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# The separation of some inorganic compounds by liquid-liquid extraction

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THE SEPARATION OF SOME INORGANIC COMPOUNDS BY LIQUID-LIQUID  
EXTRACTION

by

45  
Raymond A. Foos

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

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## I. INTRODUCTION

Liquid-liquid extraction is becoming widely used for the separation of inorganic salts in industrial as well as in laboratory processes. Consequently, this technique was investigated as a method for the separation of some inorganic salts which are of current interest to the Atomic Energy Commission. The salt mixtures included in this study were those of niobium and tantalum, of vanadium and tantalum, of zirconium and hafnium and of yttrium and rare earths. For some of these mixtures liquid-liquid extraction afforded a very convenient method of separation.

In general a number of liquid-liquid systems containing these salts were investigated. Various compositions of the aqueous phase were contacted with a variety of partially immiscible organic solvents in single stage extractions until equilibrium was obtained. Analyses of the equilibrium phases allowed calculation of the individual distribution coefficients, mass transfers from the aqueous phase to the organic phase and separation factors for each case. These equilibrium data afforded a method whereby the separation effectiveness of the various liquid-liquid systems were compared. From the single stage data the range of the optimum operating conditions was estimated for a separation by a multistage extraction. These



conditions were tested in a multiple-contact countercurrent extractor employing as many as 20 equilibrium stages. A few multistage extraction experiments were usually required to obtain the most effective separation conditions.

The aqueous feed was usually a mineral acid solution containing the salts to be separated although basic media in some cases were also investigated. Such variables in the aqueous phase as pH, acid concentration, salt concentration, complexing agents and salting-out agents were investigated. For the organic phase factors such as acidity, complexing agents, diluents and type of organic were found to be important in making separations. Relative volumes of the organic and aqueous phases were also varied to obtain separation data. Since separation of some of these salts on a commercial scale is desired, the economics of a process was an important factor in evaluating the practicability of a liquid-liquid system.

It was found that niobium and tantalum spectrographically free of each other and hafnium spectrographically free of zirconium could be produced on a continuous basis by a multistage extraction. It was also observed that tantalum could be easily separated from vanadium. An enriched yttrium concentrate and concentrates of various rare earths resulted from extractions on the yttrium-rare earth mixtures. The use of liquid-liquid systems for separating these inorganic salts proved useful

on a laboratory scale. In a few cases the operations were scaled up to pilot plant production where they proved equally satisfactory.

## II. GENERAL ASPECTS OF LIQUID-LIQUID EXTRACTION

### A. Principle of Effecting Separations by Liquid-Liquid Extraction

In 1872 Berthelot and Jungfleisch (1) stated that if to a system composed of two immiscible liquid phases is added a third substance which is soluble in both phases, this substance will be distributed between the two liquid layers in a manner which is independent of the total amount of the dissolved substance. This statement constitutes the original form of the distribution or partition law.

Although this law has some applications many limitations have been placed on its original form. Many textbooks on thermodynamics have considered this distribution law with its variations, limitations and consequences (2,3).

The distribution coefficient as employed in this work is the ratio of the concentration of a solute in the organic phase to its concentration in the aqueous phase. Concentrations are expressed here in grams or moles of solute per liter of solvent. When the solutes x and y are distributed between two immiscible liquid phases the respective distribution coefficients are represented by  $K_x$  and  $K_y$ . Distribution values determined for single solutes in corresponding liquid-liquid systems are useful for

predicting the equilibrium conditions for extraction in a system containing multiple solutes only if the distribution values of the solutes are independent of the presence of the other solutes. Ordinarily for many liquid-liquid systems interactions between solutes prevent this direct correlation. Consequently distribution coefficients determined by experiments employing the solute mixtures are usually desired for practical liquid-liquid extraction behavior.

Separation by liquid-liquid extraction depends on differential distribution of the various solutes when they are equilibrated between two immiscible liquid phases. It is apparent that when two or more solutes are present in such a system a partial separation will result if all the components do not favor the same phase to the same degree. This means that the values of  $K_x$  and  $K_y$  in the example cited above must have different numerical values if their separation is to be effected. The ratio of the distribution coefficients of two solutes, designated as the separation factor, indicates the effectiveness of liquid-liquid extraction as a means of their separation. By definition the separation factor is always expressed as having a value of unity or greater. Under conditions where its value is unity no separation of the solutes  $x$  and  $y$  can be obtained by liquid-liquid extraction. As the value of the separation factor increases the separation

per stage increases so that the number of equilibrium stages required for solute fractionation decreases.

If in the case of two immiscible liquid solutions it is assumed that ideal behavior is exhibited by all solutes then the distribution coefficients of these solutes between the two liquid phases are all equal (2). In such a case the separation factor would be unity for each solute pair and no separation could be effected by liquid-liquid extraction. It is apparent then that separation of solutes by this means would require a deviation from ideal behavior for at least one of the solutes.

The success of purification or separation of solutes by liquid-liquid extraction depends considerably on both the magnitude and relative values of their distribution coefficients. Operation of an extraction process having a very high separation factor might not be practical if the amount of a desired material distributed in a phase were very small in comparison with its total amount present. The distribution coefficients of the solutes relative to one another in two immiscible liquid phases at equilibrium can often be varied by modifying the conditions of the system.

Variations in the pH or temperature of the system often changes the relative distribution values of the solutes and consequently their separation factors. Salting-out

agents sometimes affect the relative solubilities of the solutes at equilibrium in the liquid phases. The concentration and composition of the initial aqueous and organic phases as well as their relative volumes often change the distribution values for the solute components relative to one another. Since one variable ordinarily cannot be assumed to control the distribution coefficients and separation factors, their experimental determination remains the final test for ascertaining the possible application of liquid-liquid extraction for separation studies and for comparing results at various conditions.

When the separation factors of the solute components are close to unity a series of extractions is required to effect a quantitative separation. Since this operation becomes laborious and time consuming if carried out in separatory funnels, many liquid-liquid extractors have been designed to operate on a laboratory or a commercial scale (4-7). The four general methods of performing a liquid-liquid extraction are: (a) single stage contact, (b) multiple-contact extraction using fresh organic solvent in each case, (c) countercurrent multiple-contact extraction and (d) continuous countercurrent extraction (8). The first three methods were employed in the study presented here. Several methods of calculation based on equilibrium data and material balances to determine the

number of stages and relative flow rates for obtaining desired separations have been proposed and illustrated (8-14).

B. Application of Liquid-Liquid Extraction  
for Separating Inorganic Salts

During the past few decades liquid-liquid extraction has become one of the principle methods of performing separations, purifications and recoveries of organic compounds on both a laboratory and commercial scale. However the separation of inorganic chemicals employing this method has found only limited application. The success in separating some heavy metal salts has stimulated considerable interest in liquid-liquid extraction for purification of other inorganic mixtures. One obvious advantage of this technique is that sufficient stages can usually be added to obtain any desired purity of product. Absolute purity cannot be reached although salts spectrographically free from interfering substances have been produced. The papers contributed to the 1950 Symposium on Absorption and Extraction affords a valuable introduction to liquid-liquid extraction from a large scale production and chemical engineering viewpoint (15). Liquid-liquid extraction for separating inorganic chemicals both in the laboratory and on a commercial scale appears destined to soon

become one of the primary methods of salt fractionation.

Most of the reported work on inorganic salt separation by liquid-liquid extraction has appeared in the literature since 1948. This technique as applied to inorganic salts has been reviewed up to 1950 by Irving (16). The extraction studies cited in the present survey are treated in groups according to anions in the initial aqueous phase.

Inorganic nitrates dissolved in nitric acid have often been employed as the aqueous phase in solvent extraction studies. Extraction of uranyl nitrate by diethyl ether has been known since 1842 when Peligot (17) purified uranium starting with pitchblende. The transfer of uranium to the organic phase is increased by nitric acid (18) and many soluble nitrate salting-out agents (19). Various other organic solvents possessing an oxygen atom and capable of electron donation have been used successfully in place of the ether (20), while solvents such as benzene and carbon tetrachloride do not extract uranium from this nitrate system (21). Neptunyl and plutonyl nitrates behave very similar to uranyl nitrates (21) while americium can also be extracted from a nitrate solution (22).

Gold, cerium and thorium nitrates are extracted to a considerable degree by ether. Separation of thorium



from lanthanum employing various organic solvents and salting-out agents has been reported by Bock and Bock (18). They constructed a table indicating the extractability by diethyl ether of many metal nitrates which were dissolved in 8.0 molar nitric acid. Separations have been reported for rare earth nitrates from one another and for thorium from neodymium (11,23-29) by solvent extraction of a nitric acid system containing these salts with a wide variety of immiscible organic compounds. Warf (30) stated that ceric nitrate could be quantitatively extracted into tributyl phosphate while employing a strong nitric acid aqueous medium and that appreciable back extraction into an aqueous phase occurred only if the valence of the metal ion was reduced to three.

Scadden and Ballou (31) reported separating zirconium and niobium from radioactive products when employing a nitric acid solution of the oxalates as the aqueous phase and a 0.6 molar solution of di-n-butyl phosphoric acid in dibutyl ether as the organic phase. When the concentration of di-n-butyl phosphoric acid was decreased to 0.06 molar separation of niobium from zirconium was reported. Partial separation of niobium and tantalum was also reported in this system. The separation of hafnium and zirconium has also been accomplished when employing the nitrate system (12,32-35).

The chloride systems have probably found greatest application in solvent extraction. Extraction of ferric chloride with ethers, first proposed by Rothe in 1892, has been studied by many investigators (36). This system affords a method of separating ferric iron from ferrous iron and beryllium (37). Edwards and Voigt (38) reported antimony with a valence of five preferred isopropyl ether to a much greater degree than trivalent antimony when these two species were present in an 8.0 molar hydrochloric acid medium. Gallium and thallium trichloride are very soluble in isopropyl ether while the corresponding salts of aluminum and indium do not extract to any appreciable extent (39). Gold chlorides are easily extracted from dilute hydrochloric acid into various esters (40) while protoactinium can be separated from uranium, manganese, zirconium or titanium when employing a 6.0 molar hydrochloric acid solution and extracting into dichlorodiethyl ether (41). It has been reported that polonium can be separated from lead and bismuth by extracting a 6.0 molar hydrochloric acid solution containing these salts with a 20 per cent solution of tributyl phosphate in dibutyl ether (41). Garwin and Hixon (42) separated cobalt from nickel in a chloride solution by adding calcium chloride to the aqueous phase and extracting with 2-octanol. Morrison and Taylor (43) reported that molybdenum chloride

can be extracted from a chloride solution. Studies have also been reported on the extraction of pentavalent vanadium (44) and antimony (45) from a chloride solution. Niobium was found to be extracted quantitatively from a strong hydrochloric acid solution while the transfer of tantalum was negligible when methyldioctylamine was present (46). The possibility of extracting and separating the rare earth chlorides by solvent extraction has also been investigated (47).

The extraction of iron into ether is decreased considerably by replacing hydrochloric acid with hydrobromic acid. On the other hand, indium can be completely extracted from bromide solution while the extraction of copper and trivalent thallium is also increased (48) in presence of bromide. The extraction of bromoauric acid is much better than the corresponding chloride compound (49). At low hydrobromic acid concentration only osmium of the platinum metals can be extracted into isopropyl ether.

Solvent extraction employing fluoride solutions are almost exclusively limited to applications involving the separation of niobium and tantalum. Wilhelm, Kerrigan and Cass (50) reported many organic solvents that preferentially extract tantalum from a hydrofluoric acid solution of niobium and tantalum. Stevenson and Hicks (51) employed di-isopropyl ketone to preferentially extract tantalum from niobium when

these two salts were present in an aqueous phase containing combinations of hydrofluoric acid with other mineral acids.

Thiocyanates which form complexes with many cations are quite useful in solvent extraction. Fischer and Bock have reported an extensive study on the extraction of thiocyanates (52) by organic solvents. They are being employed industrially for separation of hafnium and zirconium (53-61). Iron, tetravalent uranium, bismuth, rhenium, cobalt, tungsten and molybdenum can be extracted into alcohols, ethers and esters when excess thiocyanate is present in the aqueous phase (62). Cobalt thiocyanate at a pH of 1.0 to 4.5 is quite soluble in a mixture of acetylacetone and isoamyl alcohol (63). Cobalt, nickel and copper thiocyanates in the presence of pyridine yield complexes which can be extracted by chloroform (64). A detailed study for extracting iron thiocyanate into tributyl phosphate was reported by Melnick and Freiser (65). While extracting a mixture of lanthanum and neodymium thiocyanates into butyl alcohol Appleton and Selwood (66) obtained a separation factor of only 1.06.

The use of inorganic perchlorates or perchloric acid media has been very limited in solvent extraction studies. Willard and Smith (67) separated potassium from a mixture of alkali metal perchlorates by extraction into organic solvents. The separation of zirconium from hafnium has been

reported while employing a perchloric acid solution of these salts as the aqueous phase (68-71).

Addition of organic reagents to the aqueous or organic phases to complex the inorganic salts and increase their extraction and separation has been reported by many investigators (16,62). Perhaps the most widely employed complexing agent of this type is dithizone (diphenylthiocarbanzone) although oxine, 1,3 diketones and cupferron (72) have also found wide application in solvent extraction studies. Generally these systems, although quite useful for analysis of mixtures, are not practical for the large scale production of pure chemicals.

Although most of the liquid-liquid systems employ an acidic aqueous phase, some purification has been reported in alkali media. Hornig and co-workers (73) when employing a 4.0 molar potassium hydroxide solution as the aqueous phase extracted the permanganate ion almost quantitatively into pyridine while the manganate ion transferred only to a limited extent. Goishi and Libby (74) dissolved separately the ammonium salts of rhenium and technetium and potassium permanganate in 4.0 molar sodium hydroxide. When each solution was extracted by pyridine a considerable difference was reported in the relative distribution coefficients although all favored the organic phase.

It is apparent from these widely diversified results that almost all anions may be employed for separation of some inorganic salts. Unfortunately most of the work has been reported on an empirical basis with few attempts to interpret the results theoretically. Consideration from this viewpoint is very difficult since many variables effect the behavior of almost every system. In the work reported here some of the variables effecting the separation of rare earth nitrates, zirconium-hafnium nitrates, niobium-tantalum fluorides and tantalum-vanadium fluorides are considered. Without doubt the use of liquid-liquid extraction for separating inorganic chemicals has already been a great help in solving many difficult purification, separation and recovery problems.

### III. APPLICATION OF LIQUID-LIQUID EXTRACTION TO THE SEPARATION OF TANTALUM FROM NIOBIUM

#### A. General History of Niobium and Tantalum Separation

In 1801 Hatchett discovered tantalum and niobium (or columbium) in a Connecticut mineral (75). Columbite and tantalite ores, the chief source of these elements, are ordinarily oxides which contain considerable amounts of iron, manganese and titanium. The columbite ores are richer in niobium while tantalite minerals contain more tantalum than niobium. Much of the world's supply of these ores is mined in Australia and Africa. Many minor deposits of these minerals have been located throughout the world.

Recently niobium and tantalum have become very useful in the field of metallurgy. Steels containing niobium or tantalum are very hard and quite chemically resistant. Niobium and tantalum metals resist the action of most acids except hydrofluoric acid. Because of their wide possible industrial applications a cheap method for recovering them from their ores is desired. Many methods have been reported for this recovery and for the separation of the niobium from the tantalum. Generally the procedures have been inadequate for low cost large scale production of pure niobium and tantalum compounds.

Several investigators have reviewed the various methods for separating niobium and tantalum salts up to about 1945 (75-77). The most widely investigated technique entails either fractional crystallization or precipitation. In the method of Marignac (75), niobic and tantalic acids were dissolved in a minimum amount of hydrofluoric acid. After saturating this solution with potassium fluoride, it was partly evaporated and cooled. This resulted in crystallization of potassium fluotantalate,  $K_2TaF_7$ . Further evaporation and cooling also yielded potassium pentafluoniobiate,  $K_2NbOF_5 \cdot H_2O$ . One gram of the tantalum salt dissolves in about 200 grams of water while an equal weight of the niobium compound requires only 12 parts water. Schoeller has devised a method of separating tantalum from niobium by fractionally precipitating their oxalates with tannin (78,79). Tannin precipitates the tantalum complex from a slightly acid solution while an excess of tannin precipitates niobium from a neutral solution. Although this technique has been quite useful as an analytical method for separating these elements it does not appear to be practical on a large scale.

Recent attempts for separating tantalum from niobium by fractional precipitation have been reported. The use of tannin with cinchonine, strychnine or brucine to obtain the separation has been reported (80-82). Repeated



precipitations of a hydrofluoric acid solution of the niobium-tantalum mixture with ferroin yielded pure tantalum (83). Fowler (84) fractionally precipitated tantalum at a pH of from 4.5 to 5 from their oxalic acid solution by slow hydrolysis of urea. After fusing the combined niobium and tantalum oxides with a mixture of potassium or sodium nitrates, chlorides or carbonates and potassium hydrogen phosphate, it was reported that tantalum containing a small amount of niobium could be leached from the residue by a 0.02 normal oxalic acid solution (85). It has also been reported that potassium iodate precipitates tantalum but not niobium (86). Golibersuch and Young (87) produced niobium containing less than 0.2 per cent tantalum by fractionally precipitating niobium from a concentrated sulfuric acid solution while Wernet (88) reported that niobium and tantalum could be separated by crystallizing from a saturated hydrochloric acid solution.

Distillation of niobium and tantalum salts as a method of effecting their separation has been reported by several investigators (89-94). Cuvellez (89) reported that niobium was separated from tantalum by roasting the ore in air at about 800 to 1200 degrees Centigrade with a basic substance which was usually calcium oxide. The residue from this roasting process was heated in a chlorine atmosphere at 800 to 1050 degrees Centigrade for several hours. Under these

conditions 70 to 80 per cent of the niobium was volatilized as the chloride or oxychloride while practically all the tantalum remained in the mixture. It has also been found useful by some investigators to preferentially reduce the niobium oxide with hydrogen before addition of chlorine gas (92-94). Kroll and Bacon observed that much more niobium oxide than tantalum oxide formed a nitride when the mixture of these oxides was treated with ammonia at 600 degrees Centigrade. When chlorine was passed over this partially nitrified mixture at about 500 degrees Centigrade niobium was fractionally distilled. In one test 88 per cent of the niobium oxide and less than 5 per cent of the tantalum oxide were removed as a chloride from a mixture initially composed of 47 per cent niobium oxide and 53 per cent tantalum oxide. Hiskey and co-workers (91) volatilized niobium and tantalum by treating the oxide mixture with a chlorinated hydrocarbon.

Several successful attempts have been reported for separating tantalum and niobium salts by preferential adsorption on cellulose (95,96) or alumina (97). These investigations were carried out on a laboratory or tracer scale. Burstall and co-workers (95,96) charged cellulose with a fluoride solution of niobium and tantalum and then elutriated this with methyl ethyl ketone. The tantalum was quantitatively transferred to the methyl ethyl ketone and

was found to contain as little as 0.10 per cent niobium. Addition of hydrofluoric acid to the eluant was required to remove the niobium from the cellulose. At a pH of 6.4 activated alumina adsorbed all the niobium and some of the tantalum when their oxalate solution was eluted with a solution of ammonium oxalate (97).

Columns charged with ion-exchange resins have been found to be effective in separating tantalum and niobium (98-101). The anion-exchange method employing a mixed hydrochloric-hydrofluoric acid solution of niobium and tantalum indicated that tantalum was preferentially adsorbed (98,99). Elution of their hydrochloric acid solution yielded the opposite trend (100). The niobium and tantalum obtained by these ion-exchange techniques were better than 99 per cent pure relative to each other. Gillis and co-workers (101) recovered 95 per cent of the niobium free of tantalum by one pass of their oxalic acid solution containing about equal weights of the two elements. It is apparent that the preparations of high purity niobium and tantalum on a small scale can be accomplished by employing adsorption and ion-exchange techniques.

The use of liquid-liquid extraction for separating niobium and tantalum has been reported by several investigators. Leddicotte and Moore (46) found that a

solution of methyldioctylamine in xylene extracted about 99 per cent of the niobium and only about 0.8 per cent of the tantalum from an 8.0 molar hydrochloric acid solution. Niobium and tantalum dissolved in nitric acid was not extracted by this organic phase when the acid concentration was as great as 10.6 molar. Scadden and Ballou (31) reported a partial separation of niobium from tantalum by preferentially extracting niobium from a nitric acid solution of their oxalates into a 0.6 molar solution of di-n-propyl phosphoric acid in dibutyl ether. The above liquid-liquid extraction experiments were all carried out at niobium and tantalum concentrations of about one gram or less per liter.

Wilhelm, Kerrigan and Cass (50) reported that many organic solvents were capable of preferentially extracting tantalum from a hydrofluoric acid solution containing high concentrations of niobium and tantalum. Stevenson and Hicks (51) successfully separated tantalum and niobium by the preferential extraction of tantalum into di-isopropyl ketone from their aqueous solution which also contained hydrofluoric acid and another mineral acid. The other mineral acids employed with the hydrofluoric were hydrochloric, sulfuric, perchloric and nitric. The hydrochloric acid was reported to be most useful. The additions of these acids to the system increased the per cent of tantalum transferred to the organic phase although the

relative changes in transfer varied with acid concentration. A niobium-tantalum separation factor of 880 was reported for extracting a nitric-hydrofluoric acid aqueous system. In one extraction series which was equivalent to two stages of extraction the aqueous product phase contained 98 per cent niobium and 2.0 per cent tantalum while the organic phase product was 99.5 per cent tantalum and 0.5 per cent niobium. The yields of the high purity niobium and tantalum were not given. However, all of the extractions of Stevenson and Hicks were carried out on aqueous solutions containing less than 2.5 grams each of tantalum and niobium per liter.

#### B. Experimental Details

Previous work in this Laboratory showed that certain organic solvents would preferentially extract tantalum from a hydrofluoric acid solution of tantalum and niobium (50). Although an excess of hydrofluoric acid was always employed in this early work, the effects of varying the concentration of niobium, tantalum and hydrofluoric acid on the extraction were not generally studied. Consequently in the present study several series of tests were carried out in which the effects of variable extraction conditions were investigated. A series of single stage and multistage extractions employing constant aqueous phase conditions was carried out to

determine the effect of the composition of organic phase. Similarly for a constant organic phase extractions were carried out for varying aqueous phase conditions. Since the solutions of niobium and tantalum containing free hydrofluoric acid react with glass, other systems were investigated. It was found that the addition of certain amines to the hydrofluoric acid solution of niobium and tantalum permits the prolonged use of glass equipment for these extraction studies.

Columbite-tantalite ore, mined in South Dakota, was the source of the niobium-tantalum mixture employed for this study. This oxide ore contained the equivalent of about 65 weight per cent of the combined tantalum and niobium pentoxides as well as appreciable amounts of iron, titanium, manganese, aluminum, silicon and tin. It was treated and purified by a caustic fusion followed by sodium hydroxide then nitric or hydrochloric acid leaches of the fusion product. The solid residue containing the niobic and tantalic acids, or earth acids, was then dissolved in aqueous hydrofluoric acid. Addition of concentrated hydrofluoric acid to the freshly prepared earth acids residue resulted in a niobium and tantalum solubility equivalent to about 530 grams of oxide per liter. However, a solution containing the equivalent of only 50 grams of oxide per liter was obtained when the hydrofluoric acid was added

to calcined pentoxides of niobium and tantalum. About six or seven moles of hydrofluoric acid per mole of niobium or tantalum were required to obtain a stable fluoride solution of these elements. The niobium-tantalum fraction in this ore in terms of oxides consisted of about 52 per cent tantalum pentoxide and 48 per cent niobium pentoxide.

One stock solution of the niobium-tantalum-hydrofluoric acid mixture was prepared. Due to the corrosive nature of an acid fluoride solution it was made up and stored in polyethylene containers. Most of the tests were carried out directly on the stock solution or its various water dilutions. The total niobium and tantalum concentration of this stock solution was equivalent to about 517 grams per liter of the combined pentoxides. Based on the average of the molecular weights for niobium and tantalum pentoxides this represents about a 1.45 molar solution. The total acidity or base equivalent of the stock solution was 17.3 moles per liter while its fluoride ion concentration was 15.3 equivalents per liter.

A large number of single and multistage extractions were carried out on this stock solution and its various water and amine solutions. A few single stage extractions were also made on an aqueous potassium hydroxide solution of niobium and tantalum. All the multistage extractions were carried out in the countercurrent multistage extractor

illustrated in Figure 1. The design, assembly and operation of this extractor has been discussed and illustrated by Wilhelm and Foos (7). For the single stage extractions of aqueous solutions containing considerable free hydrofluoric acid polyethylene equipment was employed. However, when this acid concentration was low or amine was present glass equipment was used. Equilibrium in this system is approached quite rapidly so the liquids were mixed vigorously for only about 30 seconds. The equilibrium phases were separated and assayed.

The hydrated oxides (or hydroxides) of niobium and tantalum were precipitated from the organic and aqueous phases by addition of excess ammonium hydroxide. Acetone was usually added to these phases before precipitation to aid in filtering and recovering the niobium and tantalum compounds. After filtering, the hydrated oxides were converted to pentoxides by calcining at 800 degrees Centigrade for at least two hours. These pentoxides were assayed for relative niobium and tantalum content by x-ray fluorescence (102) and spectrographic analysis (103). The first method was employed for mixtures containing between 2.0 and 98 per cent niobium and was accurate to within  $\pm 5$  per cent. The spectrographic methods of Fassel and Krotz (103) was used for samples containing less than 2.0 per cent or more than 98 per cent niobium. The accuracy of the spectrographic



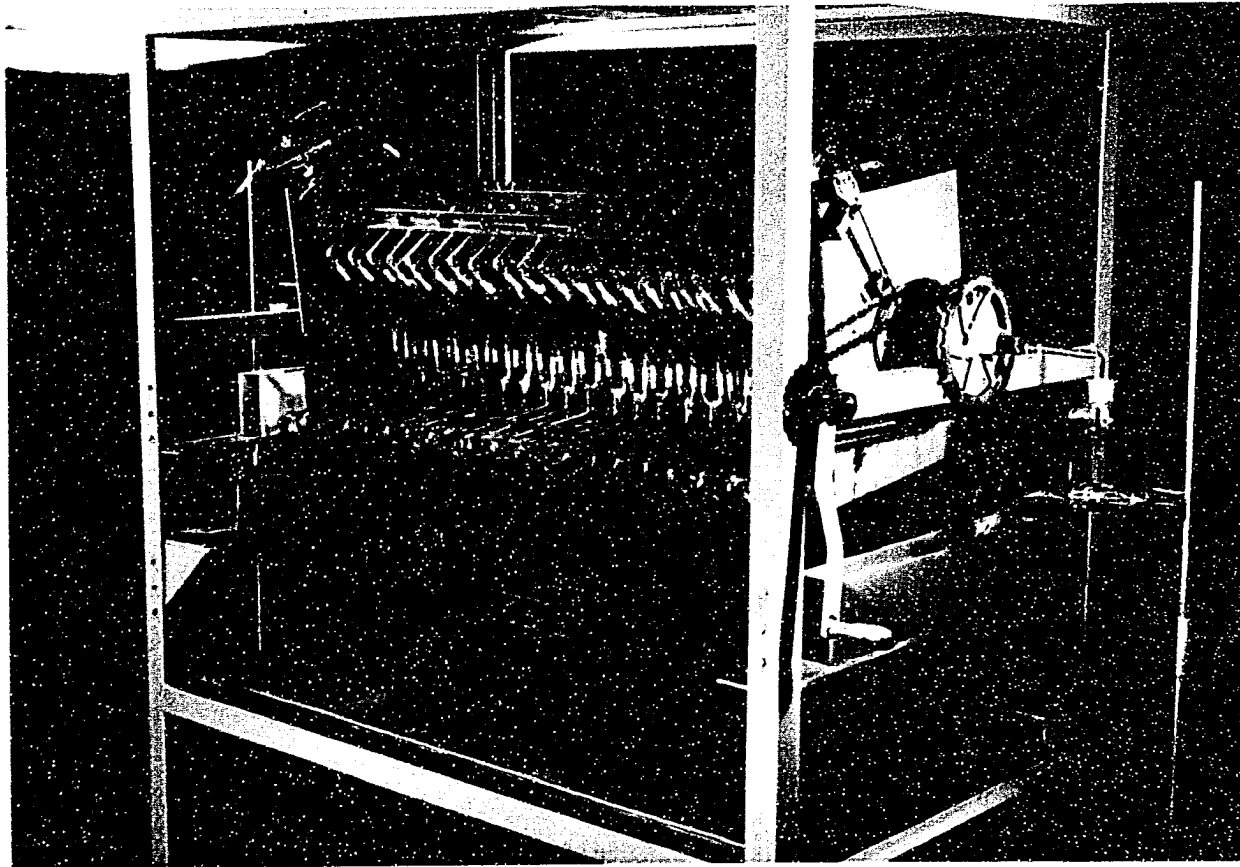


Figure 1 - Twenty Stage Countercurrent Liquid-Liquid Extractor.

methods in these high purity ranges was  $\pm 10$  per cent of the minor constituent. In all of the analytical results only the content of niobium and tantalum is considered. It is assumed that the total percentage of niobium oxide plus tantalum oxide equals 100 per cent. Since a qualitative analysis of the niobium-tantalum fraction which was used in preparing this stock solution showed that it contained only small amounts of impurities these relative percentages should also be fairly accurate on the total oxide weight basis. All qualitative analyses were carried out spectrographically.

