) Sulfurous Acid and (2) Hydrogen Peroxide

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