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Progress Report

# EXTRACTION OF INORGANIC SUBSTANCES BY ORGANIC SOLVENTS

Contract Number AT(30-1)-1663

July 1, 1955 to July 1, 1956

by

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July 15, 1955

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# EXTRACTION OF INORGANIC SUBSTANCES BY ORGANIC SOLVENTS

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# STATUS OF THE PROGRAM

## I. Chlorides

1. Aluminum Chloride.- It was expected that the study of the properties of the system: aluminum chloride-diethyl ether — water — hydrogen chloride would reach a satisfactory termination point last fall. Partly because of illness, however, Mr. D.E. Byrnes has not yet completed his study of the system. Since February 1, Mr. Byrnes has been supported as a teaching assistant rather than as a research assistant under the contract. His research objectives are still the same and are as much a part of the solvent extraction study as before except that his association with the contract is now informal.

In attempting to prepare the acid, $HAlCl_4$, which is analogous to the ether-extractible acids $HFeCl_4$ and $HGaCl_4$, two approaches have been followed. One method consists of the dissolution of pure aluminum metal chips by anhydrous hydrogen chloride in dry diethyl ether in an all-glass apparatus. As the aluminum dissolves, two liquid phases form. Crystals which separated from the heavy oily layer had the composition 1 $AlCl_3$: 1.02 HCl: 2.45 $Et_2O$. The oil appears to contain $AlCl_3$ and HCl in 1:1 ratio and ether in a non-integral ratio to aluminum. Aeration of the oil removes HCl and ether to give a substance which approaches the composition of aluminum chloride mono-etherate. Infrared spectra have been examined for the solid and liquid phases.

The second method of preparation is based on converting a known tetrachloroaluminate salt such as $LiAlCl_4$ or $NaAlCl_4$ to the acid. These salts are prepared by melting a mixture of anhydrous aluminum chloride and lithium or sodium chloride. The salts have been prepared and studied spectrophotometrically in an attempt to find an absorption of light characteristic of the $AlCl_4^-$ ion.

Both methods are being used to prepare material which should give information about the tetrachloroaluminate acid.

2. Protactinium Chloride.- Some aspects of the solvent extraction of protactinium from chloride solution were studied by Mr. D.E. Neil last summer. Pa-233 tracer was used after an appropriate license had been obtained during the summer. Radioactive decay for some of the samples was followed during the winter and spring. A manuscript for a journal article is in preparation. The manuscript will be submitted to the New York Operations Office as a classified document for declassification prior to submission to a journal. It is intended that the manuscript be ready by the end of this summer.

Mr. Neil is now in the Nuclear Engineering Department of Brookhaven National Laboratory where he is carrying out research in chemistry for his Ph.D. degree at Rensselaer.

It is hoped that the protactinium work will be continued, but the need for Q clearance has been somewhat of a deterrent factor in putting another graduate student on the problem.

3. Tantalum Chloride.- Mr. A. Behringer completed one phase of the study of the solvent extraction of tantalum chloride this June. Details of the work are reported in his thesis which was was submitted for the master's degree. Four copies have been sent to the New York Operations Office.

Mr. Behringer's results are briefly summarized below.

The distribution of tantalum as tracer (Ta-182) between hydrochloric acid and (1) methyl isobutyl ketone, (2) bis(2-chloroethyl)ether, and (3) tri-n-butyl phosphate was measured for equal-volume extraction at 25°C. for various initial concentrations of hydrochloric acid. For methyl isobutyl ketone the distribution ratio, (concentration in the organic phase)/(concentration in the aqueous phase), varied from 0.002 to 0.417 in the range of initial acid concentration of 6.10 to 9.16 M. Higher acidity was not used because of the miscibility of the two phases. For bis(2-chloroethyl)ether the distribution ratio varied as follows with initial hydrochloric acid concentration: 0.0048 at 7.10 M; 0.170 at 9.15 M; and 2.16 at 11.71 M. For tri-n-butyl phosphate the distribution ratio increased with time for each acid concentration. Distribution ratios at 7.10, 9.15 and 11.71 M hydrochloric acid increased from 2.5, 5.7 and 3.5 after 8,7 and 6 hours of contact to 42,495, and 835 after 121,120, and 119 hours, respectively.