Potentiometric titrations of the stock solution and its various water dilutions with sodium hydroxide indicated that at a pH of 9 all the hydrogen ions were replaced by sodium. Consequently the total acidity or base equivalent was determined by a direct acid-base titration using phenolphthalein as the indicator. Although the magnitude of this value may be somewhat connected with the niobium and tantalum content of the solution it gives an indication as to the concentration of hydrofluoric acid in the system. Such data also aid in reproducing extraction conditions. This titration was also employed for determining the total acidity in many of the equilibrium organic phases which had been employed in the extractions.

Determination of the fluoride ion concentration in some of the aqueous and organic phases was also desirable for characterizing these solutions. The procedure developed by Willard and Winter (104) was used for this analysis. The reagent solutions employed were:

- No. 1. About 1.0 gram of zirconyl nitrate dissolved in 250 milliliters of water.
- No. 2. About 1.0 gram of Alizarin red dissolved in 100 milliliters of ethyl alcohol.
- No. 3. Standard thorium nitrate solution.

In carrying out this titration a known volume of a diluted fluoride solution was placed in a test tube. To this fluoride solution was added about two drops of a solution prepared by mixing three parts of solution number 2 with two parts of solution number 1. The pH of this fluoride solution should be about 2 to 4 for obtaining a sharp end point. Standard thorium nitrate was then added dropwise until a permanent pink coloration resulted. If the fluoride solution was not dilute the thorium fluoride precipitate masks the color and obscures the end point.

This titration for the fluoride ion concentration was employed for many of the aqueous and organic phases containing niobium and tantalum. Ethyl alcohol instead of water, was used as a diluent for the organic phases. The fluoride ion concentration obtained by this titration for niobium-tantalum hydrofluoric acid solutions was always

slightly lower than the corresponding value for total acidity. It is believed that this value for the fluoride ion concentration is another variable whereby the conditions in any hydrofluoric acid solution of niobium and tantalum can be reproduced.

### C. Results and Discussion

#### 1. Processing columbite-tantalite ore (105)

A laboratory scale procedure developed in the Ames Laboratory for processing this particular South Dakota columbite-tantalite ore to obtain its niobium-tantalum fraction employs for each batch about 10.0 grams of the finely ground ore. A caustic mixture consisting of 8.0 grams of sodium hydroxide and 4.0 grams of sodium peroxide is heated for 30 minutes at 650 degrees Centigrade in the presence of this ore. After cooling, the fusion product is leached with about 300 milliliters of hot 1.0 molar sodium hydroxide. The solution from this basic leach which contains primarily aluminum, tin, manganese and silicon is filtered and discarded. The residue is next leached with a hot solution of about 200 milliliters of 5.0 molar nitric acid containing a trace of hydrogen peroxide. The solution from this acid leach which contains primarily iron and manganese is filtered and discarded. A minimum amount of concentrated hydrofluoric acid is added to the residue to dissolve the

earth acids. It requires about 5.0 milliliters of the concentrated hydrofluoric acid to form a stable solution of the niobium and tantalum from the ore employed. The solution is recovered from the unreacted ore by decantation or filtration.

Table 1 indicates the weights of each fraction as oxides obtained from processing 10.0 grams of this columbite-tantalite ore.

Table 1

Weights of Various Fractions from Processing 10.0 Grams of a Columbite-Tantalite Ore

Fraction	Weight of oxide
1. Soluble in NaOH leach (ppt. with $\text{HNO}_3\text{-NH}_4\text{OH}$ )	= 1.57 g.
2. Soluble in $\text{HNO}_3 + \text{H}_2\text{O}_2$ leach (ppt. with $\text{NH}_4\text{OH}$ )	= 1.60 g.
3. Soluble in HF leach (ppt. with $\text{NH}_4\text{OH}$ )	= 7.13 g.
4. Insoluble unreacted ore	= 0.32 g.
Total	<u>10.62 g.</u>

Some work to be described later was carried out with a potassium hydroxide solution of niobium and tantalum. This solution which contained an equivalent of 65 grams of combined oxides per liter was prepared by dissolving the earth acids obtained in step 2 of Table 1 in about two molar potassium hydroxide.

A qualitative analysis of the niobium-tantalum oxide fraction which was precipitated from the hydrofluoric acid solution with ammonium hydroxide indicated strong amounts of niobium and tantalum, weak amounts of silicon, tin, and titanium, very weak amounts of aluminum, iron and manganese and a trace of sodium. It can be seen from Table 1 that the ore used for this example contained about 67 per cent of the total as niobium and tantalum oxides. As reported above about 52 per cent of this fraction was tantalum oxide and about 48 per cent niobium oxide.

## 2. Single stage extractions

(a) Extraction of the stock solution or its water dilutions. A large number of single stage extractions were carried out employing the previously described stock solution or its various water dilution as the aqueous feed. All of these extractions employed equal volumes of the initial aqueous and organic phases. The data for these extractions which appear in Table 2 are classified according to the general class of organic solvent. Each organic class is subdivided alphabetically into its various compounds. The data for extraction with the mixed organic solvents are given in the last section of Table 2. For each single stage extraction the data include the composition of the organic phase, the per cent stock solution as aqueous feed, the

Table 2

Single Stage Extractions of the Aqueous Stock Solution or Its Water  
Dilutions by Various Organic Solvents

Ext. no.	Organic phase	Aq. feed		Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb Sepn. factor	% total oxide weight in org.	% total $Ta_2O_5$ in org.
		% Stock soln.	% Aq.	% $Ta_2O_5$ Aq.	% $Ta_2O_5$ Org.					
A. Alcohols										
1.	Amyl alcohol(n)	22	27.7	95.8	1.67	0.0283	59	37.1	68.4	
2.	Amyl alcohol(iso)	22	24.0	96.6	2.12	0.0234	91	38.1	70.9	
3.	Amyl alcohol(tert)	22	11.4	84.8	4.66	0.107	44	56.5	92.1	
4.	Benzyl alcohol	22	40.5	97.5	0.638	0.0114	56	24.5	45.9	
5.	Butyl alcohol(n)	22	14.3	91.1	4.48	0.0727	62	50.3	88.3	
6.	Butyl alcohol(iso)	22	16.4	91.4	3.90	0.0721	54	47.7	84.0	
7.	Butyl alcohol(sec)	22	29.9	59.9	2.05	0.586	3.5	84.5	97.7	
8.	Di-isobutyl carbinol	22	51.5	98.7	0.164	0.00235	70	8.1	15.4	
9.	Heptanol-3	22	34.3	98.5	1.09	0.00845	129	29.5	55.9	
10.	Methyl amyl carbinol	22	22.5	98.3	2.42	0.0119	203	39.0	73.8	
11.	Methyl n-hexyl carbinol	22	31.3	98.6	1.30	0.00822	158	29.2	55.3	
12.	Methyl propyl carbinol	22	15.8	95.8	4.08	0.0340	120	45.4	83.7	
13.	Octyl alcohol(iso)	22	44.9	98.3	0.371	0.00534	70	18.7	35.3	
14.	Oleyl alcohol	22	53.5	87.7	0.107	0.0175	6.2	5.9	10.0	
15.	Pentanol-27*	100	15.2	89.5	3.86	0.810	48	50.6	87.0	

\*A mixture of isomeric amyl alcohols with the primary alcohols composing about 70 per cent.

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed	Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb Sepn. factor	% total oxide weight in org.	% total $Ta_2O_5$ in org.
		% Stock soln.	% $Ta_2O_5$ Aq.	% Org.					
B. Aldehydes									
16.	Butyraldehyde (n)	100	42.0	98.6	0.607	0.00635	96	20.6	39.0
17.	Butyraldehyde (n)	25	42.9	99.7	0.530	0.00114	465	17.6	33.7
18.	Crotonaldehyde	25	10.3	95.4	8.89	0.0483	183	48.7	89.5
19.	Furfural	22	14.3	98.4	5.25	0.0147	358	45.6	86.3
20.	Heptaldehyde	25	53.5	I.S.	-	-	-	0.62	-
21.	Paraldehyde	25	49.5	98.4	0.237	0.00373	64	8.6	16.3
C. Amines									
22.	Aniline	22	15.9	66.7	11.3	1.06	11	73.5	94.4
23.	Phenyl ethyl ethanolamine	22	48.8	81.0	0.647	0.145	4.5	20.9	32.5
24.	Toluidine (meta)	22	13.9	59.8	31.6	3.44	9.2	88.7	102
25.	Toluidine (ortho)	22	15.2	70.1	11.3	0.865	13.1	70.1	94.6
26.	O-Tolyl propanolamine	22	16.8	75.3	7.25	0.480	15	62.7	90.6
D. Esters									
27.	Benzyl acetate	22	53.5	-	-	-	-	0	0
28.	n-Butyl d-tartrate	22	39.1	98.1	0.686	0.00856	80	26.2	49.3
29.	Diethyl carbonate	22	53.5	99.5	0.0123	0.0000906	136	0.63	1.21
30.	Diethyl oxalate	22	51.5	99.6	0.177	0.000557	210	5.48	10.5

I.S. = Insufficient sample.



Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed		Equil. anal.		K <sub>Ta</sub>	K <sub>Nb</sub>	Ta-Nb Sepn. factor	%	%
		% stock soln.	% Ta <sub>2</sub> O <sub>5</sub>	Aq.	Org.				total oxide weight in org.	total Ta <sub>2</sub> O <sub>5</sub> in org?
D. Esters (Continued)										
31.	Diethyl phthalate	22	52.5	99.4	0.0922	0.000557	160		5.10	9.82
32.	Ethyl acetoacetate	100	9.64	90.4	6.18	0.126	49		58.3	101
33.	Ethyl acetoacetate	50	12.4	94.7	5.71	0.0452	127		48.2	87.7
34.	Ethyl acetoacetate	22	19.6	97.1	3.52	0.0261	135		42.9	79.7
35.	Ethyl salicylate	22	53.9	-	-	-	-		0	0
36.	Methyl benzoate	22	53.5	I.S.	-	-	-		1.03	-
37.	Tributyl citrate	22	53.5	97.7	0.0440	0.00119	37		2.46	4.63
38.	Triethyl citrate	22	21.9	99.2	2.48	0.00535	464		38.1	72.7
39.	Tripropyl citrate	22	49.7	94.7	0.237	0.0131	18.1		11.7	21.3
E. Ethers										
40.	Dibutyl ether	22	53.6	-	-	-	-		0	0
41.	Diethyl ether	100	6.24	96.4	11.2	0.0282	398		49.8	92.3
42.	Diethyl ether	22	44.8	98.7	0.426	0.00472	91		14.3	27.1
43.	Di-isopropyl ether	22	53.6	I.S.	-	-	-		0.46	-
44.	Diphenyl ether	22	53.5	-	-	-	-		0	0
45.	Methyl phenyl ether	22	53.5	-	-	-	-		0	0
F. Ketones										
46.	Cyclohexanone	22	5.1	97.6	17.0	0.0223	762		50.1	94.0
47.	Diethyl ketone	100	7.24	96.8	8.33	0.0214	390		48.1	89.8

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb Sepn. factor	% total oxide weight in org.	% total $Ta_2O_5$ in org.	
		% Stock soln.	% $Ta_2O_5$ Aq. Org.						
F. Ketones (Continued)									
48.	Diethyl ketone	80	7.06	97.2	9.16	0.0197	465	47.6	88.8
49.	Diethyl ketone	60	10.0	99.0	6.70	0.00766	874	46.4	88.3
50.	Diethyl ketone	40	17.2	99.6	4.04	0.00303	1335	43.6	83.4
51.	Diethyl ketone	20	24.5	99.87	2.52	0.00124	2040	38.3	73.7
52.	Diethyl ketone	10	31.4	99.93	1.61	0.000520	3100	32.6	62.7
53.	Diethyl ketone	5	38.4	99.96	0.9107	0.000205	4475	25.5	50.0
54.	Diethyl ketone	2.5	45.2	contam- ination	-	-	-	17.4	33.5
55.	Di-isobutyl ketone	22	54.6	99.3	0.208	0.000183	113	1.16	2.17
56.	Di-isopropyl ketone	100	26.4	98.8	1.50	0.00728	200	36.2	68.8
57.	Di-isopropyl ketone	22	41.8	99.89	0.504	0.000372	1350	18.4	35.4
58.	Heptanone-2	22	37.0	99.90	0.950	0.000545	1740	27.9	53.7
59.	Heptanone-3	22	48.4	99.90	0.345	0.000336	1030	14.9	28.6
60.	Heptanone-4	22	50.6	99.3	0.258	0.00177	146	12.1	23.2
61.	Isophorone	100	2.90	95.7	22.0	0.0297	740	51.5	95.0
62.	Isophorone	22	4.71	99.3	17.0	0.00565	3000	49.0	93.7
63.	Mesityl oxide	22	8.57	99.8	8.96	0.00215	4180	46.4	93.5
64.	Methyl ethyl ketone	100	12.4	78.3	5.65	0.222	25	62.8	93.2
65.	Methyl ethyl ketone	75	12.4	87.1	6.70	0.141	48	54.4	90.5
66.	Methyl ethyl ketone	50	13.9	88.7	6.49	0.133	49	51.9	88.5

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed		Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb Sepn. factor	% total oxide weight in org.	% total $Ta_2O_5$ in org.
		% stock soln.	% Aq.	% $Ta_2O_5$ Aq.	% $Ta_2O_5$ Org.					
F. Ketones (Continued)										
67.	Methyl ethyl ketone	22	15.9	93.6	6.70	0.0875	77	48.3	87.0	
68.	Methyl n-hexyl ketone	100	30.3	99.1	1.27	0.00492	259	34.1	64.6	
69.	Methyl n-hexyl ketone	22	40.0	99.87	0.645	0.000540	1200	21.2	40.7	
70.	Methyl isobutyl ketone	22	24.0	99.1	1.95	0.00546	657	34.0	64.8	%
71.	Methyl isopropyl ketone	22	24.5	99.7	3.00	0.00304	990	43.7	84.2	
72.	Methyl phenyl ketone	22	30.7	99.4	1.28	0.00335	382	31.1	59.5	
73.	2,4 Pentanedione	22	26.8	98.2	2.56	0.0177	145	36.3	68.5	
G. Phosphates										
74.	Tributoxyethyl phosphate	22	5.79	95.4	14.7	0.0442	333	51.6	94.8	
75.	Tributyl phosphate	22	1.68	95.4	53.1	0.0438	1200	53.2	97.6	
76.	Tri-2-ethylhexyl phosphate	22	25.9	98.9	2.59	0.0117	222	42.7	81.0	
H. Phosphites										
77.	Di-2-ethylhexyl hydrogen phosphite	22	17.6	94.2	4.46	0.0586	76	48.8	88.4	

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed		Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb Sepn. factor	% total oxide weight in org.	% total Ta <sub>2</sub> O <sub>5</sub> in org.
		% stock soln.	% Aq.	% Ta <sub>2</sub> O <sub>5</sub> Aq.	% Org.					
H. Phosphites (Continued)										
78.	Tri-2-ethylhexyl phosphite	22	29.9	99.7	1.76	0.00204	865	38.5	73.9	
79.	Tri-isooctyl phosphite	22	23.0	98.0	2.84	0.0172	166	45.1	85.0	
I. Miscellaneous										
80.	Carbon disulfide	22	53.5	-	-	-	-	0	0	
81.	Chloroform	22	53.5	-	-	-	-	0	0	
82.	Heptane	22	53.5	-	-	-	-	0	0	
83.	Isoamyl nitrite	22	53.5	-	-	-	-	0	0	
84.	Nitrobenzene	22	53.5	-	-	-	-	0	0	
85.	Trichloroethylene	22	53.5	-	-	-	-	0	0	
86.	Toluene	22	53.5	-	-	-	-	0	0	
J. Mixed Solvents										
87.	40% Acetone + 60% diethyl ketone	22	19.8	98.8	4.63	0.0140	331	41.8	79.5	
88.	25% Acetone + 75% di-isobutyl ketone	22	53.5	99.0	0.0704	0.000816	86	2.75	5.2	
89.	40% Acetone + 60% di-isopropyl ketone	22	37.4	99.7	0.991	0.00655	640	25.6	48.7	

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed		Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb Sepn. factor	% total oxide weight in org.	% total $Ta_2O_5$ in org.
		% stock soln.	% Aq.	% $Ta_2O_5$ Aq.	% Org.					
J. Mixed Solvents (Continued)										
90.	25% Primene 81-T + 75% diethyl ketone**	22	1.51	60.6	288		2.88	100	88.7	103
91.	12.5% Primene 81-T + 87.5% diethyl ketone	22	1.13	83.6	129		0.292	443	65.0	104
92.	5% Primene JM-T + 95% diethyl ketone***	22	13.9	99.1	5.17		0.00750	1210	43.2	82.2
93.	25% Primene JM-T + 75% di-isobutyl ketone	22	2.26	81.3	55.7		0.349	159	65.9	103
94.	25% Primene JM-T + 75% heptane	22	13.9	79.7	8.35		0.342	24	60.8	95.0
95.	5% Primene JM-T + 95% heptane	22	43.7	97.9	0.409		0.0675	61	15.4	28.9

\*\* A technical grade amine mixture of highly branched primary amines having a tertiary alkyl structure with the number of carbon atoms per molecule varying principally from 12 to 15.

\*\*\* A primary amine similar in structure to Primene 81-T while containing essentially 18 to 24 carbon atoms per molecule.

analysis of the pentoxides recovered from the equilibrium organic and aqueous phases, the niobium and tantalum distribution coefficients, the tantalum-niobium separation factor, the mass transfer as oxide to the organic phase, and the per cent of total tantalum as oxide transferred to the organic phase. The per cent stock solution as the aqueous phase refers to its dilution with water. As an example the 22 per cent stock solution aqueous phase means that 22 milliliters of the stock solution was diluted to 100 milliliters with water and then employed as the aqueous feed. It should be emphasized that in these data the niobium and tantalum oxide are assumed equal to 100 per cent. Errors in sample preparation and analyses probably explain why the data for three of the extractions showed slightly more than 100 per cent of the tantalum oxide to be recovered from the equilibrium organic phase. Appendix A contains the sources of many of the organic compounds used in these studies.

The organic solvents employed for these niobium-tantalum extractions are listed in Table 2 and include alcohols, aldehydes, amines, esters, ethers, hydrocarbons, halogenated hydrocarbons, ketones, organic phosphates, organic phosphites, mixed organic solvents and a few miscellaneous compounds. In all cases whenever there was transfer to the organic phase a considerable preference for tantalum was

evident. This investigation showed that a great number of common water-immiscible organic compounds separate tantalum from niobium when these elements are together in a hydrofluoric acid solution.

As a general class the ketones appeared to be the most effective organic compounds for extracting pure tantalum and obtaining high tantalum-niobium separation factors. The data for the ketone extractions of the 22 per cent stock solution indicate that some of them extract appreciable quantities of high purity tantalum. Mesityl oxide, isophorone and cyclohexanone in one contact of this aqueous phase extracted about 94 per cent of the total tantalum. The amounts of niobium oxide in this tantalum as oxide were 0.2, 0.7 and 2.4 per cent respectively while the calculated tantalum-niobium separation factors were 4180, 3000 and 726, respectively for these organic liquids. It is apparent from these data that a two or three stage extraction process employing these solvents would yield quite pure tantalum and niobium with high recoveries of each.

Many other ketones extracted purer tantalum from the 22 per cent stock solution than was extracted by these three ketones. Although the purities were greater the quantities of tantalum extracted were less. Heptanone-2 and heptanone-3 extracted about 54 and 29 per cent respectively

of the total tantalum with a purity of 99.90 per cent. Di-isopropyl ketone extracted 35 per cent of the tantalum with a purity of 99.89 per cent tantalum oxide in the recovered oxide. About 74 per cent of the tantalum with a recovered oxide purity of 99.87 per cent was extracted by diethyl ketone while 84 per cent of the tantalum giving an oxide purity of 99.7 per cent was transferred into methyl isopropyl ketone. Methyl n-hexyl, methyl isobutyl (hexone) and methyl phenyl ketone (acetophenone) extracted 41, 65 and 60 per cent of the total tantalum respectively with recovered oxide purities of 99.1, 99.87 and 99.4 per cent tantalum oxide. Di-isobutyl ketone and heptanone-4 also extracted tantalum containing less than 1.0 per cent niobium although in small amounts. As is apparent from Table 2 the only ketones which did not extract tantalum with an oxide purity of 99 per cent or better from the 22 per cent aqueous stock solution was methyl ethyl ketone, 2,4 pentanedione and cyclohexanone.

Comparison of the data for the ketones above indicate that certain molecular structure features of an organic compound affects its extraction behavior. As a general rule the lower molecular weight ketones in a homologous series transferred more tantalum. The purity of the recovered oxides was as good or better than the higher members of the series. From the data for methyl ethyl, methyl isopropyl, methyl isobutyl, methyl amyl and methyl n-hexyl ketone it



is evident that the tantalum and niobium distribution coefficients and per cent mass transfers decreased with increased molecular weight of the organic. The purity of the recoverable tantalum in the organic phase remained above 99 per cent and the tantalum-niobium separation factor above 600 for all of these organic compounds except methyl ethyl ketone. Comparison of the data for dipropyl ketone (heptanone-4) and di-isopropyl ketone would indicate that the branched chain improves mass transfer and separation factor. The data for the 2, 3 and 4 heptanones indicate that as the keto group approaches the end of the chain the mass transfers and separation factors increase. The effect of unsaturation is illustrated by comparing the extractability of the tantalum by mesityl oxide (methyl isobutylene ketone) and methyl isobutyl ketone. It is apparent that in the presence of this double bond structure the amount and purity of the tantalum transferred to the organic phase were increased.

The data in Table 2 indicate further that a few pure organic solvents other than ketones extracted tantalum containing less than one per cent niobium from an approximately 22 per cent stock solution. These organic compounds were diethyl carbonate, diethyl oxalate, diethyl phthalate, triethyl citrate, tri-2-ethylhexyl phosphite and n-butyraldehyde. However the first three of these compounds each

extracted less than 11 per cent of the total tantalum. The last three of these organic liquids extracted 73, 74 and 34 per cent respectively and it is apparent that only these compounds compared favorably with most of the ketones for obtaining high purity tantalum in high yields.

The alcohols as a general class of organic compounds yielded separation factor, distribution coefficient and mass transfer data which indicated that they could be employed effectively for separating niobium and tantalum. Generally the separation factors varied from 50 to 200 while appreciable material was extracted by the organic phase. In most cases the same general trends in regard to structure and size of the alcohol molecule were observed as reported for the ketones. As the position of the hydroxy group in secondary alcohols approached the end of the molecule the tantalum-niobium separation factor and mass transfer increased. Secondary alcohols appeared to give better results than primary alcohols except for sec-butyl alcohol which was quite soluble in this aqueous phase. A comparison of the data for corresponding alcohols and ketones indicates that the alcohols gives somewhat greater mass transfers to the organic phase and considerably lower tantalum-niobium separation factors.

The few aldehydes that were used to extract this diluted stock solution indicated in general a fairly good separation

of tantalum from niobium. Crotonaldehyde which has the same formula as butyraldehyde except for a carbon to carbon double bond in the 2, 3 position extracted more tantalum but of lower purity than butyraldehyde. In light of the data for the heptanones it might be expected that butyraldehyde with a carbonyl group at the end of the molecule would yield a high mass transfer and a high tantalum-niobium separation factor. However, it extracted a relatively small amount of high purity tantalum. Commercial grade furfural yielded a tantalum-niobium separation factor and mass transfer which would work very efficiently in a large scale multi-stage extraction process.

The esters with the exception of n-butyl d-tartrate, ethyl acetoacetate and triethyl citrate extracted less than 12 per cent of the material from the 22 per cent stock solution. Benzyl acetate and ethyl salicylate failed to extract any detectable tantalum or niobium. Comparison of the data for tributyl, tripropyl and triethyl citrate indicated that the shorter the alkyl group the higher the mass transfer and separation factor. In general most of the esters do not appear practical for separating niobium and tantalum on a large scale.

Only diethyl ether of the ether organic class that was tested extracted appreciable quantities of material from the diluted stock solutions. Most of the ethers appear not

to extract any niobium or tantalum although alcohols and ketones with a similar number of carbon atoms extract appreciable amounts. No reason is known for this somewhat anomalous behavior.

Of all the organic compounds tested the water-immiscible amines generally transferred the most material to the organic phase. It is assumed that the amine salts of the fluo-tantallic and fluoniobic acid are formed and extracted. Although the mass transfer was high the separation factors were low. It is evident from the data that for the amines tested the highest tantalum-niobium separation factor was 15 while as much as 89 per cent of the material expressed as oxides was transferred to the organic phase. Although these amines do not appear practical for the separation of niobium from tantalum in a hydrofluoric acid solution they might be useful for purifying niobium-tantalum mixtures by extracting them completely into the organic phase and away from other impurities.

The organic phosphates and phosphites extracted appreciable quantities of niobium and tantalum from the dilute aqueous stock solution. A comparison of the data for the tri-2-ethylhexyl phosphate and phosphite indicates that the latter gives a much higher separation factor and a higher relative tantalum purity in the equilibrium organic phase. However, the phosphate compound extracts appreciably

more tantalum. Tributyl phosphate gave a very favorable tantalum-niobium separation factor and a favorable mass distribution. In general the organic phosphates and phosphites appear to be quite useful for separating tantalum from niobium from their aqueous hydrofluoric acid solution.

It is apparent from Table 2 that aromatic and aliphatic hydrocarbons as well as chlorinated hydrocarbons do not extract detectable amounts of niobium or tantalum from the diluted stock solution. Carbon disulfide, nitrobenzene and isoamyl nitrite also appeared inert.

The extractions employing mixed organic solvents were carried out in an attempt to combine the favorable properties of the solvents. Since the low molecular weight ketones appeared effective for separating tantalum from niobium, a mixture of acetone and an immiscible low molecular weight ketone was employed for extraction. Unfortunately acetone acted like methyl ethyl ketone by increasing mass transfer to the organic phase while decreasing the tantalum-niobium separation factor and purity of the tantalum.

Since amines were known to increase mass distribution to the organic phase, Primene 81-T and Primene JM-T were added to various organic solvents. In all cases the transfer to the organic phase increased with addition of

the Primenes while the tantalum-niobium separation factors and purity of tantalum decreased. The addition of the Primenes to heptane or di-isobutyl ketone resulted in a considerable amount of transfer to the organic phase with some separation. It is believed that the presence of these amines would cause considerable extraction of tantalum and niobium from their hydrofluoric acid solution by many otherwise inert organic solvents with some separation of tantalum from niobium.

In the above discussion only the effects of organic solvents in extracting tantalum from niobium have been considered. Studies on variations of the aqueous hydrofluoric acid solutions indicated that its composition was very important in obtaining a successful separation process. The single stage data reported in Table 2 for extraction of the stock solution and its various water dilutions illustrate the effect of changing solute concentrations although their relative concentration values remain constant. For the single stage extractions reported in Table 3 the hydrofluoric acid concentration was kept constant while the total concentration of niobium and tantalum was varied. The single stage data in Table 4 indicate the effect of varying the hydrofluoric acid concentration at a constant concentration of niobium and tantalum.

Table 3

Single Stage Extractions of a 12.8 Molar HF Solution of Niobium and Tantalum with Diethyl Ketone

Initial Aq. Phase	Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb Sepn. factor	% total oxide weight in org.
	% $Ta_2O_5$					
	Aq.	Org.				
41	17.0*	73.4	4.28	0.316	14	59.5
66	17.0	77.8	4.02	0.232	17	55.0
205	18.2	85.7	2.75	0.103	27	49.3
256	20.4	93.4	2.47	0.0448	55	47.8
310	19.3	95.5	2.17	0.0245	92	43.3
375	25.0	98.5	1.74	0.00885	197	40.6
506	26.0	99.5	1.63	0.00318	514	38.3

\* Calculated value.

Table 4

Single Stage Extractions of a Niobium-Tantalum-Hydrofluoric Acid Solution Containing the Equivalent of 172 Grams of Oxide Per Liter with Diethyl Ketone

Initial Aq. Phase HF conc. (molar)	Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb Sepn. factor	% total oxide weight in org.
	% $Ta_2O_5$ Aq.	Org.				
4.58	37.0	99.93	0.960	0.000390	2460	26.1
5.50	16.4	99.6	3.48	0.00271	1280	41.0
9.14	15.8	95.8	3.70	0.0302	123	46.0
12.8	18.2	86.5	2.98	0.105	28.4	48.6
14.7	23.5	82.9	2.40	0.153	15.7	53.4
20.2	48.4	62.5	1.12	0.593	1.89	60.4*
23.9	52.5	59.2	0.998	0.757	1.32	72.7*

\*Additional weight probably caused by reaction of HF with containers.



Figure 2 shows the variation of mass transfer with per cent stock solution for extractions with methyl ethyl ketone, diethyl ketone and ethyl acetoacetate. For these organic solvents as well as all the others tested the per cent of material transferred to the organic phase decreased with per cent stock solution. The percentage of the total tantalum extracted by the organic phase showed a similar trend. It is apparent from Figure 2 that as the concentration of the stock solution decreased below 20 per cent the mass transfer to diethyl ketone decreased markedly.

From Figure 3 it can be noted that the material extracted by diethyl ketone contained higher purity tantalum as the per cent stock solution and mass transfer shown in Figure 2 decreased. These dilution effects were observed for all the organic liquids so tested. The greatest rate of change in percentage niobium oxide recovered from the organic phase occurred in the extraction of the 50 to 80 per cent stock solution. The tantalum which was extracted from the 5.0 per cent stock solution by diethyl ketone contained only 360 ppm niobium.

As the per cent stock solution decreased the tantalum-niobium separation factors increased. Figure 4, which shows this relationship, indicates that for an extremely dilute stock solution the separation factors would approach infinity. According to the laws of heterogeneous equilibrium when finite volumes of solutions containing

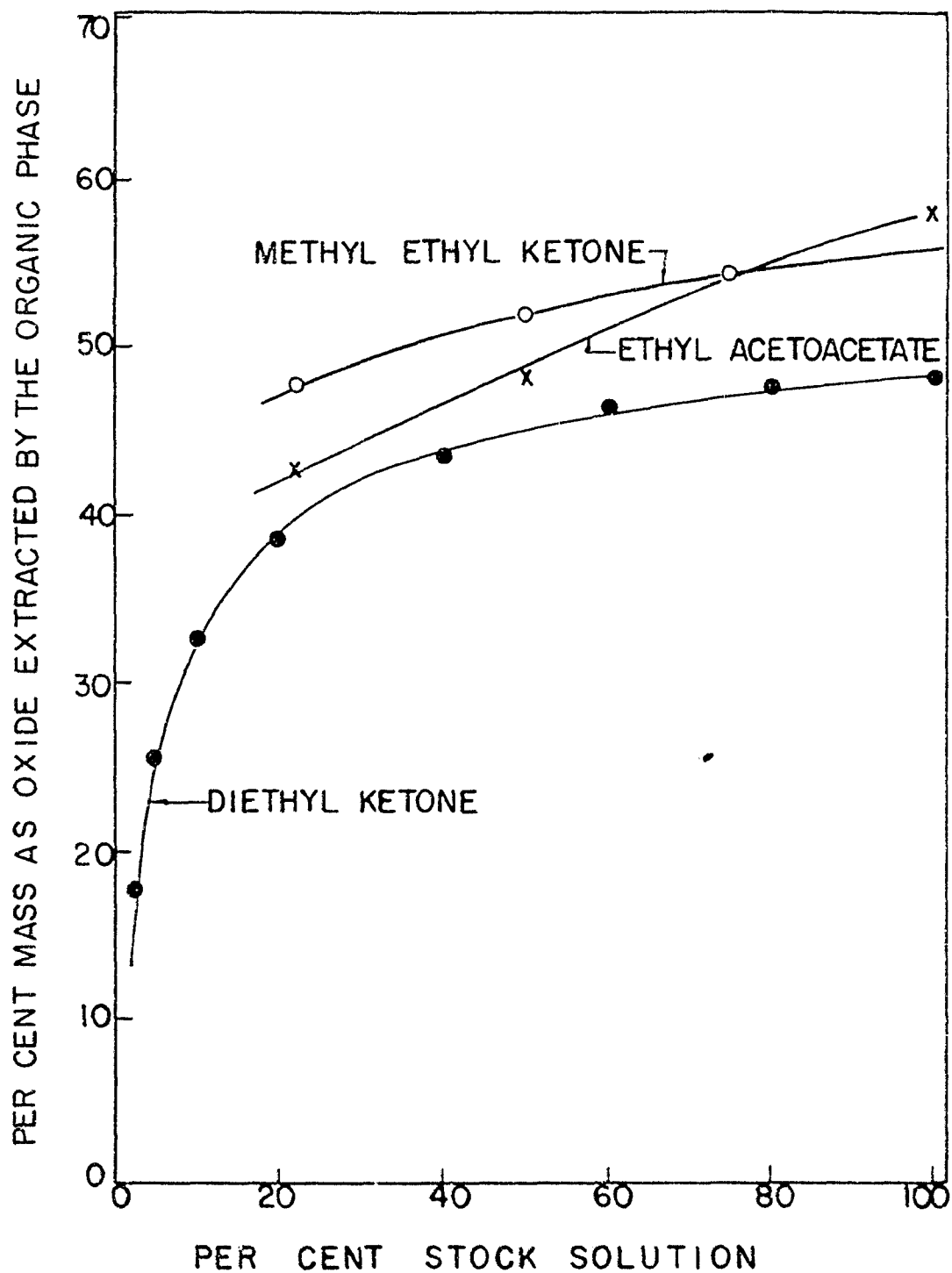


Figure 2 - Extraction of Niobium and Tantalum at Various Water Dilutions of the Stock Solution.

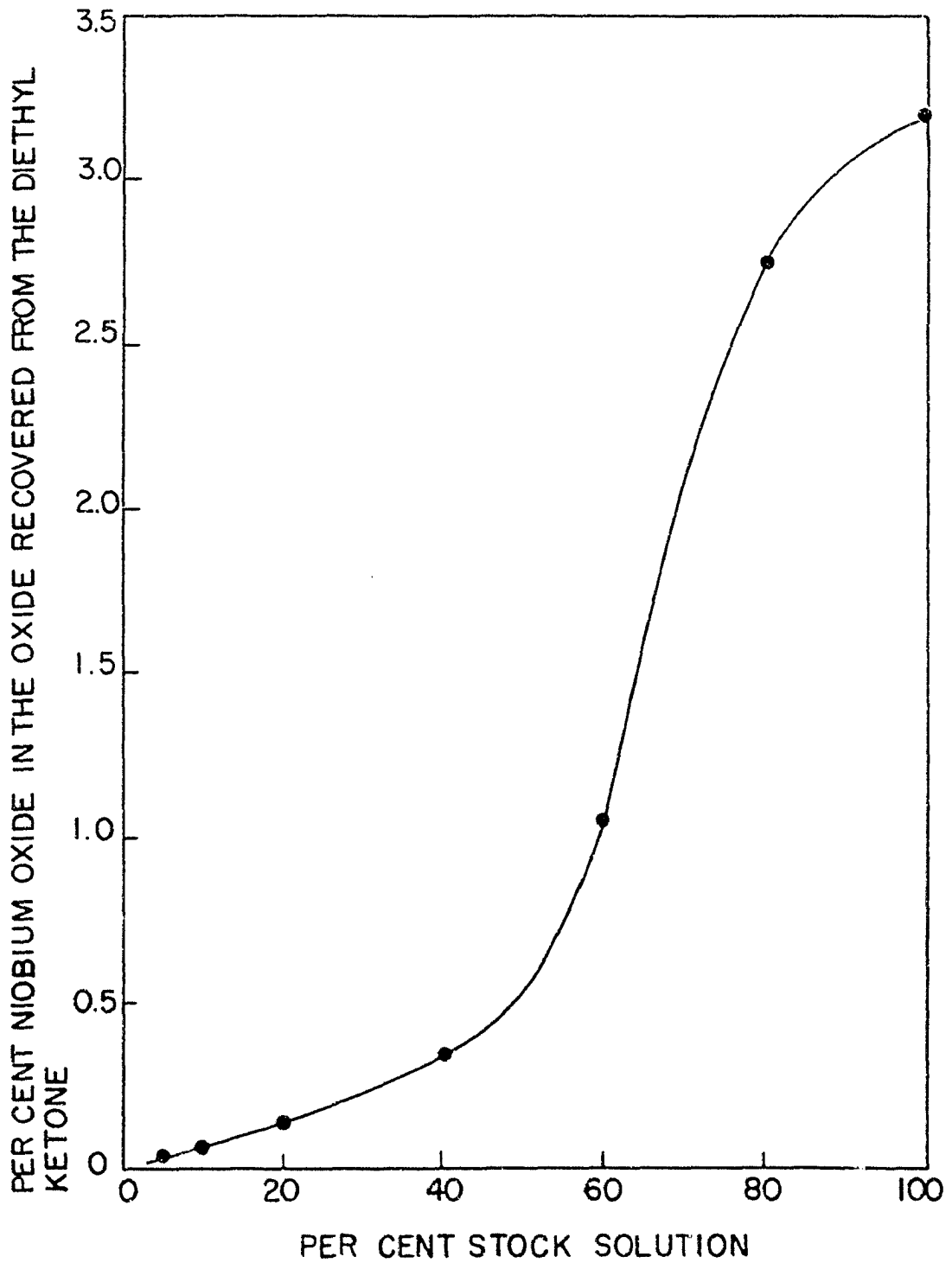


Figure 3 - Composition of the Product from Diethyl Ketone Extractions of Various Dilutions of the Stock Solution.

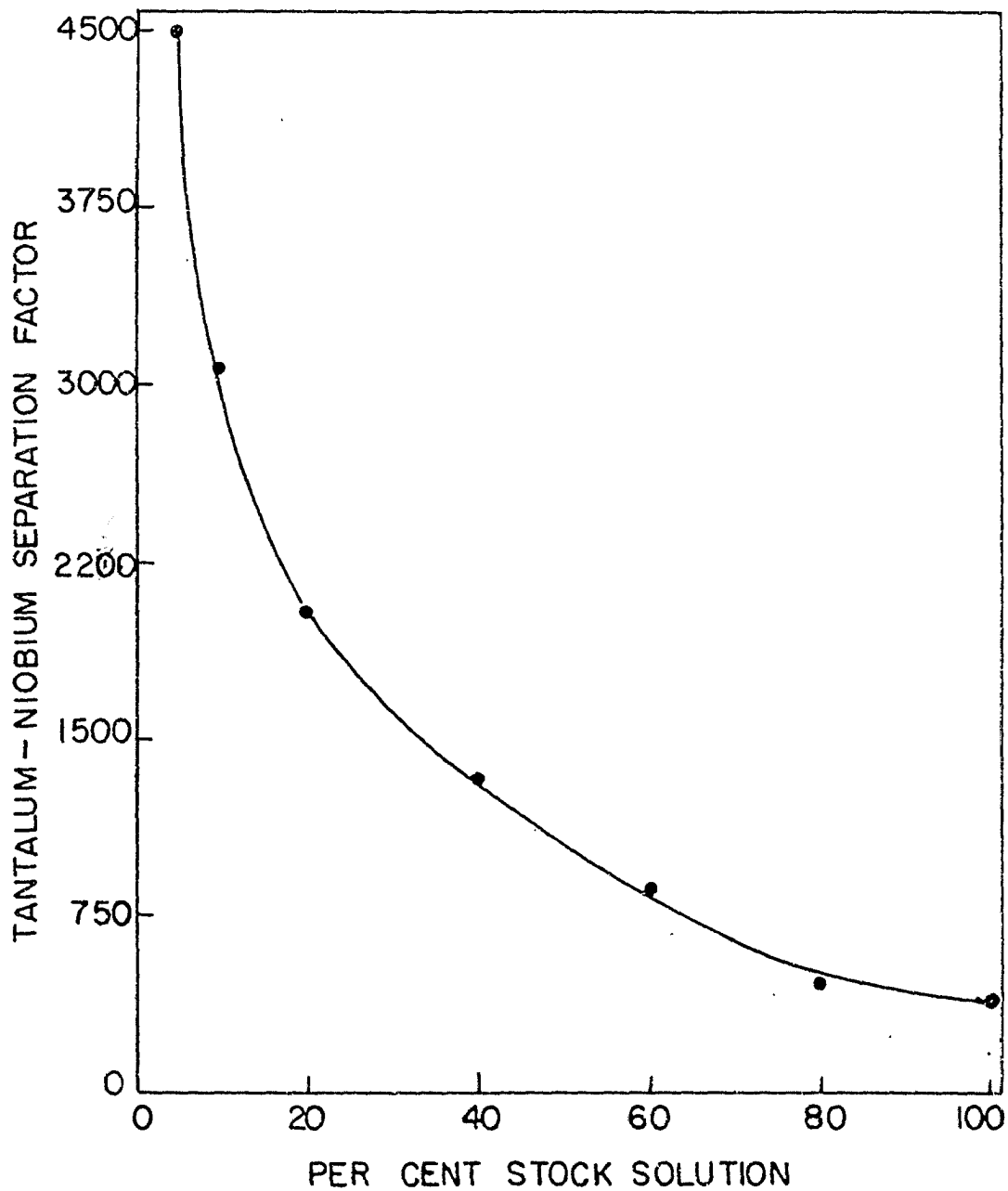


Figure 4 - Tantalum-Niobium Separation Factors for Extracting Various Dilutions of the Stock Solution with Diethyl Ketone.

finite amounts of niobium and tantalum are extracted, then there will be finite amounts of niobium and tantalum in both phases. The equilibrium organic phase could not become free of niobium by a practical extraction process. However the niobium concentration might go below the limit of analytical detection, consequently for practical purposes the product extracted by the diethyl ketone organic phase could approach a purity considered to be free of niobium.

In Figure 5 it is shown that the variation in the tantalum-niobium separation factor with mass transfer for diethyl ketone is linear over the range studied. In light of the above data it is apparent that as the mass transfer approaches zero, or as dilution of the stock solution approaches infinity, the separation factor must become increasingly large. Consequently this variation of separation factor with mass distribution, shown in Figure 5, might not remain linear over the range of low mass transfer not covered in the figure.

Another series of single stage extractions was carried out employing pure diethyl ketone as the organic phase. The aqueous phases were prepared by dissolving various amounts of the mixed hydrated oxides in 12.8 molar hydrofluoric acid. This hydrated oxide mixture was obtained by precipitating various volumes of the stock solution with ammonium hydroxide. The data for these extractions appear in Table 3.

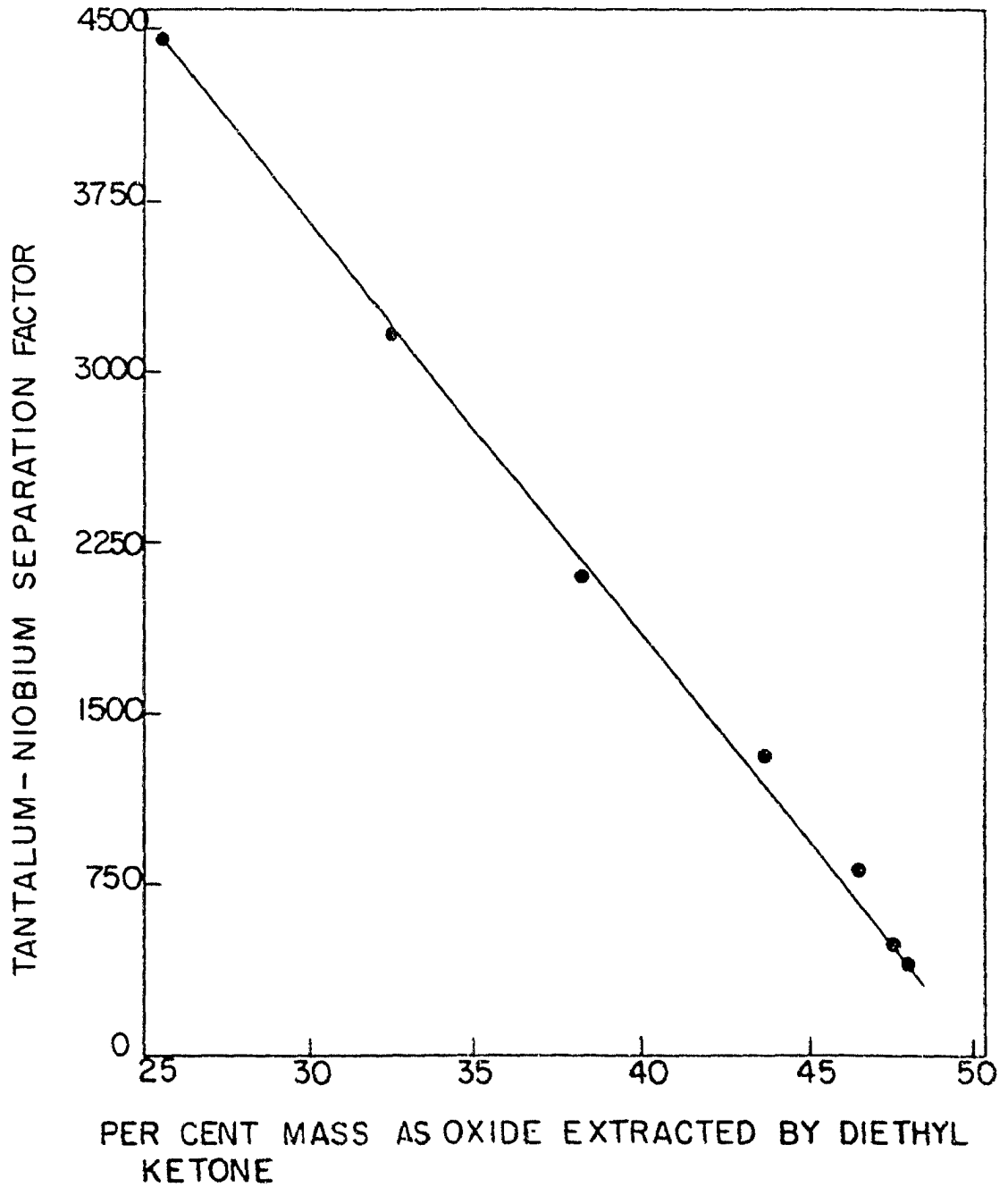


Figure 5 - Tantalum-Niobium Separation Factors at Various Mass Distribution Values.

This variation of mass transfer to the organic phase with concentration of niobium and tantalum in the initial aqueous phase is illustrated graphically in Figure 6 while the relationships between the equivalent oxide concentration in the aqueous and organic phases appear in Figure 7. It is apparent from the data of Table 3 and Figure 6 that an increase in the concentration of niobium and tantalum in the initial aqueous phase resulted in a decrease for per cent mass transfer to the organic phase. However the material which was extracted by the organic phase increased in relative tantalum purity. It can be seen in Table 3 that the distribution coefficients for niobium and tantalum decreased with increasing oxide concentration. It is obvious that the concentration of free hydrofluoric acid in the system decreased as the amounts of niobium and tantalum increased. It appears from these data that the presence of excess free hydrofluoric acid reduces the effectiveness of the separation of tantalum from niobium although increasing their transfer to the organic phase.

This possibility was investigated further by carrying out a series of single stage extractions employing diethyl ketone as the organic phase and an aqueous phase containing 172 grams of combined niobium and tantalum oxides per liter at various hydrofluoric acid concentrations. The data from these extractions appear in Table 4.

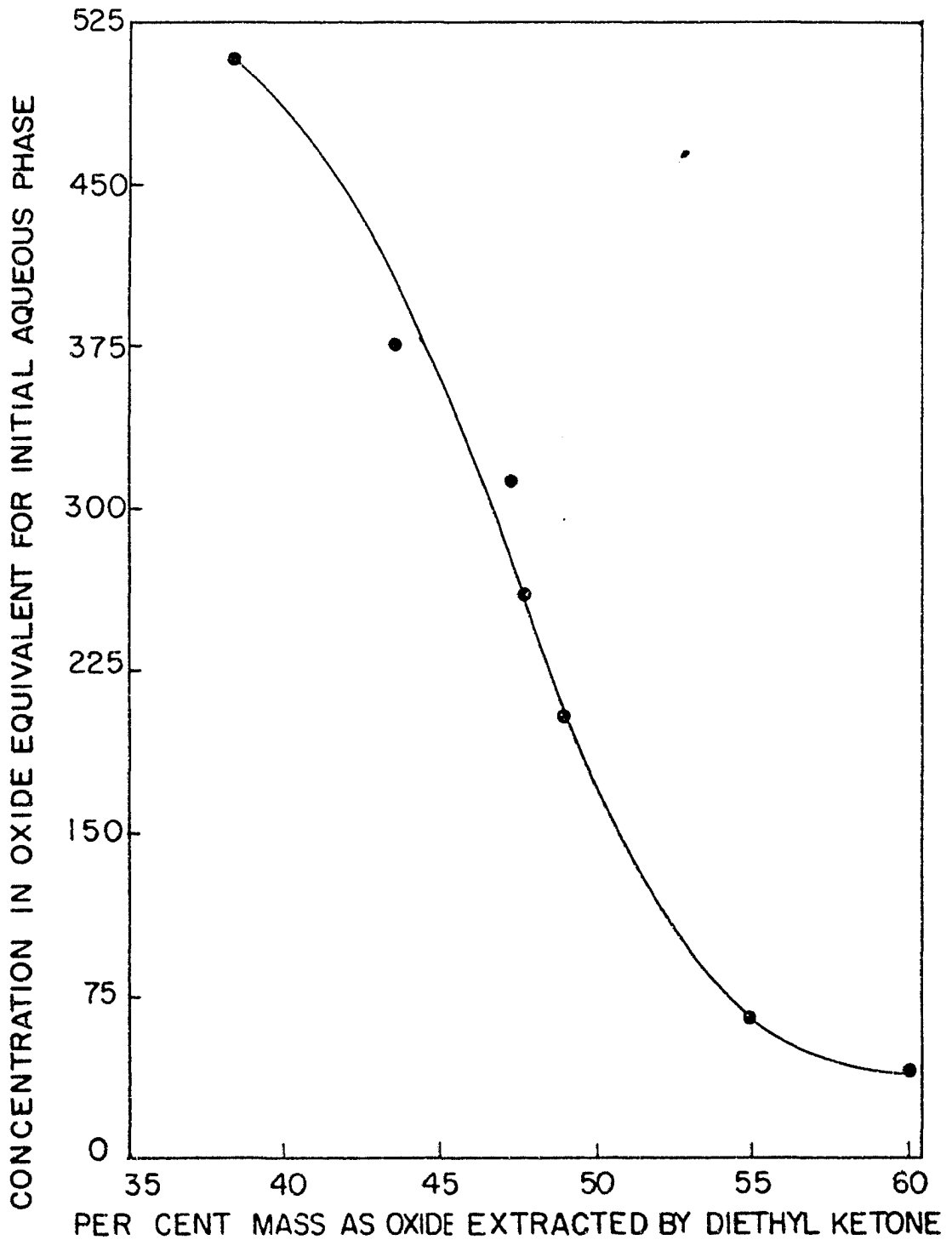
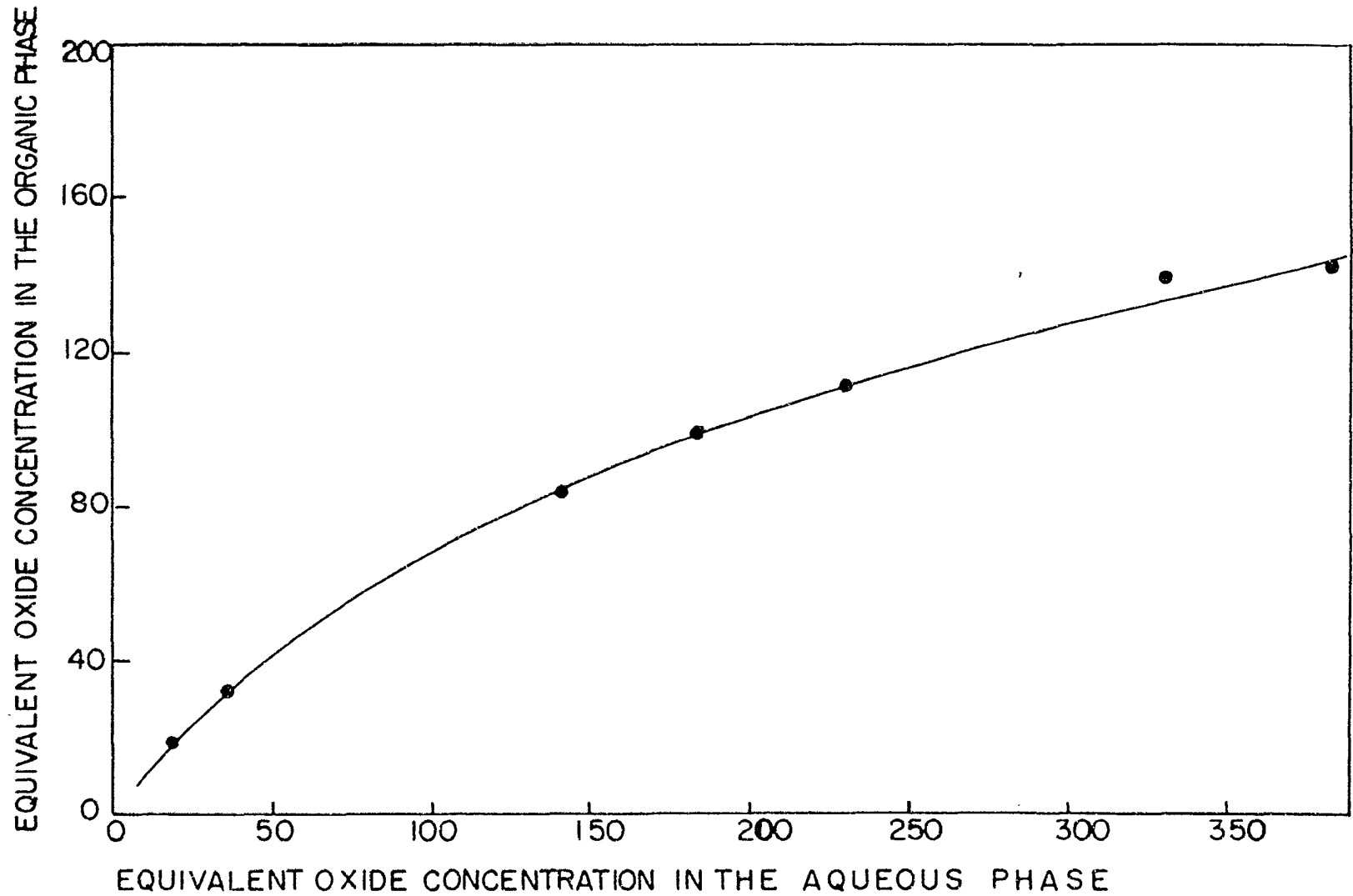


Figure 6 - Effect of Niobium and Tantalum Concentration on Mass Distribution at Constant Fluoride Concentration.





EQUIVALENT OXIDE CONCENTRATION IN THE AQUEOUS PHASE  
Figure 7 - Distribution of the Niobium-Tantalum Mixture between Aqueous Hydrofluoric Acid and Diethyl Ketone.

These data show that the addition of hydrofluoric acid to the system at a constant niobium and tantalum concentration increases the mass transfer to the organic phase while decreasing the tantalum-niobium separation factor. The purity of the tantalum relative to niobium extracted by the organic phase also decreased. The distribution coefficient for niobium gradually increased with hydrofluoric acid concentration while the tantalum distribution values reached a maximum at about 9 molar hydrofluoric acid. This indicates that hydrofluoric acid increases the extractability of niobium by diethyl ketone while decreasing the extractability of tantalum over much of the acid range. This is indicated by the very rapid decrease in the tantalum-niobium separation factors for the addition of hydrofluoric acid. It can be noted in Table 4 that the separation factor was 2460 for the practically saturated solution of earth acids in hydrofluoric acid while for the 23.9 molar acid system the separation factor was only 1.32.

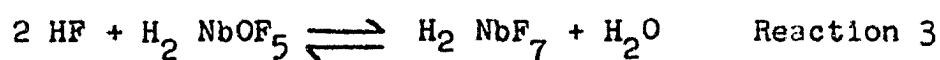
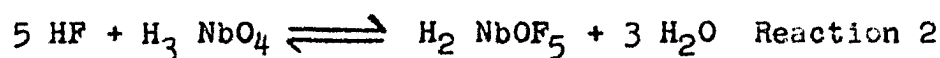
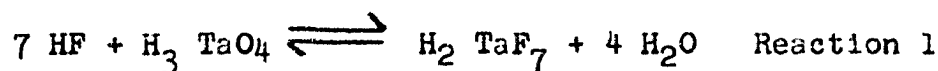
The data in Tables 2, 3 and 4 for the single stage extractions of the hydrofluoric acid solution of niobium and tantalum with diethyl ketone illustrate several important points. Dilution of the stock solution with water did not change the numerical value of the ratio of hydrofluoric acid concentration to niobium plus tantalum concentration. Extractions of these diluted aqueous stock

solutions yielded very pure tantalum in the equilibrium organic phase. The data in Tables 3 and 4 indicate that when this ratio of acid concentration to the niobium plus tantalum concentration increased, the amount of material transferred to the organic phase increased while its tantalum purity decreased. When this ratio was decreased the opposite trends were observed. It appears therefore that the concentration of tantalum, niobium and hydrofluoric acid as well as their ratios are important in determining the purity and amount of tantalum extracted by the organic phase.

For highly preferential extraction of tantalum from niobium when they are together in hydrofluoric acid solution, it appears that the ratio of acid concentration to the niobium and tantalum concentrations should be as low as possible. This means that the earth acids should be dissolved in a minimum amount of hydrofluoric acid. However if a large excess hydrofluoric acid is present a dilution of the aqueous solution with water permits a highly preferential extraction of tantalum from niobium. It is apparent that the amount of hydrofluoric acid, niobium, tantalum and water dilution is determined by the desired purity and recovery of tantalum.