The stability of hydrochloric acid solutions of tracer tantalum was studied also. Stability was found to increase with increasing hydrochloric acid concentration. About 80 per cent of tantalum remained in solution in 11.71 M hydrochloric acid for at least 25 days at about 25°C.

Mr. Behringer's work also included measurement of the distribution of HCl between water and methyl isobutyl ketone; preparation of solutions of $K_2Ta_6O_{19}$ for use as tantalum carrier; and a preliminary study of colorimetric methods for the determination of tantalum.

Initially, radioactivity measurements for Ta-182 were carried out by drying the samples and beta-counting with a thin-window Geiger counter. Later, samples were gamma-counted in liquid form in a well-type scintillation counter.

Mr. Behringer was not supported under the contract except for his using special materials and equipment not otherwise available. He is joining the Atomic Energy Project at the University of Rochester this summer.

The work on tantalum is being extended this summer by Mr. R.L. Ritzman, who will be starting his second year of graduate study this fall.

4. Ruthenium.- Mr. C.O. Hommel has been carrying out experimental work on ruthenium chloride as a part-time research assistant under the contract since the beginning of the spring semester in February.

Hydrochloric acid solutions of ruthenium chloride have been examined spectrophotometrically with Beckman Models B and DU spectrophotometers for various concentrations of hydrochloric acid. A solution of $RuCl_3$ in water shows no distinct absorption peaks, but absorbs strongly in the ultraviolet region with the absorbance decreasing with increasing wavelength to a minimum at about 740 mμ where it starts to rise again. Solutions of ruthenium trichloride in hydrochloric acid are dark brown when first prepared. On standing, they turn red-brown, with absorption peaks appearing at 290, 370 and 470 mμ. The wavelengths of these peaks vary somewhat with hydrochloric acid concentration and all peaks do not appear at all acid concentrations. The 290 mμ peak, for example, is more pronounced at lower acid concentration. The peaks appear rapidly in strong acid; quite slowly in weak acid.

Solvent extraction of ruthenium from hydrochloric acid was tried first with diethyl ether. Analysis showed no extraction. Tri-n-butyl-phosphate was tried next with positive results. Figure 1 shows the dependence of the distribution coefficient, (conc. Ru in organic phase)/(conc. Ru in aqueous phase), on initial acid concentration. Points on the curve are average values of duplicate experiments. The organic phase shows a strong absorption peak at 291 mμ and weaker ones at 370 and 470 mμ. The extracting species has not yet been identified but it appears to absorb predominantly at 291 mμ and to exist most readily at low acid concentration, i.e., about 1 to 2 molar.