A possible explanation for the lack of preferential extraction of tantalum at high hydrofluoric acid concentrations results from consideration of the probable niobium

and tantalum species in this acid aqueous medium. It has been reported that fluotantalates,  $\text{TaF}_7^-$ , and pentafluoniobates,  $\text{NbOF}_5^-$ , crystallize from a supersaturated fluoride solution. Consequently for nearly saturated solutions of niobium and tantalum it appears reasonable to assume that these species are present in the aqueous phase. The formation of these species by the reaction of hydrofluoric acid with the earth acids probably results according to the over-all reactions 1 and 2. However in the presence of excess hydrofluoric acid it is possible that the product from reaction 2 might tend to undergo a further reaction 3. These reactions are:



It is apparent that the products of reactions 1 and 3 are very similar while the niobium and tantalum salts from reactions 1 and 2 are quite different. It would be expected that the relative extractability of the fluotantalates and the fluoniobates might be similar while for the fluotantalates and the pentafluoniobates it might be different. If this assumption is correct an amount of hydrofluoric acid insufficient to yield appreciable amounts

of reactions 3 should result in a considerable relative difference in niobium and tantalum extractability. Although this approach is very qualitative, it does offer an explanation of the high tantalum-niobium separation factors at low hydrofluoric acid concentrations and low separation factors at high acid concentrations.

(b) Extraction of the amine neutralized stock solution or its water dilutions. A great number of common water-immiscible organic liquids separate tantalum from niobium when these elements are together in a hydrofluoric acid solution. However, this system because of its corrosive nature toward glass and most metals cannot be employed in ordinary equipment for continuous separation work. Therefore, other effective liquid-liquid systems for the separation of niobium from tantalum were developed in an effort to obtain conditions of extractions that would permit prolonged use of glass equipment.

Before these extraction separation studies could be considered, an essentially non-corrosive aqueous solution of niobium and tantalum was required. Consequently various organic amines were added to the 22 per cent stock solution of niobium and tantalum to neutralize the free hydrofluoric acid by forming the amine salt. A great variety of results were obtained. Additions of dibutyl amine, tributyl amine, tertiaryoctyl amine, phenylhydrazine, aminohydroquinone

dimethyl ether or aminohydroquinone diethyl ether caused immediate precipitation. When aniline, m-toluidine or o-toluidine was added to the aqueous phase a second liquid phase appeared at a pH of from 4 to 6 although no precipitation was immediately evident. A partially neutralized aqueous solution containing any one of these three amines was not stable for more than two hours before a precipitate would start to form. However, neutralization by o-tolyl propanolamine to a pH of about 5 gave an aqueous phase which contained only a small amount of precipitate after standing for 24 hours.

Solutions that were indefinitely stable were obtained by adding monoethanolamine, diethanolamine, triethanolamine, 3-aminopropanol, aminoethyl ethanolamine or diethyl ethanolamine to this hydrofluoric acid solution of niobium and tantalum. For the first aliphatic hydroxyamine of this series a pH of 7.5 was reached before precipitation occurred while the addition of large excess amounts of all the other compounds gave no precipitate. Phenyl ethyl ethanolamine, phenyl diethanolamine and m-tolyl diethanolamine formed a second liquid phase at a pH of from 4 to 6 when added to the 22 per cent stock solution of niobium and tantalum. This partially neutralized aqueous solution was indefinitely stable. Repetition of these experiments while employing the 100 per cent stock

solution of niobium and tantalum gave the same results. The hydroxyamines were the only class of organic amines which neutralized the hydrofluoric acid mixture of niobium and tantalum to give an indefinitely stable solution. An assumption is that the amino group reacts with the free hydrofluoric acid to neutralize the solution while the hydroxy group reacts with the fluoacids of niobium and tantalum to form a soluble complex. All pH values were determined by employing universal pH paper.

The corrosion of these amine-hydrofluoric acid solutions of niobium and tantalum on Pyrex glass was tested. Glass rings after being submerged in the various solutions for definite time increments were removed, cleaned, dried and weighed. Figure 8 shows the loss of weight of the glass per square inch of surface as a function of time submerged for the aqueous solutions having various pH values. The pH values were obtained by neutralizing the 22 per cent stock solution with different amounts of phenyl ethyl ethanolamine. It is apparent from Figure 8 that for pH values of 4 or above little variation in the weight loss of the Pyrex glass with time resulted. This is illustrated in Figure 9 where the average rate of weight loss during the first 50 hours of contact time is plotted as a function of pH. This indicates clearly that the amine-hydrofluoric acid solutions having a pH of from 4 to 6 react slowly with

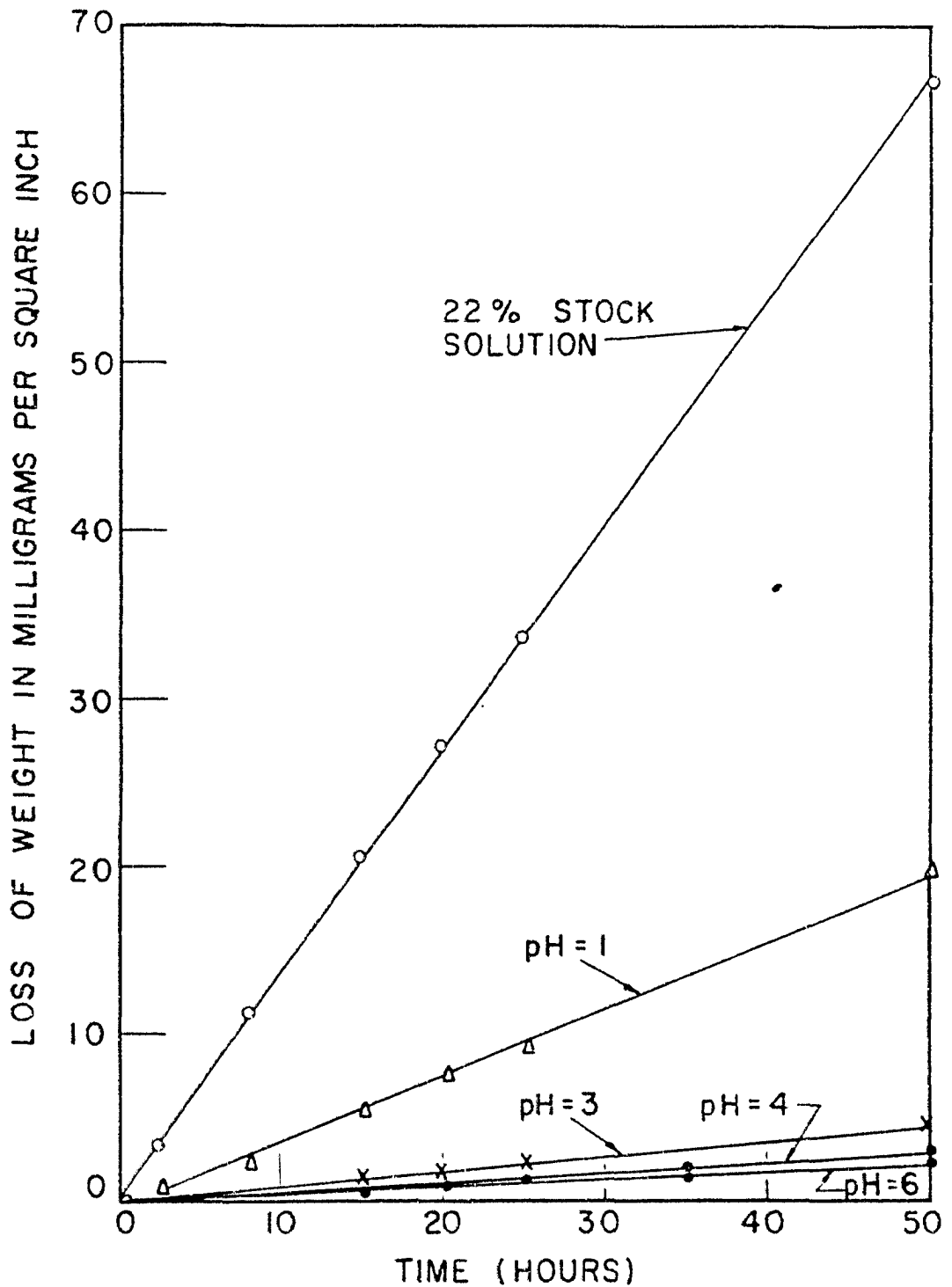


Figure 8 - Loss in Weight of Pyrex Glass Submerged in Amine Neutralized Hydrofluoric Acid Solutions of Niobium and Tantalum.



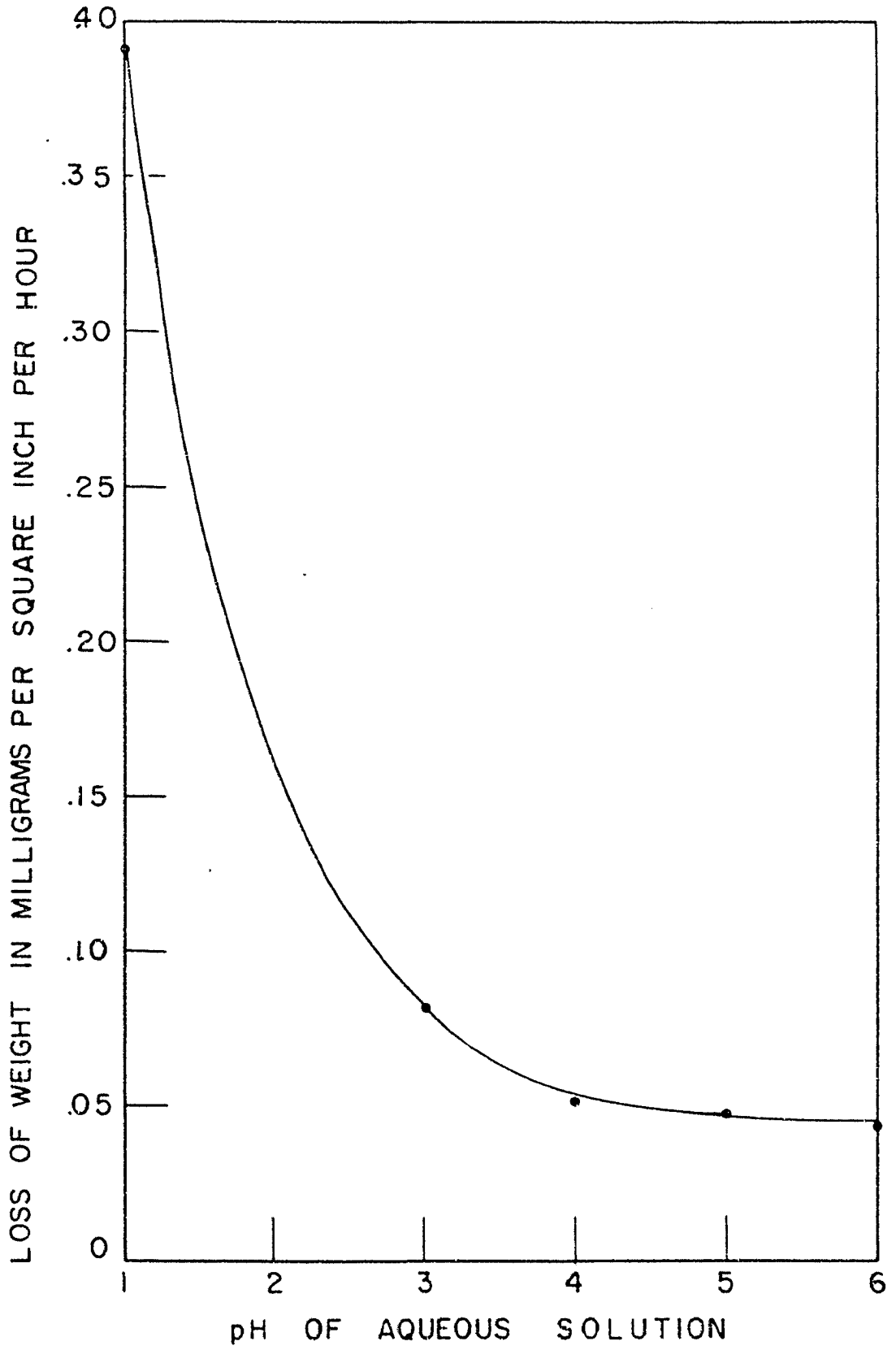


Figure 9 - Rate of Corrosion as a Function of pH.

Pyrex glass. Experiments using several other amines in place of phenyl ethyl ethanolamine for neutralizing the stock solution and its water dilutions indicated about these same rates of corrosion at the similar pH value.

The corrosion rate of 0.045 milligrams per square inch per hour which results at a pH of from about 4 to 6 represents a decrease of 33 times from the corrosion rate of the pure 22 per cent stock solution. Since these rates of corrosion were obtained for a stationary solution somewhat larger values could be expected in the presence of flowing liquids. However, these corrosion data indicate the possibility of prolonged use of the laboratory glass equipment to extract the amine-hydrofluoric acid solution of niobium and tantalum.

Although some of these amine-hydrofluoric acid salt solutions of niobium and tantalum attack glass slowly, they would be of little value in separation unless an organic solvent could be found which preferentially extracts niobium or tantalum. Consequently, a large number of single stage extractions of various partially neutralized amine-hydrofluoric acid solutions of niobium and tantalum were carried out. Unless otherwise indicated the relative volumes for these single stage extractions were two volumes of the organic liquid to one volume of the aqueous liquid. Glass equipment was used to carry out these experiments.

Table 5 contains the numbers and compositions of the various aqueous amine-hydrofluoric acid solutions of niobium and tantalum employed in this study. These aqueous phases were prepared by adding the amine to either the stock solution or its 22 per cent water solution. The amount of amine added, as shown in Table 5, is based on 10.0 milliliters of the original amine-free hydrofluoric acid solution of niobium and tantalum. When the amount of amine which was added to the aqueous solution was sufficient to form a second phase, the resulting amine feed solution was considered to be saturated with the amine.

The data for the single stage extraction of these amine-salt feed solutions are given in Table 6. The extractions are divided into groups according to the aqueous amine feed solution employed. These groups are subdivided alphabetically according to organic phase employed. When the weight of oxide obtained from one of the product phases was very small either product was analyzed.

It is apparent from the single stage extraction in Table 6 that a preferential extractability of tantalum resulted for all of these amine-hydrofluoric acid salt solutions of niobium and tantalum. The degree of extractability and the tantalum-niobium separation factors were a function of the nature and amount of amine employed to neutralize the hydrofluoric acid solution. In all cases the

Table 5

Neutralization of 10.0 Milliliters of the HF Solution  
of Niobium and Tantalum with Amines

Amine feed soln.	Amine	% stock soln.	Amount of amine added	pH	Grams oxide/ liter
1	Diethanolamine	22	1.8 ml.	5	101
2	Diethanolamine	22	3.6 ml.	7	90
3	Diethanolamine	22	5.4 ml.	9	80
4	Monoethanolamine	22	1.1 ml.	5	104
5	Triethanolamine	22	2.0 ml.	5	95
6	Diethyl ethanolamine	22	2.3 ml.	5	93
7	Aminoethyl ethanolamine	22	1.0 ml.	5	103
8	3-Aminopropanol	22	1.2 ml.	5	106
9	Aniline	22	1.0 ml.	5(sat'd)	106
10	50 Vol. % aniline + 50 vol. % mono- ethanolamine	22	1.0 ml.	5(sat'd)	105
11	Phenyl ethyl ethanolamine	22	2.1 ml.	5(sat'd)	95
12	Phenyl ethyl ethanolamine	100	10.0 ml.	5(sat'd)	260
13	m-Tolyl diethanol- amine	22	2.3 g.	4(sat'd)	95
14	Phenyl diethanol- amine	22	2.3 g.	4(sat'd)	97
15	Phenyl diethanol- amine	100	11.0 g.	4(sat'd)	262

Table 6

Single Stage Extractions of the Amine-Hydrofluoric Acid Solutions  
of Niobium and Tantalum

Ext. no.	Aq. phase		Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb sepn. factor	% total oxide weight in org.
	amine feed soln.	Organic phase (vol. %)	% $Ta_2O_5$ Aq.	Org.				
1	1	Diethyl ketone	----	I.S.	----	----	----	1.0
2	1	5% tert-octylamine + 95% diethyl ketone	43.4	69.7	0.631	0.207	3.0	43.4
3	1	Primene 81-T	I.S.	----	----	----	----	99.8
4	1	50% Primene 81-T + 50% diethyl ketone	I.S.	----	----	----	----	99.4
5	1	25% Primene 81-T + 25% diethyl ketone	I.S.	----	----	----	----	98.2
6	1	12.5% Primene 81-T + 87.5% diethyl ketone	6.40	60.0	38.9	1.77	21.9	90.0
7	1	6.3% Primene 81-T + 93.7% diethyl ketone	17.6	74.1	3.41	0.255	13.4	63.9
8	1	5.0% Primene 81-T + 95.0% diethyl ketone	20.4	82.9	2.16	0.114	19.0	53.9

I.S. = Insufficient sample.

Table 6 (Continued)

Ext. no.	Aq. phase		Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb sepn. factor	% total oxide weight in org.
	amine feed soln.	Organic phase (vol. %)	% $Ta_2O_5$ Aq.	% $Ta_2O_5$ Org.				
9	1	3.2% Primene 81-T + 96.9% diethyl ketone	33.1	88.0	0.0799	0.0537	14.8	39.1
10	1	5.0% Primene 81-T + 95% fuel oil	35.3	74.8	0.907	0.168	5.45	49.0
11	1	5.0% Primene 81-T + 95% heptane	35.3	74.5	0.910	0.171	5.33	48.0
12	1	5.0% Primene 81-T + 95% kerosene	35.7	75.8	0.945	0.167	5.65	49.6
13	1	5.0% Primene 81-T + 95% toluene	32.8	74.8	1.10	0.181	6.12	51.8
14	1	5.0% Primene 81-T + 95% turpentine	39.7	77.8	0.602	0.113	5.32	40.6
15	1	50% Primene JM-T + 50% diethyl ketone			Slurry formation			
16	1	25% Primene JM-T + 75% diethyl ketone	28.6	59.2	5.28	1.46	3.62	85.7
17	1	12.5% Primene JM-T + 87.5% diethyl ketone	25.9	69.7	2.21	0.337	6.56	65.4
18	1	5.0% Primene JM-T + 95% diethyl ketone	42.9	87.2	0.598	0.0644	9.30	36.1

Table 6 (Continued)

Ext. no.	Aq. phase		Equil. anal.				Ta-Nb sepn. factor	% total oxide weight in org.
	amine feed soln.	Organic phase (vol. %)	% Ta <sub>2</sub> O <sub>5</sub>		K <sub>Ta</sub>	K <sub>Nb</sub>		
			Aq.	Org.				
19	1	m-Toluidine	38.5	92.5	0.457	0.0230	19.8	32.1
20	2	Diethyl ketone	----	I.S.	----	----	----	0.33
21	2	25% tert-octylamine + 75% diethyl ketone	52.6	58.5	0.685	0.545	1.26	48.2
22	2	12.5% tert-octylamine + 87.5% diethyl ketone	52.6	57.8	0.346	0.281	1.23	33.5
23	2	50% Primene 81-T + 50% diethyl ketone	51.6	57.7	2.35	1.84	1.28	82.3
24	2	25% Primene 81-T + 75% diethyl ketone	53.5	60.0	0.677	0.512	1.31	56.2
25	2	12.5% Primene 81-T + 87.5% diethyl ketone	52.6	57.8	0.298	0.248	1.21	36.2
26	2	6.3% Primene 81-T + 93.7% diethyl ketone	53.4	61.9	0.151	0.107	1.41	21.4
27	2	5.0% Primene 81-T + 95% diethyl ketone	53.5	61.9	0.123	0.0870	1.41	18.0
28	2	3.1% Primene 81-T + 96.9% diethyl ketone	----	I.S.	----	----	----	11.8

Table 6 (Continued)

Ext. no.	Aq. phase		Equil. anal.				Ta-Nb sepn. factor	% total oxide weight in org.
	amine feed soln.	Organic phase (vol. %)	% $Tu_2O_5$		$K_{Ta}$	$K_{Nb}$		
			Aq.	Org.				
29	3	25% tert-octylamine + 75% diethyl ketone	----	I.S.	----	----	----	2.05
30	3	Primene 81-T	52.5	57.7	0.0642	0.0542	1.19	10.9
31	3	25% Primene 81-T + 75% diethyl ketone	----	I.S.	----	----	----	2.85
32	3	12.5% Primene 81-T + 87.5% diethyl ketone	----	I.S.	----	----	----	1.90
33	3	5% Primene 81-T + 95% diethyl ketone	----	I.S.	----	----	----	0.72
34	4	12.5% Primene 81-T + 87.5% diethyl ketone	9.94	60.5	29.6	2.12	14.0	92.3
35	4	5.0% Primene 81-T + 95% diethyl ketone	33.1	73.6	1.17	0.208	5.62	55.0
36	5	5.0% Primene 81-T + 95% diethyl ketone	31.6	75.5	1.59	0.238	6.68	59.2
37	6	5.0% Primene 81-T + 95% diethyl ketone	29.0	76.5	1.57	0.197	7.97	57.8
38	7	5.0% Primene 81-T + 95% diethyl ketone	42.9	68.1	1.07	0.381	2.82	53.4



Table 6 (Continued)

Ext. no.	Aq. phase		Equil. anal.		$K_{Ta}$	$K_{Nb}$	Ta-Nb sepn. factor	% total oxide weight in org.
	amine feed soln.	Organic phase (vol. %)	% $Ta_2O_5$ Aq.	Org.				
39	8	12.5% Primene 81-T + 87.5% diethyl ketone	7.72	60.5	37.2	2.03	18.3	91.7
40	8	5.0% Primene 81-T + 95% diethyl ketone	25.4	80.2	1.69	0.143	11.8	53.0
41	9	5.0% Primene 81-T + 95% diethyl ketone	1.60	83.9	34.1	0.106	321	60.8
42	10	5.0% Primene 81-T + 95% diethyl ketone	7.49	94.2	6.68	0.0334	200	55.6
43	10	5.0% Primene 81-T + 95% heptane	17.0	88.4	2.51	0.0672	37.3	51.2
44	11	Diethyl ketone	22.0	99.3	1.24	0.00245	506	38.8
45	11	5.0% Primene 81-T + 95% diethyl ketone	1.51	80.4	38.3	0.143	268	63.9
46	12	Cyclohexanone	18.1	81.0	4.51	0.234	19.3	59.0
47	12	Diethyl ketone*	40.5	96.7	0.652	0.0150	43.3	26.5
48	12	Diethyl ketone	32.7	98.4	0.566	0.00443	128	34.0

\*Equal volumes of the organic and aqueous phases were employed.

Table 6 (Continued)

Ext. no.	Aq. phase		Equil. anal.				Ta-Nb sepn. factor	% total oxide weight in org.
	amine feed soln.	Organic phase (vol. %)	% Ta <sub>2</sub> O <sub>5</sub>		K <sub>Ta</sub>	K <sub>Nb</sub>		
			Aq.	Org.				
49	12	Heptane	----	----	----	----	----	0
50	12	Isophorone*	27.3	94.5	1.38	0.0312	44.3	40.2
51	12	Isophorone	21.4	94.7	3.68	0.0559	65.8	46.8
52	12	Mesityl oxide*	37.4	94.5	0.850	0.0270	31.5	32.1
53	12	Mesityl oxide	25.0	96.2	3.00	0.0392	76.5	40.2
54	12	Methyl isobutyl ketone*	44.8	98.3	0.523	0.00735	71.3	23.6
55	12	Methyl isobutyl ketone	37.5	98.0	0.380	0.00477	79.8	27.9
56	12	Tributyl phosphate*	31.1	95.6	1.22	0.0256	47.8	41.2
57	12	Tributyl phosphate	17.4	92.8	1.34	0.0220	61.0	49.1
58	13	Diethyl ketone	20.4	98.9	1.43	0.00399	358	40.6
59	14	Cyclohexanone	14.6	94.6	2.12	0.0207	103	47.4
60	14	Diethyl ketone	30.8	99.7	0.690	0.00105	657	35.0
61	14	Ethyl acetoacetate	21.7	96.7	1.30	0.0124	105	41.7
62	14	Isophorone	18.7	98.1	1.39	0.00635	219	43.2

Table 6 (Continued)

Ext. no.	Aq. phase		Equil. anal.				Ta-Nb sepn. factor	% total oxide weight in org.
	amine feed soln.	Organic phase (vol. %)	% Ta <sub>2</sub> O <sub>5</sub>		K <sub>Ta</sub>	K <sub>Nb</sub>		
			Aq.	Org.				
63	14	Mesityl oxide	21.7	98.8	1.18	0.00413	286	38.9
64	14	Methyl isobutyl ketone	37.4	99.5	0.515	0.00183	281	30.8
65	15	Amyl alcohol (n)	49.7	88.0	0.163	0.0219	7.45	7.80
66	15	Cyclohexanone	8.95	76.5	3.20	0.0964	33.1	68.6
67	15	Diethyl ketone	28.2	98.4	0.675	0.00444	152	36.4
68	15	Ethyl acetoacetate	23.0	88.5	1.08	0.0420	25.7	49.1
69	15	Heptanol-3	47.3	95.3	0.0832	0.00375	22.3	9.75
70	15	Isophorone	13.0	93.6	1.92	0.0196	97.8	52.5
71	15	Mesityl oxide	20.9	96.2	1.01	0.0104	97.2	43.7
72	15	Methyl ethyl ketone	16.4	72.9	1.83	0.134	13.6	71.3
73	15	Methyl n-hexyl carbinol	48.4	96.9	0.0710	0.00212	33.4	7.94
74	15	Methyl isobutyl ketone	40.0	98.8	0.319	0.00251	12.7	26.7
75	15	Tributyl phosphate	18.2	94.1	1.19	0.0168	70.8	48.8

tantalum-niobium separation factors obtained from extracting these amine feed solutions were considerably lower than those obtained from extracting the corresponding amine-free hydrofluoric acid solutions of niobium and tantalum with the same organic compound. However, in many extractions the corresponding mass transfer to the organic phase was considerably higher for the amine feed solutions.

Many extractions of amine feed solution 1 are not listed in Table 6 because they resulted in less than 10 per cent transfer of the material to the organic phase. Two volumes of the organic phase to one volume of aqueous phase were employed for each of these unlisted extractions. The unlisted organic solvents which did not extract more than 10 per cent of the niobium and tantalum from amine feed solution 1 were: amyl alcohol (tertiary), aniline, butanol (n), dibutyl amine, ethyl acetoacetate, isophorone, mesityl oxide, methyl ethyl ketone, 2,4-pentanedione, o-tolyl propanolamine, tributyl amine and tributyl phosphate. It is evident from these data that only certain organics extracted appreciable material from amine feed solution 1. About one-third of the total initial material was extracted by m-toludine. The product from this organic phase analyzed about 93 per cent tantalum oxide. Primene 81-T on the other hand extracted essentially all the niobium and tantalum from amine feed solution 1 although about one hour was required for phase separation.

Since diethyl ketone did not extract much tantalum and niobium from amine feed solution 1, it was used as an inert solvent for diluting Primene 81-T. It is apparent from extractions 3 to 9 inclusive in Table 6 that decreasing the amount of Primene 81-T also decreased the mass distribution to the organic phase. However, as little as 3.2 volume per cent Primene 81-T in diethyl ketone extracted about 40 per cent of the material in terms of oxide. The tantalum-niobium separation factors which resulted from the extractions of amine feed solution 1 with a solution of Primene 81-T in diethyl ketone ranged in value from 13 to 22 with no apparent definite trend. However, the purity of the tantalum oxide obtained from the organic extraction solutions rapidly increased as the amount of Primene 81-T decreased (or as pure diethyl ketone was approached).

Similar extractions were carried out employing a solution of Primene JM-T (extractions 15 to 18 inclusive) or tertiaryoctylamine (extraction 2) in diethyl ketone as the organic phase. The same general trends as reported above resulted although under similar extraction conditions Primene JM-T yielded lower tantalum-niobium separation factors and mass transfer than Primene 81-T. Tertiaryoctylamine, which is similar in structure but has a lower molecular weight than either Primene 81-T or Primene JM-T, resulted in lower separation factors than these Primene compounds under similar conditions of extraction. However,

its corresponding mass transfer was greater than obtained for the Primene JM-T system although less than for the Primene 81-T system. It is apparent therefore that for similar conditions of extraction Primene 81-T yields a greater tantalum-niobium separation factor and mass transfer to the organic phase than either of these other two tertiary alkyl amines.

Since diethyl ketone is a relatively expensive diluent for Primene 81-T (about 75 cents per pound in 55 gallon drum lots) several cheaper water-immiscible organic liquids were substituted in its place. The data obtained by extracting amine feed solution 1 with these systems (extractions 10 to 14 inclusive) indicated that the use of fuel oil, heptane, kerosene, toluene or turpentine in place of diethyl ketone generally decreased only slightly the mass transfer to the organic phase. However, the tantalum-niobium separation factors resulting from the use of these cheaper organic solvents had a value of approximately 5.5 as compared to 19 for diethyl ketone. Perhaps the ketone forms a complex with Primene 81-T making it more selective for extracting tantalum while the hydrocarbon solvents are incapable of forming such a complex. It is apparent however that the material for diluting Primene 81-T is also an important factor in separating tantalum from niobium when they are together in an amine-hydrofluoric acid salt solution.