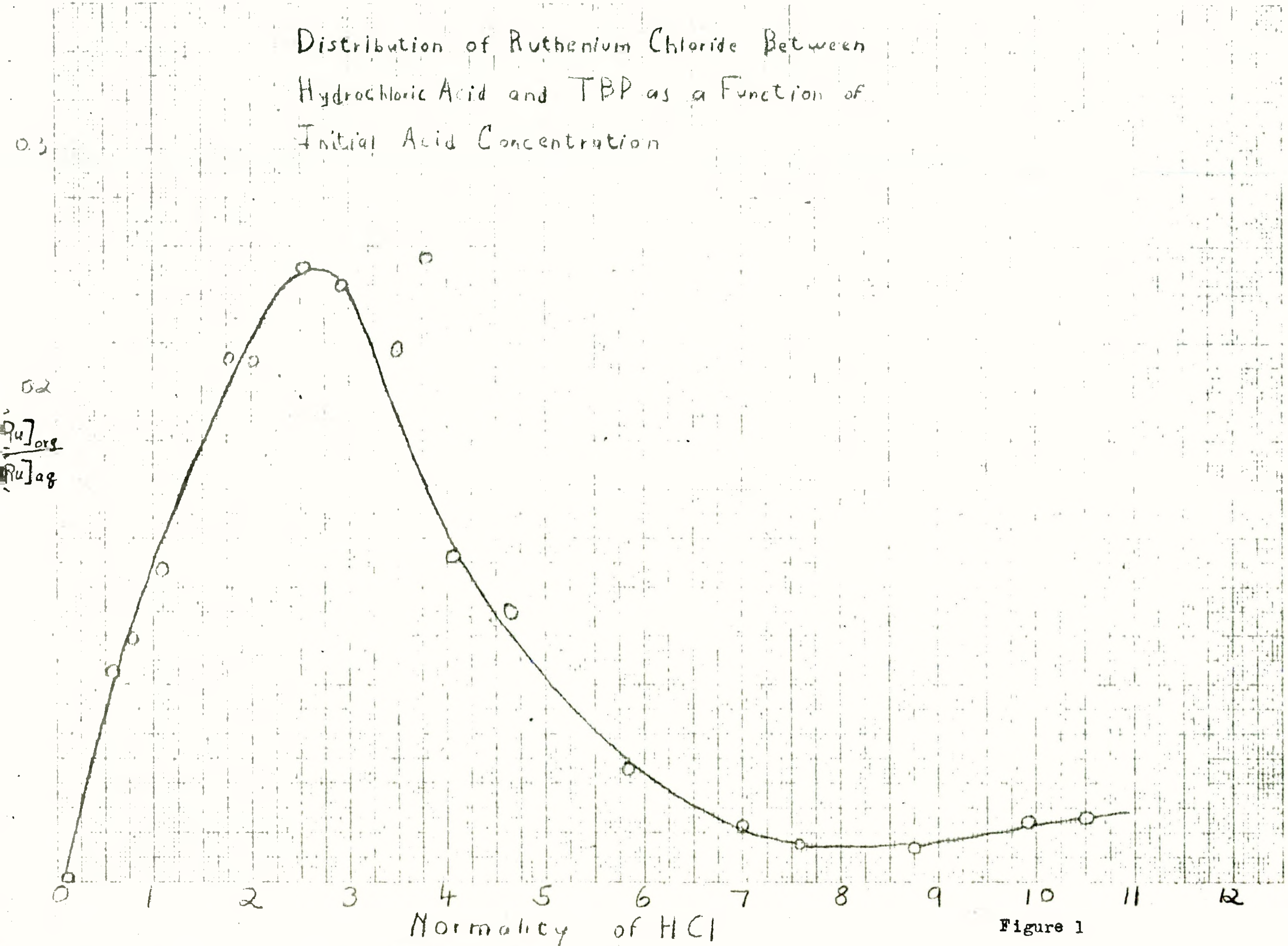
Distribution of Ruthenium Chloride Between
Hydrochloric Acid and TBP as a Function of
Initial Acid Concentration
0.3
0.2
[Ru]org / [Ru]aq
0
1
2
3
4
5
6
7
8
9
10
11
12
Normality of HCl

Figure 1

Further work on both ends of the distribution curve is planned for the future. Radioruthenium, Ru-106, will be used to extend the range of analysis beyond that attainable by the thiourea colorimetric method. Future work will include:

1) Identification of the extracting and extracted species.
2) Extraction of HCl itself into TBP at high concentration.
3) Effect of oxidation and reduction on the extraction of ruthenium.
4) Effect of other solvents on the extraction of ruthenium,

## II. Bromides

Ferric Bromide.- Mr. G.S. Golden has been continuing his study of the ferric bromide—water—diethyl ether—hydrobromic acid system as a research assistant under the contract since February 1st. Methods for the analysis of the aqueous and organic phases have been developed. The study of the visible absorption spectra of the system was carried on. The distribution of HBr between $H_2O$ and diethyl ether was determined. The extraction of a ferric bromide-hydrobromic acid solution by diethyl ether is being studied at present.

In hydrobromic acid concentrations up to 6 M, the visible spectrum of the ferric ion exhibits a peak at 410-420 mμ. At higher HBr concentrations two peaks appear at 390 and 460 mμ with a reduction in the relative height of the 420 peak. The spectrum of the ethereal layer of a ferric bromide extraction from 3.5 M HBr shows the same peaks as that of ferric iron in concentrated hydrobromic acid. In analogy with the $FeCl_3$-HCl-ether system, the indication is that the ethereal iron species is the tetrabromoferrate ion.