Comparison of the data for extracting amine solutions 1, 2 and 3 illustrate the effect of pH, or the amount of diethanolamine present, on mass transfer and niobium and tantalum separation. In each case where the organic phase was the same, the per cent material transferred to the organic phase decreased as the pH of the initial aqueous phase increased. For extraction of amine feed solution 3 the amount of transfer to the organic phase was generally too small to obtain a niobium and tantalum analysis. The tantalum-niobium separation factors also decreased with increasing pH of the initial aqueous phase. The separation factors obtained by extracting amine feed solutions 2 and 3, where the pH values were 7 and 9 respectively, were never greater than 1.4. However, tantalum was still preferentially extracted by the organic phase. These data indicate that addition of excess diethanolamine decreases considerably the extractability and effective separation of tantalum from niobium. Evidently the pH of the amine solution must be kept quite acidic if mixtures of niobium and tantalum are to be separated in a relatively few stages.

The data for the extraction of the amine feed solutions 1, 4, 5, 6, 7 and 8 of Table 5 with a solution of Primene 81-T in diethyl ketone illustrate the relative effects of the presence of several aliphatic hydroxyamines. It is assumed that in preparing each of these amine feed solutions

essentially the same number of equivalents of the amino group was added per unit volume of the 22 per cent stock solution. Since the pH value of 5 was determined by employing universal pH paper small deviations resulted. Based on density values and the molecular weight of the aliphatic hydroxyamines it was calculated that on an average 0.0187 equivalent of the amino group was required to neutralize 10.0 milliliters of the 22 per cent stock solution to a pH of 5.

Comparison of the results for the extraction of these aliphatic hydroxyamine feed solutions indicated similar mass distribution but varying tantalum-niobium separation factors. For the extraction with a 5.0 per cent solution of Primene 81-T in diethyl ketone the mass transfer to the organic phase calculated as oxide varied from 53 to 59 per cent. However, the tantalum-niobium separation factor ranged from a value of 2.8 for amine feed solution 7 to a value of 19 for feed solution 1. The separation factors obtained for extraction of all the other aliphatic hydroxyamine solutions varied from 6 to 12. No explanation can be given for these variations in the tantalum-niobium separation factor. However, it is apparent that the choice of the aliphatic hydroxyamines for neutralizing the hydrofluoric acid solution of niobium and tantalum does effect their separation.



Since these aliphatic hydroxyamines yielded relatively low tantalum-niobium separation factors other systems non-corrosive to glass were investigated. The aniline neutralized solution, or amine feed solution 9, was stable for only 30 minutes. However, when it was extracted with a 5.0 per cent solution of Primene 81-T in diethyl ketone, as is indicated by extraction 52 of Table 6, a mass transfer of about 61 per cent and a tantalum-niobium separation factor of 321 resulted. Evidently the presence of an amine such as aniline is much more effective than the aliphatic hydroxyamines for separating tantalum and niobium. However these aniline-neutralized hydrofluoric acid solutions of tantalum and niobium because of their instability would probably have to be processed soon after their preparation.

It was reported above that the aliphatic hydroxyamine feed solutions were indefinitely stable but upon extraction yielded low tantalum-niobium separation factors. On the other hand, the aniline-neutralized feed solution gave the opposite results. Consequently, a series of stability tests were carried out on the 22 per cent stock solution. After additions of various mixtures by volume of aniline and monoethanolamine to this hydrofluoric acid solution of tantalum and niobium until a pH of 5 was reached, the time required for a precipitate to form was observed. Precipitation started in about one hour for the 80 per cent

aniline and 20 per cent monoethanolamine mixture while about 48 hours were required for precipitation from their 50-50 mixture. After 12 days all the samples which were neutralized with the mixture containing more than 30 per cent aniline had considerable amounts of precipitate present.

Since 48 hours was selected as an acceptable stability time the amine feed solution 10 was prepared by neutralizing the 22 per cent stock solution to a pH of 5 with a 50-50 volume per cent mixture of aniline and monoethanolamine. As indicated by extractions 42 and 43 of Table 6 this feed solution was extracted with a 5.0 per cent solution of Primene 81-T in both diethyl ketone and heptane. In the former extraction the resulting mass transfer of 55.6 per cent and tantalum-niobium separation factor of 200 were about intermediate in value to those obtained for extracting the corresponding feed solutions which had been neutralized with pure aniline or pure monoethanol amine. The use of heptane as a diluent for Primene 81-T decreased the separation factor considerably and the mass transfer percentage slightly. It is apparent from these data that the proper combination of monoethanol amine, aniline, Primene 81-T and diethyl ketone affords an effective system for separating tantalum and niobium from their hydrofluoric acid solution.

It is evident from the above data that extraction of an aqueous phase containing both aniline and an aliphatic hydroxyamine gave not only a relatively stable solution but also a favorable separation of tantalum from niobium. Consequently a series of extractions was carried out on a feed solution which consisted of a hydrofluoric acid solution of tantalum and niobium which had been partially neutralized with a derivative of aniline containing a hydroxy group. As is apparent from Table 5 these amines were phenyl ethyl ethanolamine, phenyl diethanolamine and m-tolyl diethanolamine. The amine feed solutions 11 to 15 inclusive which contained these aromatic hydroxyamines were indefinitely stable.

From the data for these extractions certain generalities are evident. Generally, extraction of these aniline derivative feed solutions resulted in smaller tantalum-niobium separation factors and mass transfer to the organic phase than was reported above for extraction of the corresponding hydrofluoric acid solution. The separation of tantalum from niobium was much more effective when extracting these aromatic hydroxyamines feed solutions than when extracting the aliphatic hydroxyamine feed solutions. Consequently, from the standpoints of both chemical separation and corrosion the aniline derivative feed solutions appear to be more desirable than either the pure

hydrofluoric acid solutions or the aliphatic hydroxyamine solutions.

The separation factor and per cent transfer trends for extracting the amine feed solutions 11 to 15 inclusive with various organic solvents were similar to those reported above for extracting the amine-free hydrofluoric acid solutions of niobium and tantalum. The ketones were the most effective organic class of compounds although the esters, organic phosphates and alcohols also yielded favorable separation factors and mass transfer values. The hydrocarbons do not appear to extract either tantalum or niobium from these amine feed solutions while Primene 81-T causes considerable extraction of material by any organic phase.

Upon comparison of the results for extracting amine feed solutions 11, 13 and 14 it appears that for the same organic phase the tantalum-niobium separation factors increased progressively for the following amines: *m*-tolyl diethanolamine, phenyl ethyl ethanolamine and phenyl diethanol amine. The reverse trends resulted for mass transfer to the organic phase. From the data for extractions 58, 44 and 60 or amine feed solutions 11, 13 and 14 where diethyl ketone constituted the organic phase it can be seen that the tantalum-niobium separation factors were 358, 506 and 657 respectively, while the corresponding

mass transfer to the organic phase on an oxide basis was 40.6, 38.8 and 35.0 per cent. Comparison of the data for extracting amine feed solutions 12 and 15 indicated that in all corresponding extraction the tantalum-niobium separation factor was highest for the amine feed solution containing phenyl diethanolamine.

The effect of the initial aqueous phase concentration can be observed by comparing the data for extracting amine feed solution 11 and 12 and amine feed solutions 14 and 15. It is apparent that increasing the concentration of tantalum, niobium and amine salts in the initial aqueous phase resulted in an increase in the mass transfer to the organic phase while decreasing the tantalum-niobium separation factor. The data obtained from extracting amine feed solution 12 with different volume ratios of organic phase to aqueous phase indicate that the larger relative volume of organic phase to aqueous phase not only increases the mass transfer to the organic phase but also the tantalum-niobium separation factor. The use of these aromatic hydroxyamine feed solutions appears to be practical for the separation of tantalum from niobium.

(c) Extraction of the potassium hydroxide solution of niobium and tantalum. In the columbite-tantalite ore treatment section it was stated that the earth acids were soluble in potassium hydroxide solution. A slightly basic

solution containing the potassium salts of niobium and tantalum should not react with glass to any appreciable extent. Consequently extraction of this system was investigated as a possible technique for separating niobium and tantalum.

A basic feed solution was prepared by dissolving the earth acids in excess potassium hydroxide. This feed solution had a pH value above 14 and contained the equivalent of about 65 grams per liter of combined niobium and tantalum pentoxides. The titration of this basic solution with standard hydrochloric acid employing phenolphthalein as the indicator gave a base concentration equivalent to 1.63 moles per liter. Since niobium and tantalum partially precipitated during this titration some of the hydrochloric acid must have reacted with the potassium niobate and tantalate.

This potassium hydroxide solution of niobium and tantalum could not be precipitated by addition of ammonium hydroxide. However it was precipitated immediately by the addition of acids such as hydrochloric, sulfuric, nitric, acetic, butyric, propionic, oxalic, maleic, tartaric and salicylic in excess. It was also precipitated by ethyl alcohol, ethylenediamine, diethanolamine, diethylaminoethanol, sodium hydroxide and sodium chloride. Malic acid precipitated the solution at a pH of about 9 while citric

acid (105) even in sufficient excess to give a pH of about 4 did not form a precipitate.

Many single stage extractions were carried out directly on the potassium hydroxide solution of niobium and tantalum. It was reported that all the organic compounds tested, which included ketones, alcohols, amines, ethers, esters, hydrocarbons and organic phosphates, extracted no detectable amounts of niobium or tantalum (105). However, when citric acid was added to this basic solution to neutralize it to a pH of below 7 a small amount of material was extracted by certain organic liquids. The tantalum and niobium were precipitated from the equilibrium product phases by addition of hydrofluoric acid followed by ammonium hydroxide. Without first adding the hydrofluoric acid the ammonium hydroxide will not precipitate the niobium and tantalum from a citric acid solution. It is presumed that the hydrofluoric acid destroys the citric acid complex which is stable in the presence of only ammonium hydroxide.

In a typical experiment the initial aqueous phase was prepared by adding 7.0 grams of citric acid to 20.0 milliliters of the basic feed solution. The pH of the resulting aqueous solution buffered at about 4.0. Extraction of this aqueous phase with an equal volume of a 25 volume per cent solution of Primene JM-T in methyl ethyl ketone resulted in a mass transfer to the organic phase of 9.4 per cent in

terms of oxides. The products from the organic phase was 44 per cent tantalum oxide while the product from the aqueous phase was 55.0 per cent tantalum oxide. The tantalum-niobium separation factor was 1.58 for this extraction.

It is apparent from these data that for the extraction of this citric acid-potassium columbate and tantalate solution the niobium favored the organic phase while tantalum preferred the aqueous phase. Several other extractions of this aqueous feed solution showed similar trends. It is apparent that these phase preferences are opposite to those reported for extractions of the hydrofluoric acid or hydrofluoric acid-amine salt solutions. An extensive extraction study was not carried out on these basic or citric acid solutions because of the seemingly low mass transfers and separation factors which resulted from these preliminary investigations.

### 3. Multiple-contact batch extraction tests

It is apparent from the data for the single stage extractions of the stock solution and its various water dilutions that a great number of common water-immiscible organic compounds separate tantalum from niobium when these elements are together in a hydrofluoric acid solution. It was observed that essentially niobium-free tantalum could easily



be produced in a single stage extraction but that the preparation of tantalum-free niobium would require a series of extractions. Consequently, a number of separate multiple-contact batch extraction tests were carried out in an effort to prepare tantalum-free niobium with a high recovery. All percentages for mass transfer and recovery of material were calculated on the basis of the total oxide weight present in the initial aqueous phase. As discussed in a previous section, niobium containing less than 300 ppm tantalum is considered to be spectrographically free of tantalum while tantalum containing less than 50 ppm niobium is considered to be spectrographically free of niobium. The conditions and results of these batch extraction tests appear below.

(a) Batch extraction test 1. In this batch extraction test the hydrofluoric acid stock solution constituted the starting aqueous phase while di-isopropyl ketone was the organic phase. After four successive extractions of the aqueous phase with equal volumes of pure di-isopropyl ketone greater than 95 per cent of the starting niobium oxide remained in the aqueous phase. This niobium oxide product from the aqueous phase analyzed less than 300 ppm tantalum. The organic product phase from the first of the four contacts contained about 70 per cent of all of the tantalum. This first portion of organic was scrubbed twice with a 0.77 molar hydrofluoric acid aqueous solution. For each

of these two extractions only one volume of the aqueous phase was used to 10 volumes of the organic phase. This resulted in 50 per cent of the original tantalum, analyzing spectrographically free of niobium, remaining in the organic phase. However, had all four portions of the organic phase been combined without further treatment, it was calculated that the resulting tantalum would have had a purity of greater than 90 per cent.

(b) Batch extraction test 2. In the second batch extraction test the 22 per cent hydrofluoric acid stock solution was contacted with five successive equal volume portions of pure di-isopropyl ketone. In each extraction the oxide recovered from the organic phase analyzed greater than 99.8 per cent tantalum oxide with respect to the sum of the combined tantalum and niobium oxides. Furthermore the total extracted oxide from the five contacts represented a 68 per cent recovery of the tantalum oxide originally present in the aqueous phase. As the extractions progressed the amount of tantalum transferred to the organic phase steadily decreased so that the fifth organic contact resulted in a transfer of only 1.9 per cent of the initial weight of combined oxides. After the fifth extraction the aqueous phase still contained 25.9 per cent tantalum oxide and 74.1 per cent niobium oxide. It was determined that a rapid decrease in the concentration of fluoride ion in the

equilibrium organic phase paralleled the decrease in the transfer of material. A very large number of such extractions would be required for complete removal of tantalum unless more hydrofluoric acid were added to the system. Tantalum spectrographically free of niobium was prepared by extracting a portion of the organic phase from the first contact with three separate portions of a 0.77 molar hydrofluoric acid aqueous solution. The relative volumes for these back-extractions were 10 volumes of organic to one volume of aqueous.

(c) Batch extraction test 3. The third batch extraction test employed the 22 per cent stock solution as the initial aqueous phase and virgin tributyl phosphate as the organic phase. This aqueous phase was given two successive contacts with equal volumes of the tributyl phosphate. The residual aqueous phase contained 88 per cent of the original niobium oxide with less than 300 ppm tantalum oxide. Two back-extractions of the first equilibrium organic phase with a 0.72 molar hydrofluoric acid solution resulted in a 92 per cent recovery of the original tantalum oxide containing less than 0.40 per cent niobium oxide. The relative volumes for these back-extractions were also 10 volumes of the organic phase to one volume of the aqueous phase. One more such back-extraction would probably have yielded spectrographically pure tantalum.

(d) Batch extraction test 4. In the fourth batch extraction test the 22 per cent stock solution was contacted three separate times with diethyl ketone. The equilibrium organic phase from the first contact contained about 41 per cent of the total starting oxide weight and analyzed 0.12 per cent niobium oxide. In the second organic contact 8.8 per cent of the total starting oxide weight was extracted and an analysis showed it to contain 0.35 per cent niobium oxide. Combination of these two organic portions resulted in about a 96 per cent recovery of the total tantalum oxide which analyzed about 0.15 per cent niobium oxide. Since the aqueous phase product after these two extractions with diethyl ketone still contained about 3.7 per cent tantalum oxide a third extraction with diethyl ketone was made. This extraction resulted in the transfer of another 1.8 per cent of the total starting oxide weight to the third portion of the organic. This portion analyzed about 75 per cent tantalum oxide. The residual aqueous phase product contained better than 99 per cent of the starting weight of niobium oxide and analyzed approximately 1.0 per cent tantalum oxide. Further contacts of this aqueous phase with diethyl ketone would probably have yielded pure niobium.

(e) Batch extraction test 5. It is apparent from batch extraction test 4 that two diethyl ketone extractions of the

22 per cent stock solution yielded a good recovery of high purity tantalum. Since several more extractions with this ketone are necessary for producing pure niobium oxide, the use of other organic solvents for the third contact of the aqueous phase were investigated. These investigations constitute batch extraction tests 5 and 6.

In batch extraction test 5 the two contacts of the 22 per cent stock solution with diethyl ketone described in batch extraction 4 were carried out. An equal volume of pure tributyl phosphate was employed for the third extraction of the aqueous phase. This tributyl phosphate contact extracted 11 per cent of the total starting oxide weight which analyzed about 14 per cent tantalum oxide and 86 per cent niobium oxide. The niobium oxide in the residual aqueous phase contained less than 300 ppm tantalum oxide.

It is apparent that these three separate extractions of the aqueous solution yielded three niobium-tantalum fractions. One fraction contained 96 per cent of the total tantalum oxide weight analyzing only 0.15 per cent niobium oxide while a second fraction contained about 80 per cent of the total niobium oxide weight spectrographically free of tantalum. The third or intermediate fraction was primarily niobium oxide and contained 11 per cent of the total initial oxide weight.

(f) Batch extraction test 6. In an attempt to decrease the oxide weight of the intermediate fraction while maintaining the high purity of niobium in the final aqueous product phase, an equal volume of isophorone was employed for the third extraction of the aqueous phase. This resulted in transfer of 2.3 per cent of the initial oxide weight to the organic phase. The material transferred gave a product which analyzed about 73 per cent tantalum oxide and 27 per cent niobium oxide. The equilibrium aqueous phase contained about 99 per cent of the total niobium which analyzed less than 300 ppm tantalum. It is apparent from this batch extraction test that 99 per cent of the niobium and 96 per cent of the tantalum were recovered in high relative purity.

(g) Batch extraction test 7. In this batch extraction test, two similar contacts of the 22 per cent stock solution with diethyl ketone as reported in batch extraction 4 and also employed in batch extractions 5 and 6 were carried out. The single stage extraction data on the hydrofluoric acid solution of niobium and tantalum indicated that the presence of excess hydrofluoric acid increased the extraction by the organic phase. Consequently, in batch extraction test 7 the base equivalent of the aqueous phase which after the second diethyl ketone extraction was 2.3 equivalents per liter was changed to a value of 3.0 equivalents per liter by addition of hydrofluoric acid. This aqueous solution was then extracted with an equal volume of diethyl ketone.

The product from this third ketone extraction contained about 2.3 per cent of the total starting oxide weight and it analyzed about 75 per cent tantalum oxide and 25 per cent niobium oxide. The residual aqueous product phase contained about 99 per cent of the total niobium contaminated by less than 300 ppm tantalum. It is apparent that the addition of 0.7 of an equivalent per liter of hydrofluoric acid followed by extraction with diethyl ketone gave the same effects as the third extraction with isophorone reported in batch extraction test 6.

Two other batch extraction tests were carried out in which 1.7 and 2.7 equivalents per liter of hydrofluoric acid were added to the aqueous phase before the third extraction with diethyl ketone. The aqueous product phases from these third diethyl ketone extractions contained niobium contaminated with less than 300 ppm tantalum in either case. When 1.7 equivalents of hydrofluoric acid was added about 97 per cent of the niobium oxide was recovered in the highly purified state while for the addition of 2.7 equivalents per liter only about 94 per cent was recovered. It is evident that these slight increases in hydrofluoric acid concentration decreased the recovery of purified niobium. However the purity of the niobium prepared with the higher hydrofluoric acid concentration was possibly greater but the analytical method employed was not sensitive below 300 ppm tantalum.

It is apparent from multiple-contact batch extraction tests 6 and 7 that in a three stage extraction of the 22 per cent stock solution 99 per cent of the niobium as oxide spectrographically free of tantalum and 96 per cent of the tantalum as oxide containing only 0.15 per cent niobium oxide were recovered. The initial mixture contained about 48 per cent niobium oxide and 52 per cent tantalum oxide. The third or intermediate fraction which constituted only 2.3 per cent of the initial total oxide weight and was mainly tantalum could be allowed to accumulate in large scale operations and then given a special processing. However, if the intermediate fraction was added to the high purity tantalum fraction, the resulting mixture would contain essentially 100 per cent of the tantalum with a purity of about 99 per cent relative to niobium. The purity of such a mixture could probably be increased somewhat by varying further the conditions for the third extraction of the aqueous phase.

The conditions for the quantitative separation of tantalum from niobium have been developed for their nearly equal weight mixtures. However, the same general conditions should apply for separating any composition of these two elements. As long as the concentration of free hydrofluoric acid is kept very low only small relative amounts of niobium are extracted by diethyl ketone. If the earth acids are



dissolved in a minimum amount of hydrofluoric acid and then diluted with water several extractions of this aqueous mixture with organic solvents such as diethyl ketone should produce essentially a quantitative recovery of pure tantalum and niobium. It is believed that these extractions could readily be developed to afford a convenient analytical method for separating tantalum from niobium.

If a suitable material of construction were available this hydrofluoric acid system could be used in a counter-current extractor for the continuous separation of tantalum from niobium. A column fabricated from a plastic material such as polyethylene would withstand the attack of this acid fluoride solution. However the construction and operation of such an extractor would require some development work. The single stage data from the extraction of the stock solution indicated that about 5 to 10 stages should be sufficient for a quantitative separation of tantalum from niobium at these high concentrations. This extraction would require such organic compounds as diethyl ketone, hexone, isophorone, tributyl phosphate or methyl isopropyl ketone although many other solvents would suffice. The separation of niobium and tantalum on a large scale by liquid-liquid extraction would probably be a very simple process if a suitable extractor were available.

#### 4. Multistage extractions

The single stage and batch extraction data indicate that many organic solvents extract high purity tantalum from a hydrofluoric acid solution containing niobium and tantalum. Under these conditions only a few stages would probably be required for a quantitative separation. It was also noted from the single stage extraction data that tantalum could be easily extracted from an amine-hydrofluoric acid salt solution containing niobium and tantalum. The addition of amine markedly reduced the attack of the solution on glass. Consequently these amine aqueous solutions were used as the feed for three separate countercurrent multistage extractions for separating tantalum from niobium. The extractor shown in Figure 1 was used in each case.

(a) Extraction 1. The amine feed solution 11 whose composition is given in Table 5 constituted the aqueous feed for this multistage extraction while pure diethyl ketone was the introduced organic phase. The aqueous scrub solution was diluted hydrofluoric acid which had been saturated with phenyl ethyl ethanolamine giving a fluoride salt concentration of about 0.5 molar and a pH value of about 4. Only 10 stages of the 20 stage extractor were used for this extraction. For each cycle of operation there was added 10.0 milliliters of the aqueous feed solution at

stage 7, 5.0 milliliters of the aqueous scrub solution at stage 10 and 30 milliliters of diethyl ketone at stage 1.

The product phases for every fifth cycle of operation were analyzed for total oxide content and for relative percentages of niobium and tantalum oxides. These analyses indicated that about 20 cycles were required to reach essentially steady state conditions. After 55 complete cycles the process was discontinued, the liquids collected from the stages and oxide analyses carried out on both phases from each stage. The results of these stagewise analyses appear in Table 7.

The data from the cycle analyses showed that tantalum was not detected in the niobium of the aqueous product although the lower limit of detection of tantalum in niobium by the spectrographic method employed was about 300 ppm. This high purity of the niobium product is substantiated by the data for the aqueous phase of stages one and two in the stagewise analyses appearing in Table 7. It can be seen in this table that these niobium oxide samples were 99.97 per cent or better in relation to tantalum.

Analyses of the cycle product phases showed that for the first 50 cycles of operation only about 100 ppm of niobium oxide was present in the tantalum oxide from the organic product. However, the stagewise data indicate that the oxide recovered from the organic product phase from stage 10 should have contained 0.054 per cent (540 ppm)

Table 7

Stagewise Data for the First Niobium and Tantalum  
Multistage Extraction

Stage no.	<u>Organic phase</u>		<u>Aqueous phase</u>	
	Grams oxide/ liter	Per cent Nb <sub>2</sub> O <sub>5</sub>	Grams oxide/ liter	Per cent Nb <sub>2</sub> O <sub>5</sub>
1	0.12	*	37.7	> 99.97
2	0.038	*	36.1	99.97
3	0.97	*	37.5	99.1
4	1.20	*	38.4	97.5
5	2.24	1.42	40.2	90.0
6	5.27	0.50	47.0	72.3
7	19.8	0.24	51.2	64.0
8	18.8	0.17	47.2	1.78
9	15.8	0.030	40.9	0.080
10	19.0	0.054	10.8	0.84

\*Insufficient sample for analysis by x-ray fluorescence; per cent Nb<sub>2</sub>O<sub>5</sub> outside range for the spectrographic technique employed. Values estimated at above 2.5 per cent Nb<sub>2</sub>O<sub>5</sub>.

niobium oxide. A new supply of aqueous scrub was employed for the last few cycles of operation and it is possible that this scrub contained a small amount of niobium. A slight contamination of the scrub with niobium would also explain the lower percentages of niobium in both phases in stage 9 with higher niobium percentages in stage 10. Since this laboratory is also used for other problems involving these elements, this contamination is conceivable.

The data in Table 7 show that the maximum oxide concentrations of both the aqueous and the organic phases were in stage 7, the feed stage. It is also apparent that very little material was extracted into the organic phase in stages one and two. The over-all material balance, based on average analyses, concentrations and volumes of product indicated that the organic product phase delivered from stage 10 and the aqueous product phase delivered from stage one contained about 51 per cent and 49 per cent respectively of the total weight of tantalum and niobium oxides.

Figure 10 shows the variation of the oxide composition, expressed as niobium pentoxide percentage, with stage number for both the organic and aqueous phases. It is apparent from the data that very little niobium transferred to the organic phase in any stage. Since the large variation in niobium percentage in the aqueous phase is

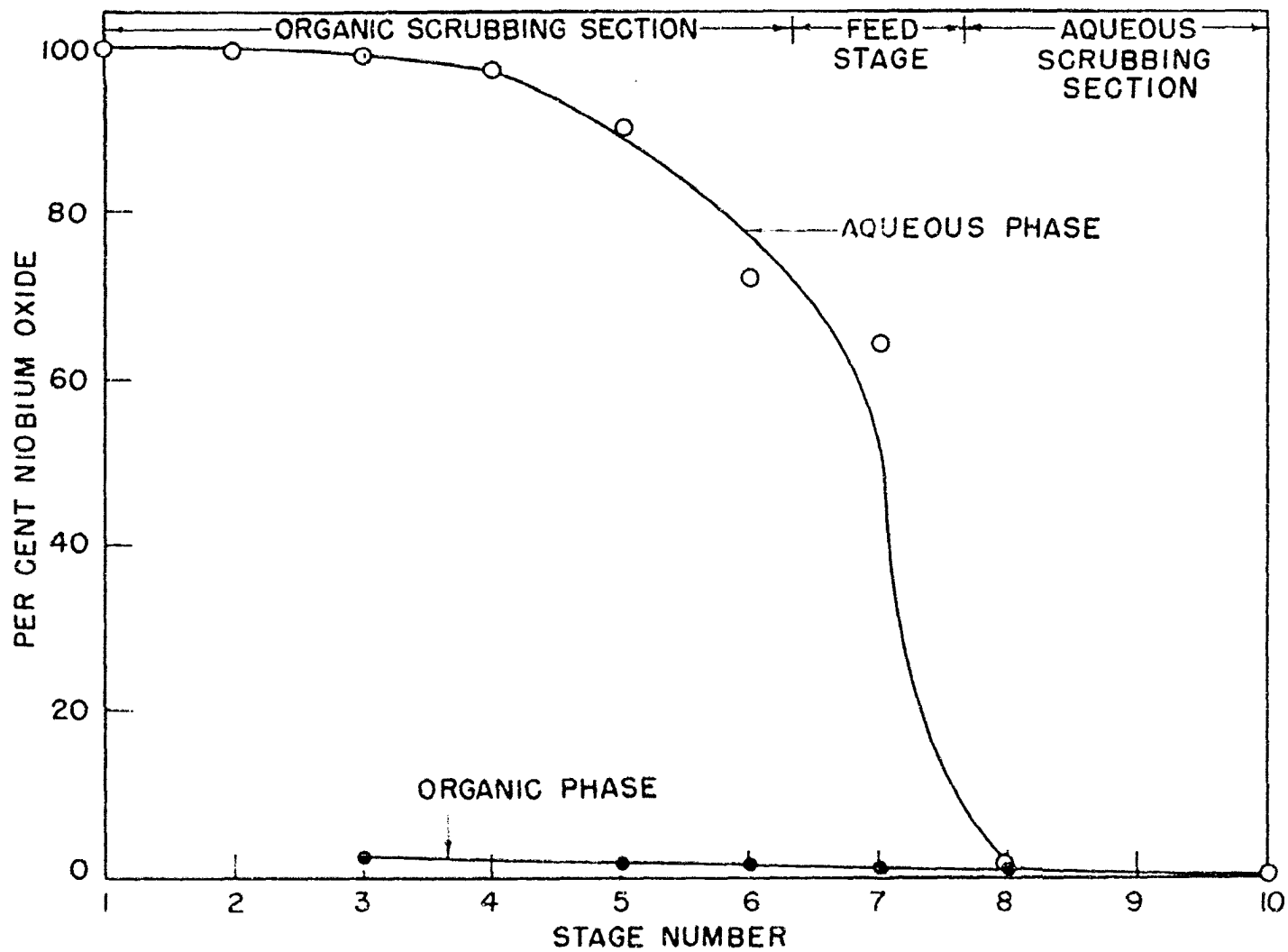


Figure 10 - Niobium Oxide Percentages in the Equilibrium Liquid Phases as a Function of Stage Number.

due mainly to the distribution of tantalum to the organic phase, the separation then depends essentially on the selective transfer of tantalum. Consequently the prime operation factor in this separation is the organic scrubbing of the aqueous feed solution. It was observed therefore that in this extraction employing an approximately 50-50 mixture of niobium and tantalum that there was a quantitative separation into a tantalum fraction containing 100 ppm niobium and a niobium fraction spectrographically free of tantalum.

(b) Extraction 2. The results from the first multi-stage extraction indicated that a nearly quantitative separation of tantalum and niobium resulted when extracting their phenyl ethyl ethanolamine-hydrofluoric acid salt solution with diethyl ketone. From the data for the single stage extractions it was observed that phenyl diethanolamine was a more effective amine for obtaining this separation of niobium and tantalum. Consequently this amine was employed for preparing the feed solution. A higher concentration of tantalum and niobium in the aqueous feed was also employed in order to increase the rate of production of tantalum and niobium. Since the tantalum-niobium separation factor decreases with an increase in concentration of niobium, tantalum and amine, 15 stages were used in this extraction.

Amine feed solution 15 (see Table 5) constituted the aqueous feed solution while diethyl ketone was the organic phase. The aqueous scrub solution was prepared by partially neutralizing a 0.50 molar hydrofluoric acid solution to a pH of 4 with phenyl diethanolamine. For each cycle of operation 10.0 milliliters of the amine feed solution, 30.0 milliliters of diethyl ketone and 5.0 milliliters of the aqueous scrub were added at stages 9, 1 and 15 respectively. The extraction process was carried out for 83 cycles although the products from every tenth cycle were analyzed. Analyses of the liquid phases in each stage were carried out after the extraction process was completed.

The cycle analyses indicated that about 40 cycles of operation were required to reach essentially steady state. These analyses showed that the niobium delivered in the aqueous product phase contained less than 300 ppm tantalum. These data were substantiated by the stagewise data which appear in Table 8. It can be noted from the data in this table that the niobium in the equilibrium aqueous phase of stages 1, 2 and 3 was spectrographically free of tantalum. Since high purity niobium was obtained in these three end stages it is probable that the contamination of the niobium by tantalum in the aqueous product phase was considerably lower than 300 ppm, the lower limit of detection.



Table 8

Stagewise Data for the Second Niobium and Tantalum  
Multistage Extraction

Stage no.	Organic phase			Aqueous phase		
	Vol. (ml.)	Grams oxide/ liter	Per cent Nb <sub>2</sub> O <sub>5</sub>	Vol. (ml.)	Grams oxide/ liter	Per cent Nb <sub>2</sub> O <sub>5</sub>
1	31.5	.096	*	11.0	119	> 99.97
2	31.8	.044	*	12.8	113	> 99.97
3	32.0	.204	*	13.3	113	> 99.97
4	33.2	.760	*	12.2	110	99.3
5	31.0	2.26	1.25	11.9	112	98.5
6	31.1	5.96	0.64	12.7	112	96.5
7	32.6	12.2	0.50	13.8	123	89.7
8	32.8	25.2	0.51	16.2	131	73.6
9	33.0	52.5	0.60	16.0	149	55.5
10	34.8	50.7	0.038	5.9	68.0	3.47
11	36.2	52.7	0.007	5.7	58.6	0.27
12	35.7	49.7	0.005	5.8	66.4	0.14
13	34.4	50.1	< 0.005	6.0	54.5	0.14
14	34.5	50.1	0.017	5.9	51.5	0.14
15	31.2	45.7	0.019	5.7	47.1	0.18

\*Refer to Table 7.

Analyses of the organic product phase indicated that the tantalum in this phase contained about 0.020 per cent (200 ppm) niobium on the oxide basis. It can be noted from the stagewise data for the organic phase that a minimum for the per cent niobium in tantalum occurred in stage 13. In this stage the tantalum was spectrographically free of niobium since it contained less than 50 ppm. It appears that the aqueous scrub solution, introduced at stage 15, must have been contaminated by niobium. This would also explain the relatively high values for the niobium oxide percentages in the equilibrium aqueous phase in the aqueous scrubbing section of the extractor.

A qualitative analysis of this amine scrub solution indicated that moderate to strong amounts of both niobium and tantalum were present. In order to determine the source of this contamination qualitative analyses were carried out on the hydrofluoric acid and phenyl diethanolamine which were employed in preparing this amine feed solution. The pure amine was relatively free of niobium or tantalum but the hydrofluoric acid contained moderate amounts of both. A qualitative analysis on a portion of hydrofluoric acid obtained from a new bottle indicated the absence of niobium or tantalum. Consequently it was assumed that the hydrofluoric acid employed in preparing this amine feed solution was contaminated prior to its use in this multistage

extraction. This probably also explains the contamination error observed in the first niobium-tantalum multistage extraction.

An over-all material balance based on the average analyses, concentrations and volumes of the product phases indicated that about 52 per cent of the material on an oxide basis was delivered by the organic product phase. As in the case of the first multistage extraction of niobium and tantalum, the maximum oxide concentration for both phases was in the feed stage. Very little niobium oxide was extracted by the organic phase of any stage.

The stagewise data indicated that niobium spectrographically free of tantalum could have been produced even if two stages were eliminated in the organic scrubbing section of the extractor. Had an amine scrub solution free of niobium been employed, it is apparent from the stagewise data that tantalum spectrographically free of niobium could have been obtained with two less stages in the aqueous scrubbing section of the extractor. Consequently it is probable that when employing this system tantalum spectrographically free of niobium and niobium spectrographically free of tantalum could be produced on a continuous basis in an 11 stage extractor.

(c) Extraction 3. In the second multistage niobium-tantalum extraction a system was indicated for preparing

niobium and tantalum spectrographically free of each other on a continuing basis. The system employed for this third multistage extraction was similar to the one used in extraction two. The concentrations of amine, niobium and tantalum in the feed solution were the only variation. In preparing the feed solution only sufficient phenyl diethanolamine was added to the stock solution to give a pH of about one and a niobium-tantalum concentration equivalent to about 300 grams per liter. According to the single stage extraction data a decrease in the pH value, or amount of phenyl diethanolamine present, would increase the tantalum-niobium separation factor. On the other hand, the increase in niobium and tantalum concentration should decrease this separation factor. For either variable change the per cent mass transfer from the aqueous to the organic phase was not expected to change appreciably.

The aqueous scrub and the organic liquid employed for this multistage extraction had the same compositions as those used in the second multistage extraction. A qualitative analysis on the aqueous scrub indicated that it was free of niobium and tantalum. The flow rates and stages of introduction of all three influents and the delivery stages of both product phases were the same as employed for extraction two. The product phases from every tenth cycle

of operation were analyzed for niobium and tantalum. About 30 cycles were required to essentially reach a steady state condition. After 64 cycles were completed the extraction was discontinued. The liquids in each stage were removed, separated and their volumes measured. They were then analyzed for niobium and tantalum content. Table 9 contains the results from these stagewise analyses.

It is apparent from the stagewise data that the organic product phase, delivered from stage 15, contained tantalum spectrographically free of niobium (or less than 50 ppm). All the equilibrium portions of the organic phase in stages 10 to 15 inclusive were free of niobium. The portions of the equilibrium aqueous phase from stages 12 to 15 inclusive were also free of niobium. This indicated that under the conditions of the extraction not more than three stages in the aqueous scrubbing section of the extractor would be required to obtain tantalum spectrographically free of niobium.

These stagewise data also show that the aqueous product phase, delivered from stage one, contained the equivalent of 98.7 per cent niobium oxide and 1.3 per cent tantalum oxide. This indicates that with the flow rates employed more stages are required in the organic scrubbing section to produce high purity niobium. An over-all material balance based on average volumes and analyses indicated

Table 9

Stagewise Data for the Third Niobium and Tantalum  
Multistage Extraction

Stage no.	Organic phase			Aqueous phase		
	Vol. (ml.)	Grams oxide/ liter	Per cent $\text{Nb}_2\text{O}_5$	Vol. (ml.)	Grams oxide/ liter	Per cent $\text{Nb}_2\text{O}_5$
1	34.0	0.253	*	12.5	129	98.7
2	33.8	1.17	*	13.8	120	97.3
3	31.5	1.39	*	13.4	123	93.9
4	33.8	3.06	*	13.0	125	93.0
5	34.2	3.40	1.8	13.5	123	92.7
6	32.8	6.70	1.0	14.0	127	86.4
7	37.0	9.60	0.70	13.9	127	84.4
8	37.0	21.2	0.60	14.5	140	72.2
9	34.3	59.5	0.48	15.0	155	58.2
10	30.8	59.4	< 0.005	6.2	85.4	4.5
11	31.0	57.4	< 0.005	6.6	67.0	0.058
12	29.6	60.4	< 0.005	6.4	61.0	< 0.005
13	29.8	54.9	< 0.005	6.5	52.2	< 0.005
14	29.0	57.0	< 0.005	6.5	43.7	< 0.005
15	29.3	51.2	< 0.005	6.3	35.0	< 0.005

\*Refer to Table 7.

that about 50 per cent of the oxide by weight was delivered by each product phase. Evidently the decrease in the amount of amine in the system resulted in a decrease in the per cent of the material transferred to the organic phase. It is probable that an increase of organic volume to about 33 to 35 milliliters per cycle would have yielded the desired oxide split with the number of stages employed. The data from multistage extraction two showed that the addition of more amine to form a saturated solution yielded the proper oxide split by weight.

This third multistage extraction showed that tantalum spectrographically free of niobium could be produced on a continuous basis from a concentration niobium and tantalum solution. It was also observed that the effect of decreasing amine concentration must be overcome by increasing the relative organic phase flow rate. It is believed that the conditions employed in this extraction could easily be adjusted to obtain at the same time both niobium and tantalum spectrographically free of each other on a continuous basis.

These three multistage extractions indicated the applicability of countercurrent extraction for continuously preparing spectrographically pure niobium and tantalum. The industrial application of such a process entails the recovery and recycling of the organic solvent and amines.

Small scale experiments indicated that about two equal volume contacts of the organic phase with water will back-extract almost all of the niobium and tantalum. It was also determined that from 60 to 80 per cent of the amine fed to the extractor was delivered from the extractor by the organic product phase. For a continuous operation some of the amine could probably be added to the system by the influent organic phase. This would possibly eliminate recovering the amines from the organic product phase. The addition of such bases as ammonia or calcium oxide to the aqueous phase regenerates the amine which is insoluble. Consequently the amine separates as a second layer and can be recovered by decantation.

#### D. Conclusions

##### 1. Ore processing

The niobium-tantalum fraction in a columbite-tantalite ore was rendered soluble by carrying out a series of treatments starting with a caustic fusion. A sodium hydroxide leach of the fusion product followed by a nitric or hydrochloric acid leach of the residue removed most of the common impurities. The remaining insoluble fraction which was essentially niobium and tantalum acid oxides was dissolved in either hydrofluoric acid or potassium hydroxide.



## 2. Single stage extractions

a. Many water immiscible organic solvents preferentially extract tantalum from a hydrofluoric acid solution containing tantalum and niobium. Tantalum essentially free of niobium was produced in a single stage extraction while the preparation of niobium free of tantalum required a series of extractions. As a general class the ketones appeared to be the most effective for obtaining pure tantalum although many alcohols, aldehydes, amines, phosphites, phosphates, ethers, esters and mixed organic solvents were also decidedly effective.

b. An increase in the concentration of free hydrofluoric acid decreased the niobium-tantalum separation factor but increased the mass transfer from the aqueous phase to the organic phase.

c. The dilution of the hydrofluoric acid solution of niobium and tantalum with water resulted in an increased preferred extractability of tantalum.

d. Certain aliphatic and aromatic hydroxyamines form a stable partially or completely neutralized solution when added to the hydrofluoric acid solution of niobium and tantalum. These amine systems did not react appreciably with glass.

e. The transfers of niobium and tantalum to the organic phase and the tantalum-niobium separation factors

were generally quite low when their hydrofluoric acid solutions were neutralized with the aliphatic hydroxyamines and then extracted with pure organic solvents. The presence of Primene JM-T or Primene 81-T in the organic solvent increased considerably the mass transfer to the organic phase while not affecting appreciably the tantalum-niobium separation factors.

f. The presence of an inert diluent in the organic phase decreased the mass transfer as well as the tantalum-niobium separation factor.

g. Extractions of the hydrofluoric acid solution which were neutralized with the aromatic hydroxyamines yielded high purity tantalum in the equilibrium organic phase, appreciable mass transfer and favorable tantalum-niobium separation factors. The same general trends for the organic solvents that were reported when extracting the amine-free hydrofluoric acid solution of niobium and tantalum were observed here. Phenyl diethanolamine appeared to be the most effective aromatic amine for neutralizing the excess hydrofluoric acid from both a cost and chemical separation viewpoint.

h. The extraction of a potassium hydroxide solution of the earth acids which had been neutralized to a pH of 4 with citric acid indicated that niobium was preferentially extracted by the organic phase. The amount of material

extracted by the organic phase and the tantalum-niobium separation factor in this system were much smaller than those observed with the hydrofluoric acid system of niobium and tantalum.

### 3. Multiple-contact batch extractions

a. A series of batch extraction tests employing the hydrofluoric acid solution of niobium and tantalum were carried out. In three contacts of the 22 per cent stock solution with diethyl ketone 96 per cent of the total tantalum oxide containing 0.15 per cent niobium oxide and 99 per cent of the total niobium oxide spectrographically free of tantalum were obtained. The intermediate or third fraction which was primarily tantalum contained 3.2 per cent of the total weight as oxide. A small amount of hydrofluoric acid solution was added to the aqueous phase after the second extraction with diethyl ketone.

b. Two extractions of the 22 per cent stock solution with diethyl ketone and a third extraction with isophorone without the addition of hydrofluoric acid yielded the same three fractions reported in 3a.

c. The three stage extraction of the 22 per cent stock solution with diethyl ketone resulted in a quantitative recovery of the tantalum with a 99 per cent purity relative

to niobium and 99 per cent recovery of niobium spectrographically free of tantalum.

d. A procedure was presented whereby any mixture of niobium and tantalum could probably be effectively separated into its pure components.

e. A countercurrent extractor consisting of from about 5 to 10 equilibrium stages should effectively separate niobium and tantalum on a continuing basis by employing one of the many organic solvents tested for the extraction of a hydrofluoric acid solution of niobium and tantalum.

#### 4. Multistage extractions

a. Three multistage extractions of the aromatic hydroxyamine neutralized hydrofluoric acid solution of niobium and tantalum were carried out to prepare the spectrographically pure salts.

b. Niobium spectrographically free of tantalum and tantalum containing about 100 ppm niobium were prepared on a continuing basis in 10 stages. The feed solution was saturated with phenyl ethyl ethanolamine and contained the equivalent of about 95 grams of niobium and tantalum oxide per liter.

c. In 15 stages niobium spectrographically free of tantalum and tantalum containing about 200 ppm niobium was obtained on a continuing basis. The feed solution was saturated with phenyl diethanolamine and contained the

equivalent of about 260 grams of niobium and tantalum oxides per liter. Stagewise analyses and a qualitative analyses of the aqueous scrub indicated that this scrub solution was contaminated with niobium. The tantalum would probably have been spectrographically free of niobium if this contamination had not existed.

d. Tantalum spectrographically free of niobium and niobium containing 1.3 per cent tantalum oxide were obtained in 15 stages on a continuing basis. The feed solution was neutralized to a pH of one by phenyl diethanolamine and contained the equivalent of about 300 grams of niobium and tantalum oxides per liter.

e. Ten to 15 stages was sufficient for a quantitative separation of both tantalum and niobium spectrographically free of each other on a continuing basis when they were fed to the extractor together in an amine-hydrofluoric acid solution.

#### IV. APPLICATION OF LIQUID-LIQUID EXTRACTION FOR THE SEPARATION OF TANTALUM FROM VANADIUM

##### A. Introduction

The separation of vanadium and tantalum is not a very important problem industrially as these two elements seldom occur together in nature. However, since the vanadium-tantalum alloys were being studied in this laboratory, a method of separating them was desired. Liquid-liquid extraction was considered as a possible method of effecting this separation. Niobium and tantalum which appear in the same chemical family as vanadium were easily separated by extracting their fluoride solution with many common water-immiscible organic compounds. Since the position of vanadium in the periodic table is closest to niobium it was expected that pentavalent vanadium could also be separated from tantalum by extracting their acid fluoride solution. The data given below verify this assumption. This inorganic salt separation illustrates another application of liquid-liquid extraction.

##### B. Experimental Details

The aqueous feed solution which contained tantalum and vanadium was prepared as follows. A hydrofluoric acid solution contained the equivalent of 16.5 grams of tantalum

pentoxide per liter and a base equivalent of 3.25 moles per liter. About 22.0 grams of vanadium pentoxide was dissolved in a liter of this tantalum hydrofluoric acid solution. The total content of vanadium and tantalum in terms of oxide was 38.5 grams per liter. Analysis indicated that the oxide mixture recovered from this solution was composed of about 55 weight per cent vanadium oxide and 45 weight per cent tantalum oxide. This hydrofluoric acid solution of vanadium and tantalum was stored in polyethylene containers.

A series of single stage extractions employing this aqueous feed solution was carried out. In each extraction equal volumes of the aqueous and organic phases were used. After mixing the phases for about 60 second they were allowed to separate. The volumes of these equilibrium phases were measured and then each phase analyzed for vanadium and tantalum content. Vanadium and tantalum were precipitated from both the aqueous and organic phases by the addition of excess ammonium hydroxide and acetone. The addition of considerable acetone was essential for decreasing the solubility of the hydrated vanadium oxide. The hydrated oxides of vanadium and tantalum were filtered and calcined at about 450 degrees Centigrade for at least two hours to give the pentoxides of niobium and tantalum.

A method developed in this Laboratory (106) was employed for analyzing these pentoxide mixtures for their vanadium

content. The tantalum content was calculated by difference since it was assumed that the samples were composed entirely of vanadium and tantalum pentoxides. In this analytical method the pentoxides were dissolved in a mixed hydrofluoric-sulfuric acid solution. After the solution was fumed to remove the excess hydrofluoric acid, zirconium was added to complex the fluoride ions in solution. Sulfur dioxide gas was then added to reduce the pentavalent vanadium to tetravalent vanadium. The tantalum was not reduced by this treatment. The content of vanadium in this solution was then determined by a titration with 0.1 normal potassium permanganate. It was estimated that at the time of these analyses an error of not more than a  $\pm$  10 per cent of the vanadium content existed for this method.

### C. Results and Discussion

The results of these single stage extractions appear in Table 10. It is apparent from these data that tantalum was preferentially extracted by all of the organic solvents tested. More than 85 per cent of the original tantalum was transferred in one stage to most of these organic compounds. Relatively small amounts of vanadium were extracted by all the solvents except methyl ethyl ketone. These data indicate that pentavalent vanadium acts similar to pentavalent niobium in liquid-liquid extractions of their fluoride solutions.



A tantalum-vanadium separation factor of 736 and 496 was obtained by the extraction with tributyl phosphate and diethyl ketone respectively. With such high separation

Table 10

## Single Stage Extractions of Tantalum from Vanadium

Organic solvent	Equil. anal.		$K_V$	$K_{Ta}$	Ta-V sepn. factor	% oxide wt. in org.
	Aq. % $V_2O_5$	Org.				
Diethyl ketone	84.1	1.0	0.00619	3.07	496	36.7
Ethyl acetoacetate	86.8	4.4	0.0305	4.40	144	39.6
Isophorone	86.3	3.2	0.0224	4.28	192	43.8
Methyl ethyl ketone	85.7	15.5	0.140	7.86	56	43.7
Tributyl phosphate	92.0	1.6	0.0129	9.50	736	48.2

factors and favorable mass transfers to the organic phase a three or four stage extraction would probably give a quantitative separation of tantalum from vanadium. Since the conditions employed for these extractions were probably not optimum, it is assumed that a more satisfactory system could be obtained. At the present time this method for separating tantalum from vanadium appears to be of limited interest. However it might eventually be a useful step in processing tantalum or vanadium ores as well as a rapid analytical procedure for analyzing such mixtures.

#### D. Conclusions

a. The extraction of a hydrofluoric acid solution containing pentavalent tantalum and pentavalent vanadium with some common water-immiscible organic solvents indicated that tantalum was preferentially transferred to the organic phase. A tantalum-vanadium separation factor as great as 736 was obtained with more than 95 per cent of the total tantalum extracted by a single contact of the aqueous phase with tributyl phosphate.

b. It was observed in this liquid-liquid extraction study on an acid fluoride solution that pentavalent vanadium resembles pentavalent niobium very closely.

## V. APPLICATION OF LIQUID-LIQUID EXTRACTION FOR THE SEPARATION OF ZIRCONIUM FROM HAFNIUM

### A. General History of Hafnium-Zirconium Separations

Zirconium was first isolated by Klaproth in 1789 as the carbonate salt although it was 1824 before Berzelius reduced this salt to the metal. Complete agreement on the characteristics of this new element was not possible until 1923 when Coster and von Hevesy (107) separated the hafnium from the zirconium. It has since been found that all known natural occurring zirconium ores are contaminated by a hafnium fraction which varies in composition from a few tenths of a per cent to as much as 16 per cent by weight. A great deal of work on the separation of these two chemically similar elements has been reported during the past three decades.

The similarity in chemical behavior appears to be related to the electronic configuration of the valence electrons. This configuration is  $4d^2, 5s^2$  for zirconium and  $5d^2, 6s^2$  for hafnium. Even though the hafnium nucleus has 32 more protons than the zirconium nucleus the difference in ionic radii for their tetravalent ions is only 0.01 of an angstrom (108). Other properties such as atomic radius, atomic volume, refractive index and solubility are quite similar for these two elements.

The use of hafnium-free zirconium has become very important in the field of atomic reactors. Zirconium metal is a useful material in the building of atomic reactors since it is highly resistant to water corrosion at elevated temperatures and has favorable neutron capture cross section values. The cross sectional areas for thermal neutron capture by zirconium and hafnium atoms are about 0.2 and 103 barns respectively (109). It is apparent that since this value for hafnium is several hundred times greater than that of zirconium, slight amounts of hafnium in zirconium would considerably increase its thermal neutron capture. Consequently, considerable research has been carried out since 1947 in an effort to remove most of the hafnium from zirconium. There has developed also a limited interest in high purity hafnium for use in basic research. The preparation of hafnium free of zirconium was the main purpose of the work described in this section.

The first widely employed technique for separating hafnium from zirconium was fractional crystallization and precipitation. Generally, the hafnium salts are slightly less soluble and tend to concentrate in the first crystals or precipitates. Some of the systems and techniques employed for this method of separation have been the double alkali fluorides (110), sulfates (111), oxychlorides (112), fluorides (113), higher oxysalts (114), oxalates (115), ammonium citrate solutions

(116), oxides (117), phosphates (118), ferricyanides (119), triethyl phosphate hydrolysis (120) and hydroxides (121). In general fractional crystallization or precipitation is not economically feasible for large scale separation of zirconium and hafnium.

Fractional distillation of a mixture composed of the chlorides or oxychlorides of zirconium and hafnium in phosphorus pentachloride has been reported by several investigators (122-125). While employing a reflux ratio of 20 to 1 and 50 distillation plates about 40 per cent of a hafnium-zirconium mixture which originally analyzed 3.0 per cent hafnium remained in the still and analyzed less than 0.1 per cent hafnium (124).

Hafnium and zirconium have been separated by employing paper chromatography (126,127), by adsorption on silica gel (128-131) and by use of ion-exchange resins (132-140). Hansen and Gunnar (128) passed a methanol solution of the tetrachlorides of zirconium and hafnium through silica gel to preferentially adsorb hafnium and recover high purity zirconium. Beyer, Jacobs and Masteller (131) concentrated a mixture containing originally two per cent hafnium to 90 per cent hafnium in two passes through silica gel. In the ion-exchange method of separation, the hafnium-zirconium mixture is generally first mixed with the resin in a separate batch process. This resin-hafnium-zirconium mixture is elutriated after being placed on top of a column which contains the same

resin. The order of elution for the anion-exchange resins is inverse to the cation-exchange resins. Zirconium is more difficult to elute from a cation-exchange resin. A zirconium product containing 0.1 per cent hafnium (132) and a hafnium product containing 0.04 per cent zirconium (135) have been reported from work employing this technique. These ion-exchange column experiments were all carried out on a milligram scale. Neither ion-exchange, adsorption on high surface materials or distillation have been used for large scale separation of hafnium and zirconium.

At the present time liquid-liquid extraction is being employed industrially for the separation of hafnium from zirconium. In 1947 Fischer and co-workers (52,53) reported that when the thiocyanates of zirconium and hafnium were distributed between water and ether, hafnium concentrated in the ether phase. The original ether contained 1.0 molar thiocyanic acid while the aqueous phase was a sulfuric acid solution of hafnium, zirconium and ammonium thiocyanate almost saturated with sulfate ions. In a typical case a starting material with a hafnium content of 0.5 per cent yielded in one extraction an organic phase product containing 7 per cent hafnium with a recovery of 50 per cent of the total hafnium.

Extensive investigation of the Fischer system for separating hafnium from zirconium has been carried out at the

Oak Ridge National Laboratory (54-61). Some of the extraction variables studied were flow rates, temperature, complexing agents, organic solvents and composition and concentration of the acidic aqueous phases. Fischer's original system was eventually varied since a hexone-hydrochloric acid system employing thiocyanate was found to be more practical. Hafnium also favored the organic phase in this variation of the thiocyanate extraction. Large scale extractions now in operation employ an aqueous solution containing 1.0 molar zirconium tetrachloride, a few per cent hafnium and 1.5 molar ammonium thiocyanate. The organic phase consists of hexone which is 2.0 molar in thiocyanic acid. The flow ratios are about 3.7 volumes of the organic phase to one volume of the aqueous phase. Starting with a mixture containing about 2 per cent hafnium and about 98 per cent zirconium approximately 75 per cent of the zirconium containing 75 ppm hafnium is produced on a continuous basis. Higher recovery of zirconium can be maintained although its purity in regards to hafnium is decreased. Production of some zirconium believed to contain less than 20 ppm hafnium has also been reported.

Further purification of the hafnium obtained from the above large scale liquid-liquid extraction process has been reported. The hafnium in the organic product phase was back-extracted into an aqueous phase by a series of scrubs employing either hydrochloric or sulfuric acid. This concentrate which

was recovered from the aqueous phase contained about 93 per cent hafnium with respect to zirconium. It was dissolved in concentrated hydrochloric acid and diluted to obtain a hafnium-zirconium concentration equivalent to 27 grams of oxides per liter. This aqueous phase was made 2.0 molar in ammonium thiocyanate. The organic hexone phase contained 1.9 molar of thiocyanic acid per liter. A 0.3 molar sulfuric acid solution was employed as the aqueous scrub. When using this system in a 12 stage mixer-settler extractor 94 per cent of the input hafnium containing approximately 200 ppm zirconium was recovered from the organic product phase. This was the purest hafnium in respect to zirconium ever produced at that time on a continuous basis. It was believed that zirconium contamination in the equipment limited the purity of hafnium at about 200 ppm zirconium.

Another liquid-liquid extraction system for the separation of zirconium from hafnium was introduced by Connick and McVey (68). Several investigators (69-71) have reported hafnium-zirconium separation factors of about 20 with these systems. In general the organic phase consists of a benzene solution of such 1,3-diketones as 2-thenoyltrifluoroacetone, 2-furoyltrifluoroacetone, 2-pyrryltrifluoroacetone or trifluoroacetylacetone. A perchloric or hydrochloric acid solution containing about  $1 \times 10^{-3}$  molar hafnium and zirconium constituted the organic phase. When these two phases are contacted zirconium



favors the organic phase although attainment of equilibrium between phases requires approximately two hours. Because of this slow equilibrium time, high cost of most 1,3-diketones and low hafnium-zirconium concentration of the aqueous phase this system has not been employed industrially.

In 1950, Wilhelm, Walsh and Kerrigan (32-34) reported that tributyl phosphate would preferentially extract zirconium from hafnium when they were present in a mixture of nitric and hydrochloric acids. Ordinarily the oxychloride salts of zirconium and hafnium were dissolved in this mixed acid system and a salting-out agent such as calcium chloride added. When carrying out a 13 stage countercurrent extraction zirconium containing less than 100 ppm hafnium was produced on a continuous basis.

An all nitrate aqueous phase which contained hafnium and zirconium but no salting-out agent was employed in a 14 stage mixer-settler extractor by Peterson and Beyer (12,35) for the separation of zirconium from hafnium. The initial aqueous phase which was 1.0 molar in zirconium contained about two weight per cent hafnium. Both the aqueous feed and scrub solutions were about 5.2 molar in nitric acid. The organic phase containing 0.65 molar nitric acid was composed of 60 volume per cent tributyl phosphate and 40 volume per cent heptane. At steady state the organic product phase contained zirconium with less than 100 ppm hafnium with an over-all zirconium recovery of about 97 per cent. The aqueous phase product was

about 45 per cent hafnium. The chief advantage of such a process over the use of the thiocyanate system described above is that zirconium is reduced of many minor impurities when transferred to the organic phase. However, transfer of the major constituent to the organic phase is less desirable in large scale production because of the usually increased relative organic flow rates required.

In the work reported here the separation of a small amount of zirconium from a hafnium concentrate was effected by employing a modification of the Wilhelm, Walsh and Kerrigan system (32-34). A nitric acid solution of the hafnium and zirconium as oxychlorides was employed as the aqueous feed solution. The purpose of this study was to develop a procedure and to prepare a few hundred pounds of a high purity hafnium salt essentially free of zirconium. The purified hafnium salt was to be converted to hafnium metal for basic studies of the metal and its alloys.