The distribution of HBr between $H_2O$ and diethyl ether was studied at 25°C. At initial hydrobromic acid concentrations of 0.8 to 4 M, the ethereal HBr concentration increased linearly from $10^{-5}$ to $10^{-3}$M. At higher aqueous concentrations there was a large increase in the HBr ethereal solubility, and a concomitant increase in the solubility of the ether in the aqueous phase. The maximum aqueous equilibrium HBr concentration attained was 3.7 M when an initial concentration of 6 M was used. With solutions more concentrated initially the equilibrium concentration was slightly less due to the increased solubility of the ether. The results appear to be similar to those obtained with the isopropyl ether-HCl-$H_2O$ system.

The preparation of ferric bromide solutions was investigated. The most satisfactory appears to be the dissolution of $Fe_2O_3$ in concentrated hydrobromic acid. The reaction is slow, several days being needed for complete solution. $FeBr_3$ is easily reduced by both heat and light. Because of this, all work is done, where possible, in low actinic glassware.

In extraction studies difficulty has been experienced due to the reduction of the ethereal iron to ferrous iron and bromine. Investigations as to the extractability of ferrous bromide proved negative. A study of the distribution of bromine between the ether and aqueous phases proved unfeasible because of reaction between the bromine and the ether. Reduction of the iron is hindered by mixing the phases at low temperature followed by gradual warming to 25°. Experiments showed that 48 hours is sufficient time for equilibrium to be established. Work in progress on the distribution of ferric bromide between ethereal and aqueous phases as a function of hydrobromic acid concentration is in agreement with scattered data in the literature. Data thus far obtained are listed in the following table:

| (HBr) M, initial | (HBr) M, equilibrium | $\frac{(Fe^{+++})_{ether}}{(fe^{+++})_{aqueous}}$ | $\frac{(Br^{-})}{(Fe^{+++})_{ether}}$ |
|---|---|---|---|
| 1.88 | 1.78 | .0068 | 3.70/1 |
| 2.59 | 2.44 | .265 | 3.86/1 |
| 3.85 | 2.98 | 4.97 | 4.25/1 |
| 4.19 | 3.44 | 7.25 | 4.45/1 |
| 4.48 | 3.38 | 38.5 | 4.41/1 |
| 5.12 | 3.65 | 46.2 | 4.75/1 |
| 6.05 | 3.55 | 12.5 | 4.91/1 |

Observations indicate that extractability increases with a decrease in temperature.

Proposed work will include the determination of the distribution of ferric bromide between hydrobromic acid and ether as a function of hydrogen ion concentration, bromide ion concentration, iron concentration, and temperature. The isolation and analysis of the ethereal iron species will also be undertaken.

## II. APPROXIMATE STATEMENT OF EXPENSES

Period of November 1, 1953 to October 31, 1954

| | Salaries | Indirect Charges | Materials, Supplies, etc. | Total |
|---|---|---|---|---|
| AEC | $3580 | $ 568 | $2137 | $6285 |
| RPI | 900 | 2255 | .... | 3155 |
| Total | $4480 | $2823 | $2137 | $9440 |

Period of November 1, 1954 to October 31, 1955

| | Salaries | Indirect Charges | Materials, Supplies, etc. | Total |
|---|---|---|---|---|
| AEC | $3607 | $ 500 | $2385 | $6492 |
| RPI | 900 | 2024 | .... | 2924 |
| Total | $4507 | $2524 | $2385 | $9416 |

Period of November 1, 1955 to July 31, 1956

| | Salaries | Indirect Charges | Materials, Supplies, etc. | Total |
|---|---|---|---|---|
| AEC | $4085 | $ 480 | $1833 | $6398 |
| RPI | 675 | 2186 | .... | 2861 |
| Total | $4760 | $2666 | $1833 | $9259 |

Estimate for Period August 1, 1955 to October 31, 1956

| | Salaries | Indirect Charges | Materials, Supplies, etc. | Total |
|---|---|---|---|---|
| AEC | $1773 | $ 160 | $ 150 | $2083 |
| RPI | 225 | 959 | ... | 1184 |
| Total | $1998 | $1119 | $ 150 | $3267 |