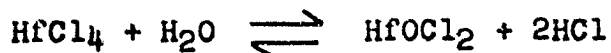
#### B. Experimental Details

Since tributyl phosphate was reported to extract zirconium in preference to hafnium from an aqueous nitric acid solution medium, this system was ideal for separating small amounts of zirconium from hafnium. Consequently, a series of single and multistage extractions was carried out in which the composition of the organic phase and content

of nitric acid in the system were varied. A saturated or nearly saturated solution of the hafnium-zirconium mixture was used in each extraction.

The zirconium-hafnium mixture used in this investigation was obtained from the Bureau of Mines Separation Plant operated for the United States Atomic Energy Commission at Albany, Oregon. It was essentially the mixture delivered by the organic product phase in the hexone-thiocyanate extraction of hafnium from zirconium. The hexone phase was scrubbed with dilute mineral acid to back-extract hafnium and zirconium. These elements were precipitated by the addition of ammonium hydroxide and were subsequently converted to oxides and then to the tetrachlorides. This resulting tetrachloride mixture was the starting material for the investigation described here. It contained from 2.0 to 4.0 per cent zirconium with respect to hafnium. The metal content analysis of one of the shipments as received appears in Table 11.

Addition of water to the solid tetrachloride mixture as received caused the formation of the oxychloride salts according to the following over-all reaction:



Since the resulting aqueous solution was usually quite cloudy a small amount of carbon was added and the solution filtered. The filtrate was then evaporated until the hydrochloric acid concentration in the hot solution reached a value of about

6.0 to 8.0 molar. At this concentration range the solubility of hafnium and zirconium oxychlorides has a minimum value. When this solution was cooled about 95 per cent of the hafnium and zirconium crystallized as their oxychloride octahydrates. This white crystalline mixture was filtered, washed with acetone and air dried. Its solubility in water is approximately 800 grams of the oxychloride salt per liter. The aqueous phases employed for the extraction studies were prepared by dissolving the oxychlorides in the water or acid and adjusting to the desired concentrations.

In these single and multistage extractions the organic phase consisted of either pure tributyl phosphate or its solution with dibutyl ether. Since equilibrium conditions were rapidly approached a mixing time of about 30 seconds was employed. After the liquids had separated some or all of the following analyses were performed on the equilibrium phases: zirconium and hafnium oxide weights and percentages, chloride ion concentration, hydrogen ion concentration and nitrate ion concentration.

Hafnium and zirconium are completely precipitated as the hydroxides (or oxyhydroxides) by addition of excess ammonium hydroxide. The aqueous phase product was precipitated directly while acetone was first added to the organic phase to maintain only one liquid phase. This addition of acetone also aided in the filtering operation. It is possible

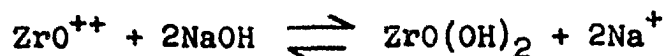
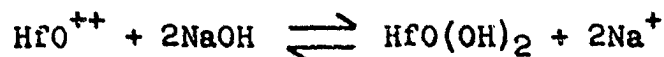
to back-extract all the hafnium and zirconium from the organic phase product by three consecutive separate equal volume extractions with water. After filtering, the precipitates were calcined at 600 degrees Centigrade for two hours to yield the zirconium and hafnium oxides.

All qualitative and quantitative analyses of these highly refractory oxides were done spectrographically. The hafnium and zirconium percentages are given relative to the total amount of only these elements with all impurities disregarded. The method of Fassel and Anderson (141) was employed for analyzing mixtures containing up to 98 per cent hafnium while the procedure of Fassel and Gray (142) was used for assaying mixtures containing more than 98 per cent hafnium. In the former method the standard deviation was given as  $\pm 2$  per cent of the entire zirconium content while for the latter case the accuracy was believed to be within  $\pm 10$  per cent of the true value for this minor constituent. The lower limit of detection is about 20 ppm of zirconium in hafnium.

An anion and cation balance on the aqueous and organic phases required determination of hydrogen, zirconium, hafnium, chloride and nitrate ion concentrations. The concentrations and percentages of hafnium and zirconium were readily determined by the ammonium hydroxide precipitation combined with the spectrographic analyses described above. A sodium hydroxide titration using phenolphthalein as the indicator was

employed to determine the total acidity of the solution. This was done by adding excess standard base to the aqueous phase until all the zirconium and hafnium was precipitated and the hydrogen ions neutralized. The precipitate was filtered and washed well with water to remove all the residual basic liquid. After combining the filtrate and washing, the excess base was back-titrated with standard acid. It was observed that the end point of this titration was much more precise and reproducible if the precipitates of zirconium and hafnium were first removed. When assaying the organic phase for total acidity the only difference in the procedure was the addition of acetone to the organic phase to insure only one liquid phase.

From the data on total acidity the free hydrogen ion concentration can be calculated. Although the knowledge of zirconium and hafnium solution chemistry is limited it is generally believed that in an acid solution the zirconyl ions,  $ZrO^{++}$ , and hafnyl ions,  $HfO^{++}$ , exist primarily. Since these are divalent two equivalents of hydroxide ions are required per equivalent of hafnium or zirconium according to following equations:



As the concentrations of both hafnium and zirconium were known

in each phase, the moles of base reacting with them can be calculated. Consequently, the remaining base was assumed to react with the free hydrogen ions.

For the chloride analysis of the aqueous and organic phases the method of Volhard was employed. In the aqueous phase excess silver nitrate was added to precipitate all the chloride ions. About two milliliters of nitrobenzene was used to produce a thin film on the silver chloride in order to prevent its reaction with other reagents (143). This eliminates the need for filtering the silver chloride. Approximately a milliliter of a saturated aqueous solution of ferric alum constituted the indicator. The excess silver nitrate was titrated with standard potassium thiocyanate until a yellow-orange color appeared indicating the end point. The chloride analysis of the organic phase was carried out in a similar manner except that sufficient acetone was added to maintain a one liquid phase system. Determination of the concentration of chloride ion was calculated from the amount of silver nitrate consumed.

Since the concentration of all the ions in each phase except the nitrate ion is known, the molarity of this ion could then be calculated. As in the case of the chloride ion, it is not possible to assign any one definite cation to balance the nitrate ion. However, the nitrate molarity could probably be expressed quite accurately in terms of nitric acid.

Single stage extractions were carried out in ordinary glass separatory funnels while for the multistage extractions the extractors shown in Figure 1 and Figure 11 were employed. This latter multistage extractor, consisting of 17 stages, will be discussed in detail in another publication (144). However, during one cycle of operation (or 360 degrees rotation about its axis) two separate mixing and settling steps are performed although only one portion of each of the aqueous and the organic product phases was delivered.

### C. Results and Discussion

#### 1. Composition of the initial hafnium-zirconium mixture

The purpose of this work was to prepare very pure hafnium with respect to zirconium when starting with the hafnium concentrate obtained from the thiocyanate-hexone system. The tetrachloride mixture of hafnium and zirconium was first converted to the oxychloride and then employed for the preparation of aqueous feed solutions. Although there were slight variations in the relative zirconium and hafnium compositions the mixtures contained between two and four per cent zirconium. As stated above all the hafnium and zirconium percentages are relative values which are based only on the total hafnium and zirconium content of the sample. Table 11 contains quantitative data on this mixture as reported by the Bureau of Mines. All values except one for iron were



determined spectrographically.

Table 11  
Analysis of the Initial Hafnium-Zirconium Mixture  
(Received as Tetrachlorides)

Element	ppm	Element	ppm	Element	ppm
Al	50	Fe	> 3000	B	0.5
Sn	< 5	Cr	100	Co	< 10
Cu	200	Mn	20	V	< 20
Pb	30	Ni	200	Cd	< 1
Mg	> 500	Si	50	Zr	2.5%
				Hf + Zr	
Zn	< 50	Ti	500	Hf	97.5%
				Hf + Zr	
Fe	3300 (chem.)	Mo	< 10		

## 2. Single stage extractions

Several single stage extractions were carried out at room temperature in order to determine favorable conditions to employ in the multistage extractor for effective separation of the hafnium-zirconium mixture. The effect of dibutyl ether as an organic diluent and of the nitric acid concentration in the initial aqueous phase was studied. Equal volumes of the organic and aqueous phases were employed in all single stage

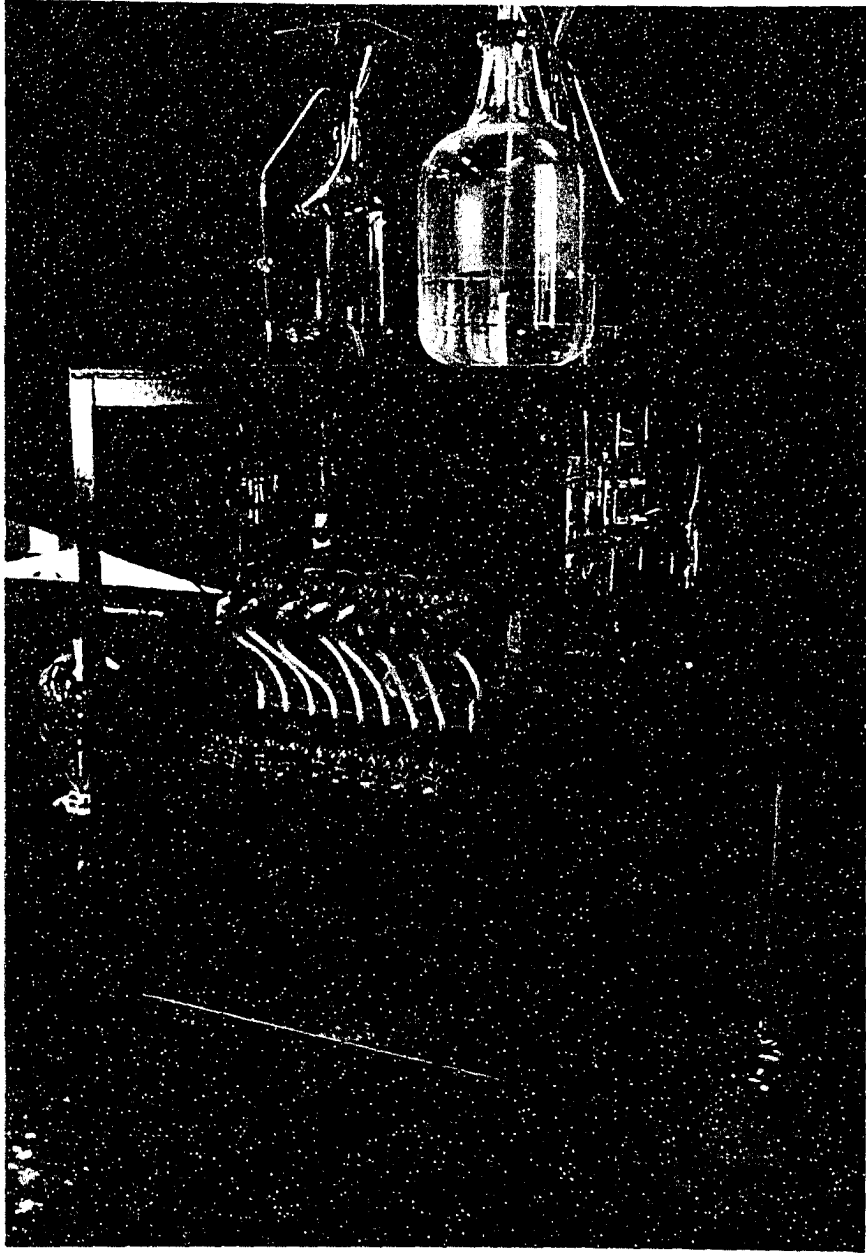


Figure 11 - Seventeen Stage Countercurrent Liquid-Liquid Extractor.

extractions. Figures 12 to 17 inclusive illustrate the data that were obtained from these experiments.

The initial aqueous phase, or feed solution, employed for these single stage extractions was a saturated hafnium-zirconium salt solution. The zirconium content of these aqueous solutions was almost negligible since it composed only a small part of the mixture. The nitric acid concentrations of the feed solutions determined the solubility of this hafnium-zirconium mixture. Figure 12 shows the variation in solubility of the zirconium-hafnium oxychloride mixture expressed as oxides with variable nitric acid concentrations. It is apparent from this figure that an increase in the nitric acid concentration generally decreased the solubility of the hafnium-zirconium mixture.

The effect of nitric acid concentration in the initial aqueous phase on mass transfer from the aqueous to the organic phase for both pure and diluted tributyl phosphate is shown in Figure 13. It is apparent from this figure that an increase in nitric acid concentration results in an increase in the per cent of the total zirconium and hafnium extracted by the organic phase. This relationship appears to be linear over the complete range that was studied. The use of the diluent, dibutyl ether, resulted in a decrease in the mass transfer for any given nitric acid concentration. The difference between the per cent mass transfer values for extractions with diluted and undiluted tributyl phosphate decreased as

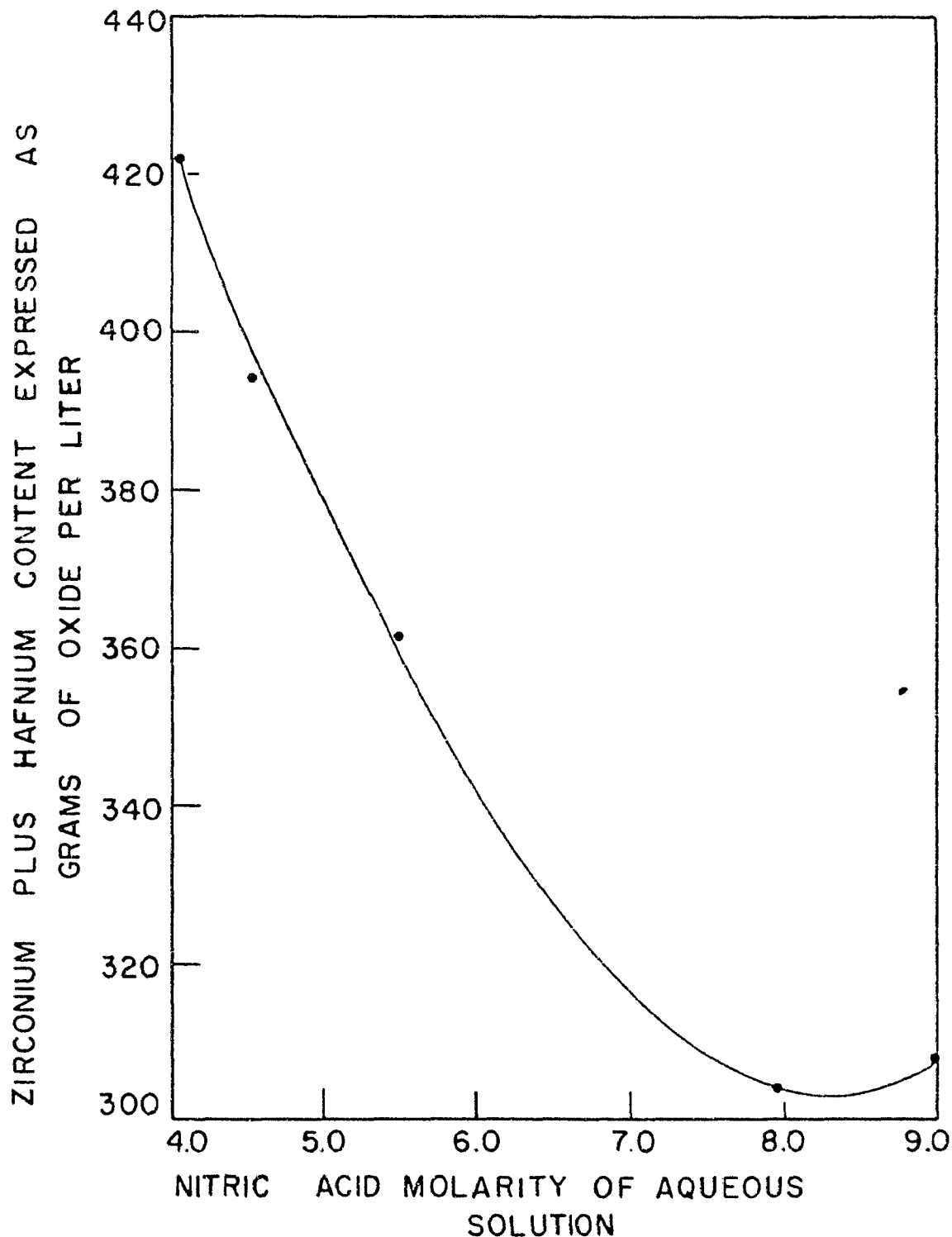


Figure 12 - Solubility of the Hafnium-Zirconium Mixture Expressed as Oxide Equivalent for Various Nitric Acid Solutions.

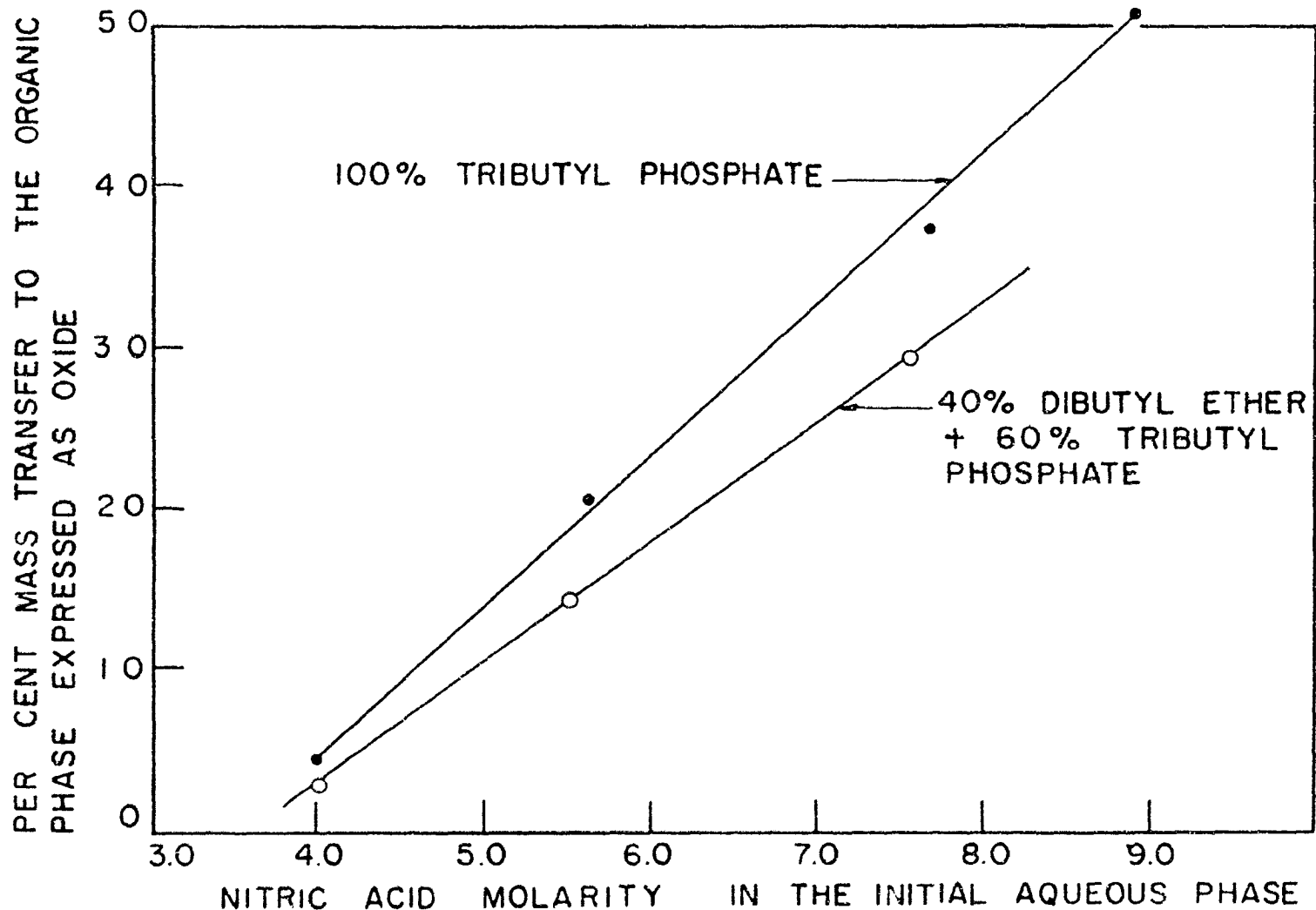


Figure 13 - Mass Distribution of the Hafnium-Zirconium Mixture at Various Nitric Acid Concentrations in Pure and Diluted Tributyl Phosphate.

the nitric acid concentration decreased. When both curves were extrapolated to zero per cent transfer they converged at about 3.6 molar nitric acid.

The hafnium oxide analyses of the aqueous product phases that were obtained from these single stage extractions are given in Figure 14. The zirconium oxide content in the product phases can be obtained by subtracting the hafnium oxide percentage from 100. It is apparent from this figure that the hafnium oxide percentage in the aqueous product phase increased with increasing nitric acid concentration in the initial aqueous phase. It can also be noted that the aqueous product phase contained the greatest percentage of hafnium oxide when the initial aqueous solution was extracted with pure tributyl phosphate. On a weight basis less hafnium would be recovered by extracting the aqueous solution with pure tributyl phosphate because of the large mass transfer to the organic phase (see Figure 13). However, as shown by Figure 14, the hafnium oxide purity in the aqueous phase product was as great as 99.3 per cent in a one stage extraction. As stated above, the composition of the aqueous phase product depends not only on the nitric acid concentration but also on the amount of diluent added to the tributyl phosphate.

The zirconium and hafnium distribution coefficients are shown in Figures 15 and 16, respectively as functions of the nitric acid concentration in the initial aqueous phase. In

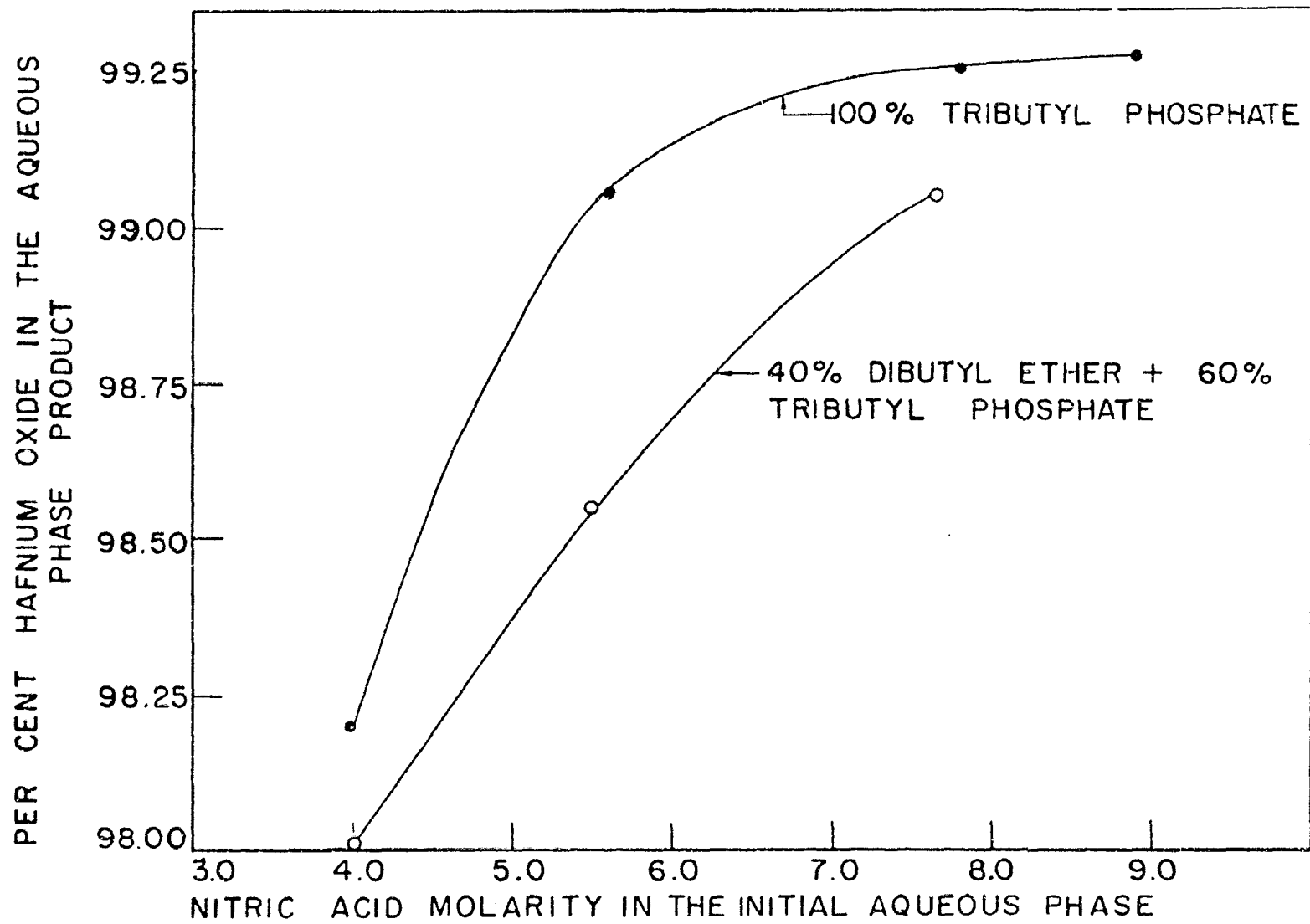
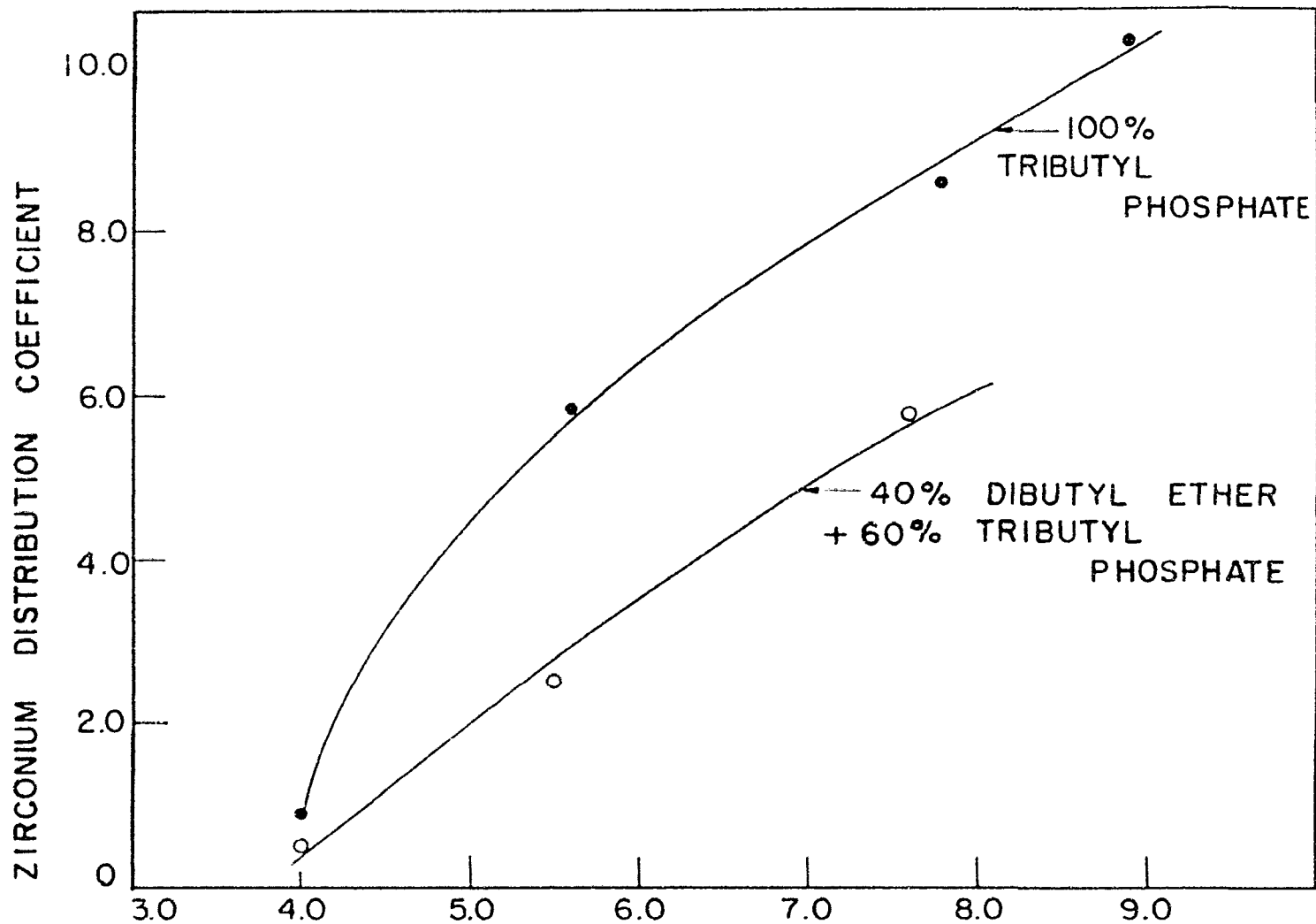
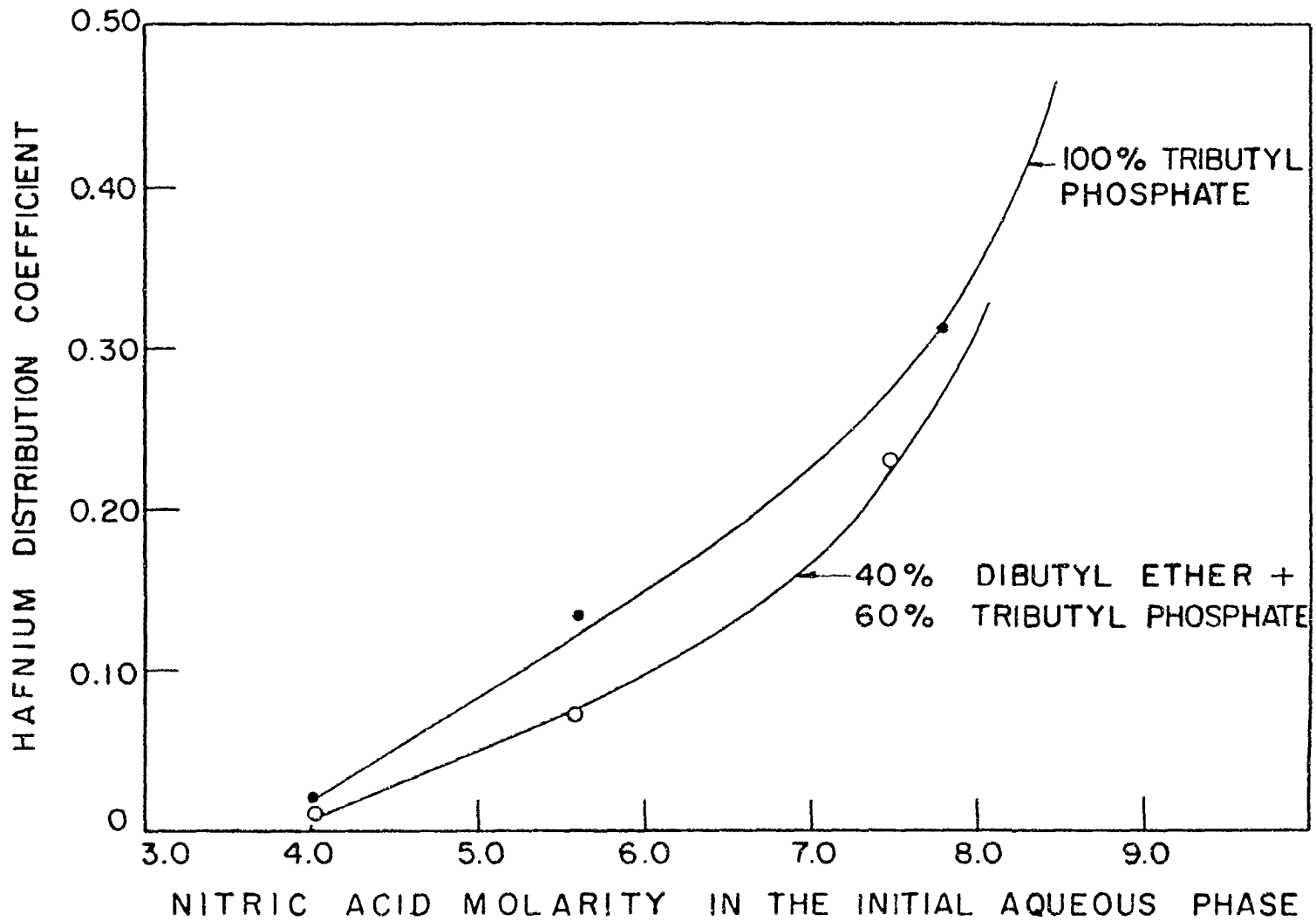


Figure 14 - Per Cent Hafnium Oxide in the Equilibrium Aqueous Phase at Various Nitric Acid Concentrations.



NITRIC ACID MOLARITY IN THE INITIAL AQUEOUS PHASE  
 Figure 15 - Zirconium Distribution Coefficient as a Function of Nitric Acid Content.





NITRIC ACID MOLARITY IN THE INITIAL AQUEOUS PHASE  
 Figure 16 - Hafnium Distribution Coefficient as a Function of Nitric Acid Content.

practically all of the extractions the distribution coefficient for zirconium was considerably greater than unity while the value for the hafnium distribution coefficient was always less than unity. Figures 15 and 16 indicate that the distribution coefficients are greatest when the aqueous solutions of hafnium and zirconium were extracted with undiluted tributyl phosphate. As the mass distribution data presented in Figure 13 would indicate, the distribution coefficients increased with the nitric acid content of the system.

The effect of the nitric acid concentration in the initial aqueous phase on the hafnium-zirconium separation factor is indicated in Figure 17. It is apparent from this figure that an increase in the nitric acid concentration resulted in a decrease in the value of the separation factor. Beyer and Peterson (35) when extracting an aqueous nitric acid solution containing a mixture of 98 per cent zirconium and 2.0 per cent hafnium with diluted tributyl phosphate reported a similar trend. A hafnium-zirconium separation factor of 57 was obtained when the 4.0 molar nitric acid solution of hafnium and zirconium was extracted with undiluted tributyl phosphate. For given concentrations of nitric acid and hafnium and zirconium in the aqueous phase the use of pure tributyl phosphate as the organic phase gave a higher separation factor than extraction with tributyl phosphate which had been diluted with dibutyl ether. The separation factor was higher even

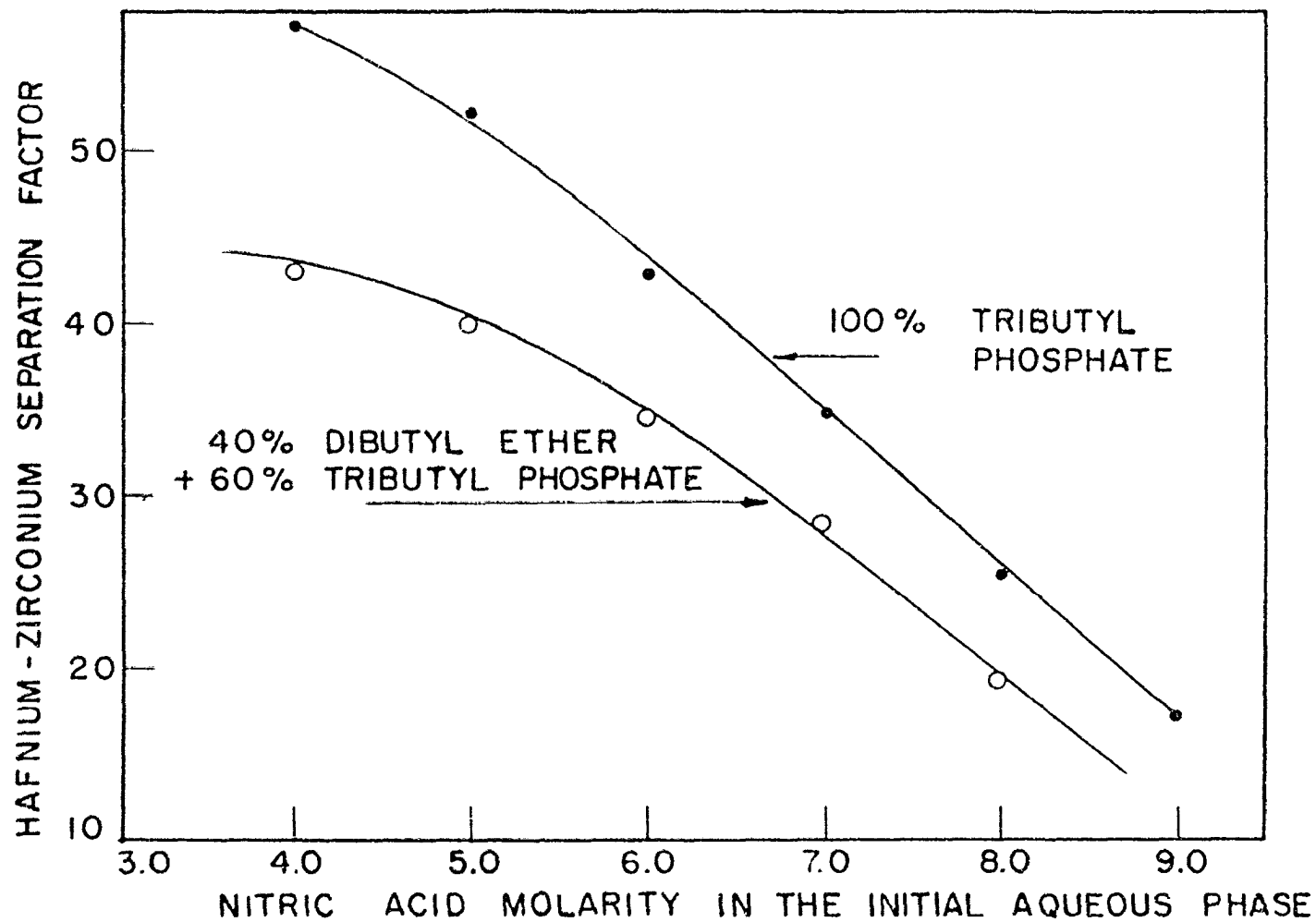


Figure 17 - Hafnium-Zirconium Separation Factors at Various Nitric Acid Concentrations.

though more material was extracted by pure tributyl phosphate. These data indicate that the lower concentrations of nitric acid are most effective for separating zirconium from hafnium.

Several important trends resulted from these single stage extractions of the saturated solutions of the hafnium-zirconium mixtures. In general, the addition of nitric acid to the system increased mass transfer to the organic phase while decreasing the hafnium-zirconium separation factors. The use of pure tributyl phosphate as the organic phase resulted in greater mass transfers and hafnium-zirconium separation factors than the use of tributyl phosphate which was diluted with dibutyl ether. These single stage extraction data were used to determine approximate extraction conditions for operating the multistage extractors in order to efficiently separate zirconium from hafnium on a continuing basis.

### 3. Multistage extractions

Since the primary goal of this work was to produce high purity hafnium on a pilot plant scale a nearly saturated solution of hafnium and zirconium was employed as the feed solution. Extractor 2 (shown in Figure 11) which consisted of only 15 stages (at that time) was to be employed for these production experiments. Consequently in the small scale extractions which were carried out in Extractor 1

(shown in Figure 1) only 15 of its 20 stages were used. The first three multistage extractions were carried out in Extractor 1 while two large scale extractions required the use of Extractor 2.

The single stage data indicated that favorable hafnium-zirconium separation factors as well as mass transfers could be obtained when preferentially extracting zirconium with tributyl phosphate from a saturated solution of a hafnium-zirconium oxychloride mixture dissolved in nitric acid. Pure tributyl phosphate gave the most favorable separation and mass distribution data. Unfortunately this pure organic solvent tended to form an emulsion and consequently at least five minutes were required for complete phase separation. When 40 or more volume per cent of dibutyl ether was added to tributyl phosphate, this phase separation time was reduced to about 20 to 50 seconds depending on the acid concentration of the system. Consequently the organic phase used in all these multistage extractions was a mixture composed of 40 volume per cent dibutyl ether and 60 volume per cent tributyl phosphate.

In addition to the organic phase composition other similarities existed in each of these five multistage extractions. In each extraction the organic phase was introduced and the aqueous product phase delivered at stage 1. Similarly the aqueous scrub phase was introduced and the organic product

phase delivered at stage 15 for all the multistage extractions except the last one. Since 17 stages were employed in this extraction the 17th stage was used to add the aqueous scrub and deliver the organic product phase. The aqueous feed was introduced at stage 9 for all of these multistage extractions except for the last one where stage 11 was used. The relative volumes of the organic phase, aqueous scrub phase and aqueous feed phase were the same in all of these multistage extractions. Their relative volumes were 4,1 and 4 respectively. The actual volumes in the first three extractions were 20,5 and 20 milliliters respectively while a scale up factor of 10 was used in the last two multistage extractions. All multistage extractions were carried out at room temperature. The solutions employed for these five multistage extractions differed essentially in nitric acid content. The results of these extractions appear in Table 12 and a short discussion of each is given below. The feed material for these extractions contained in the neighborhood of two to four per cent zirconium oxide in hafnium oxide.

(a) Extraction 1. The single stage data obtained by extracting the nitric acid aqueous solutions of hafnium and zirconium indicated that at low acid concentrations the hafnium-zirconium separation factors were high while the mass transfer to the organic phase was low. Consequently an intermediate acid

concentration of about 6.0 molar nitric acid appeared to be practical since the hafnium-zirconium separation factor would be about 35 with 17 per cent of the material transferred to the organic phase. The aqueous feed contained the equivalent of 380 grams of the combined hafnium-zirconium

Table 12

## Hafnium-Zirconium Multistage Extractions

Ext. No.	Aqueous phase product		Organic phase product		
	Grams of oxide/liter	ZrO <sub>2</sub> (ppm)	Grams of oxide/liter	ZrO <sub>2</sub> (%) <sup>2</sup>	% ZrO <sub>2</sub> + HfO <sub>2</sub> delivered in org. prod.
1	310	9,500	11.6	99.93	3.0
2	284	50	19.0	50.	7.5
3	310	75	28.5	45.	7.0
4	250	20	37.0	35.	12.0
5	225	< 20	33.0	25.	14.0

oxide mixture per liter of solution. In order to maintain a nearly constant nitric acid condition in all stages of the extractor the organic phase was made 2.68 molar in nitric acid while the aqueous feed and scrub solutions were 3.15 molar in nitric acid. These nitric acid concentrations represent nearly equilibrium values.

Analyses of the products from every tenth cycle showed that essentially steady state conditions were reached at about the 40th cycle. The extraction was discontinued after 100 complete cycles and the phases from the odd numbered stages were analyzed. These stagewise data appear in Table 13 while Figure 18 indicates the variation of these analyses with stage numbers.

Table 13  
Stagewise Data for the First Zirconium and Hafnium  
Extraction

Stage No.	Organic phase		Aqueous phase		$K_{Zr}$	$K_{Hf}$	Hf-Zr Sep. factor
	Grams of oxide/ liter	Zr (%)	Grams of oxide/ liter	Zr (%)			
1	18.1	31.3	321	0.95	1.79	0.0375	47.5
3	22.5	37.1	337	1.57	1.48	0.0405	36.7
5	28.5	51.8	340	2.53	1.60	0.0387	41.4
7	30.4	50.0	336	2.44	1.74	0.0432	40.1
9	34.1	51.5	340	2.82	1.71	0.0465	36.8
11	25.1	92.9	52.5	47.5	0.878	0.0606	14.5
13	21.4	99.6	37.0	93.5	0.611	0.0337	18.2
15	10.8	99.93	22.2	98.9	0.491	0.0321	15.3

It is apparent from Table 12 and Figure 18 that for multistage extraction 1 the aqueous phase product was about



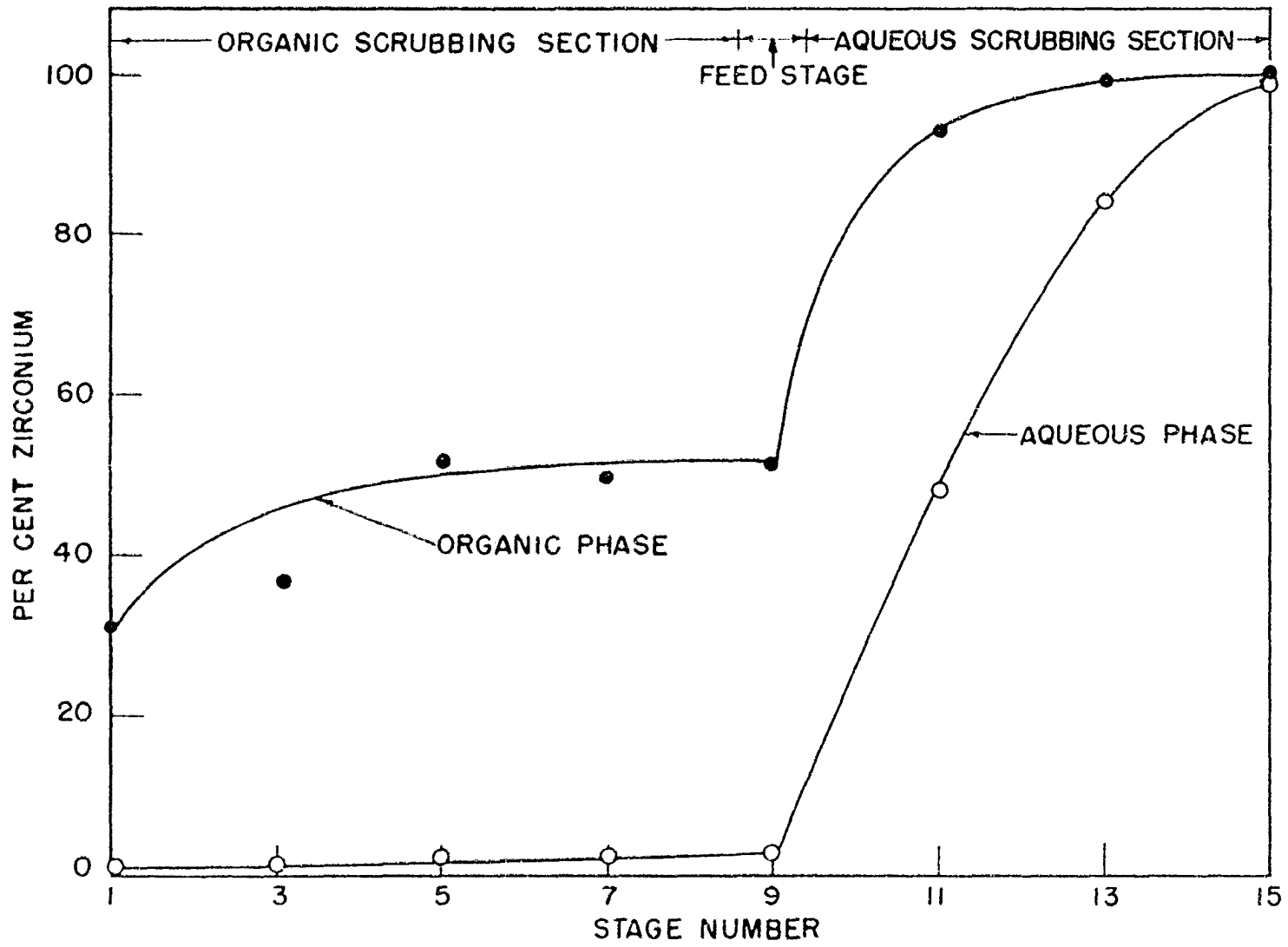


Figure 18 - Zirconium Percentage in the Equilibrium Liquids as a Function of Stage Number.

99.1 per cent hafnium oxide while the organic phase product analyzed 99.93 per cent zirconium oxide. Approximately 70 per cent by weight of the zirconium was recovered from the organic phase product while the loss of hafnium in this phase was less than 0.002 per cent of its total weight. Recovering most of the zirconium remaining in the aqueous phase product as well as obtaining a higher purity hafnium could be effected by a subsequent multistage extraction employing similar conditions. However by properly varying the operating conditions a more nearly quantitative separation could likely be effected in only one multistage extraction.

In the organic scrubbing section of the extractor, or stages one to nine inclusive, the relative flow rates were approximately five volumes of the aqueous phase to four volumes of the organic phase. The relative flow rates in the aqueous scrubbing section, stages 15 to 10 inclusive, were about four volumes of the organic phase to one volume of the aqueous phase. Figure 18 indicates that the greatest overall change in zirconium (and hafnium) percentage in either phase occurred in the aqueous scrubbing section of the extractor. According to the data in Table 13 the organic phase extracted considerable hafnium as well as zirconium in the feed stage. Although most of this hafnium was back-extracted by the aqueous scrub solution in stages 13 to 10, minor amounts of it remained in the organic product phase delivered from stage

15. A larger relative volume of aqueous scrub would have decreased the amounts of both hafnium and zirconium reaching stage 15 although the purity of the zirconium delivered would have been greater. Similarly a relatively larger volume of the organic phase would have increased the recovery of zirconium while decreasing its purity. Furthermore, changes in the number of stages employed, in the position of the feed stage and in the composition of the solutions would also effectively alter the extraction data.

It can be seen from Table 13 that the hafnium-zirconium separation factors have considerably different values in the organic and aqueous scrubbing sections of the extractor. The separation factor in the organic scrubbing section, where the percentage of hafnium in the aqueous phase resembles the feed mixture, remained fairly near to the value of 35 to 40 predicted from the single stage data for this system. The zirconium distribution coefficients apparently were influenced by the presence of the large amounts of hafnium in the organic scrubbing section of the extractor. The distribution coefficient for zirconium in stage 15 probably represents its true value for a system essentially free of hafnium. The variation of the hafnium distribution values with stage number was small throughout the entire extractor. Since the nitric acid variation in the column should be small, this large change in separation

factors was probably caused by the presence of large amounts of hafnium in the organic scrubbing section. This effect of hafnium on the zirconium distribution factor has been reported in detail from single stage extraction of varying hafnium-zirconium composition with a mixture of tributyl phosphate and heptane by Peterson and Beyer (12). They indicated a considerable variation in the zirconium distribution coefficients when a large amount of hafnium was added to form a highly concentrated hafnium-zirconium system.

Although this extraction was not successful in preparing very pure hafnium in relation to zirconium it indicates how very small amounts of zirconium in hafnium could be separated relatively free from hafnium. As stated above several changes could be made to improve the effectiveness of this 15 stage extraction. The hafnium-zirconium extractions presented below indicate primarily the effect of varying the nitric acid concentration.

(b) Multistage extraction 2. In the first multistage extraction delivery of insufficient amounts of material by the organic product phase made it impossible for high purity hafnium to reach the aqueous product outlet. According to the single stage data an increase in the nitric acid content of the system should increase the delivery of material by the organic product phase. The system employed in multistage extraction 2 contained about 1.5 molar more

of nitric acid than the system used in multistage extraction one. The nitric acid concentration employed for both the aqueous feed and aqueous scrub solutions in this second multistage extraction was about 5.0 molar while in the organic phase it was 2.92 molar. No other changes from the conditions employed for the first multistage extraction of zirconium from hafnium were made.

Cycle analyses indicated that essentially steady state was reached after 70 cycles of operation although the extraction was continued for 100 complete cycles. The aqueous phase product at steady state contained approximately 50 ppm zirconium relative to hafnium while the organic phase product contained about equal weights of zirconium and hafnium as oxides. The stagewise analyses were not significant because the organic phase employed for the last few cycles of operation was contaminated with zirconium from some unknown source.

The extraction showed that in 15 stages about 95 per cent of the hafnium containing only 50 ppm zirconium was recovered in the aqueous product phase when starting with a mixture containing from two to four per cent zirconium. A comparison of these results with those from the first multistage extraction indicates that the addition of 1.5 moles of nitric acid per liter of solution increased the mass transfer to the organic phase about 2.5 times while decreasing the zirconium content of the high purity hafnium

product about 600 times.

(c) Multistage extraction 3. For the third hafnium-zirconium multistage extraction conditions somewhat similar to multistage extraction one were employed. Although the amount of nitric acid introduced into the extractor per cycle of operation was nearly equal in both these experiments, the organic phase used for multistage extraction 3 did not contain nitric acid. While the organic phase contained no nitric acid, the aqueous feed and aqueous scrub solution were about 5.5 and 6.0 molar in nitric acid respectively. This low nitric acid concentration in the organic scrubbing section of the extractor was expected to result in the extraction of less material by the organic phase. In the aqueous scrubbing section the high nitric acid concentration should result in considerable transfer to the organic phase. The overall effect should be a greater mass transfer to the organic product phase than was obtained in the first zirconium-hafnium multistage extraction. The aqueous feed solution contained the equivalent of 380 grams of oxide per liter.

Cycle analyses, although incomplete, indicated that essentially steady state was reached after about 50 cycles of operation. As can be seen from Table 12 the aqueous phase product contained about 75 ppm zirconium relative to hafnium while the organic product phase was composed of about 55 per cent hafnium oxide. It is also apparent that approximately

7.0 per cent of the total hafnium and zirconium content as oxides were delivered by the organic product phase.

Stagewise analyses after 100 complete cycles indicated that the aqueous phase of stage two contained only 43 ppm zirconium relative to hafnium. This minimum in the zirconium percentage was also noted for the organic phase to stage two. A similar effect might have resulted in multistage extraction 2 although the large contamination in the last few cycles prevented its detection by the stagewise analyses. It appeared that the organic phase used in this extraction was contaminated by a small amount of zirconium. Before carrying out this experiment all the glassware employed for preparing the organic phase was washed with concentrated nitric acid. The organic phase mixture was also contacted four times with an equal volume of distilled water before it was added to the extractor. However the room in which this extraction was carried out as well as the extractor itself was highly contaminated with zirconium because of previous experimental work on the preparation of pure zirconium. Consequently the environment, equipment or impure chemicals could have been the source or sources of this zirconium contamination. Whenever very pure products are desired extreme care must be taken throughout the entire procedure.

Comparison of the data from the first, second and third

zirconium-hafnium extractions indicate that the nitric acid concentration of each phase introduced into the extractor as well as the total acid content influences the results. It is apparent that for these extractions that the use of an organic phase which contained no nitric acid gave the most favorable results assuming the total nitric acid content of the system was about constant. The use of the unacidified organic phase permitted approximately the same recovery of hafnium with about the same purity relative to zirconium although requiring about 1.5 mole less acid per liter. Consequently the two extractions presented below employed an organic phase containing no nitric acid.

(d) Multistage extraction 4. The liquid-liquid extractor shown in Figure 11 was used for this multistage extraction of the hafnium-zirconium mixture. Since the only previous use of this extractor was a multistage extraction of a high purity hafnium mixture it had not been contaminated by high purity zirconium. The extraction was also carried out in a different room which recently had been thoroughly scrubbed. The organic phase as well as the extractor prior to use in this experiment were treated in a manner similar to that described for multistage extraction 3.

With the exception of hafnium and zirconium concentration the conditions employed for multistage extraction 4 were essentially the same as used for multistage extraction 3.



A flow rate scale up factor of ten was employed in extraction 4. The nitric acid concentration in the aqueous scrub and feed was 5.8 and 6.2 molar respectively. This aqueous feed also contained the equivalent of 310 grams of oxides per liter. The relative amount of nitric acid introduced per cycle of operation was about the same as in extraction 3.

Cycle analyses of the product phases indicated that about 30 cycles were required to reach essentially steady state. After 65 complete cycles the extraction was discontinued, and the phases from each stage analyzed for hafnium and zirconium content, chloride concentration and total acidity. The nitrate concentration was determined by difference. These data appear in Tables 12 and 14.

From Table 12 it is apparent that the aqueous phase product was primarily hafnium which analyzed only about 20 ppm zirconium. A qualitative spectrographic analysis indicated that only trace amounts of aluminum, beryllium, magnesium, calcium, tin and copper were present. A pound of the high purity oxide recovered from this aqueous product phase from the last 20 cycles of the extraction has been submitted for analysis by other Atomic Energy Commission Laboratories to determine its purity and to compare various methods of analyzing high purity hafnium. This sample was reported to contain between 20 and 30 ppm zirconium by analysts at the Ames Laboratory. The only report which has

been received from an other laboratory indicated zirconium was not present in the sample although the method of analysis was reported to have a lower limit of detection of 50 ppm zirconium in hafnium (145).

The oxide mixture recovered from the organic product phase which contained about 12 per cent of the initial hafnium and zirconium oxide weight was about one-third zirconium oxide. This increase in mass transfer from that reported for multistage extraction 3 was probably caused by the higher ratio of nitric acid concentration to hafnium and zirconium concentration. Approximately 92 per cent of the total hafnium was delivered by the aqueous product phase as the highly purified salt.

The stagewise data obtainable only in the odd numbered stages of the extractor employed indicate that the zirconium percentage did not have a minimum value at an intermediate stage as reported in multistage extraction 3 (see Table 14). Evidently the location of and the extractor change effectively reduced the zirconium contamination at the organic inlet end of the extractor. The zirconium oxide percentage (and hafnium oxide percentage) in each phase generally showed a gradual change throughout the extractor. Operative errors and sample contamination probably explain the three deviations from this trend.

Table 1  
Stagewise Data for Hafnium-Zirconium

Stage no.	Aqueous phase							
	Vol. (ml.)	Oxide conc. (g/l.)	% ZrO <sub>2</sub>	Total acid conc. (M.)	Zr+Hf conc. (M.)	Chloride ion conc. (M.)	Nitrate ion conc. (M.)	Chloride ion conc. (M.)
1	207	250	0.0021	6.09	1.19	2.93	3.71	2.93
3	232	247	0.010	7.93	1.17	2.71	5.55	2.71
5	234	272	0.020	8.52	1.29	2.70	5.94	2.70
7	234	287	0.065	8.85	1.36	2.73	6.13	2.73
9	250	283	0.51	8.68	1.34	2.61	6.00	2.61
11	59	201	3.00	8.13	0.97	0.49	6.19	0.49
13	57	159	2.92	7.41	0.74	0.12	5.93	0.12
15	54	78.2	4.54	7.22	0.38	0.036	6.46	0.036
Feed		310	3.0	9.18	1.50	3.05	6.18	3.05
Aq. Scrub		0	0	5.80	0	0	5.80	0
Org. Phase		0	0	0	0	0	0	0



The anion and cation analysis indicated that for the organic and aqueous phases the total acidity, total molarity of hafnium plus zirconium, chloride ion concentration and nitrate ion concentration were usually a maximum in the feed stage, stage number 9. These values gradually decreased as the liquids progressed toward the ends of the extractor. The organic scrubbing section in the extractor contained greater concentrations of these ions than the aqueous scrubbing section. The aqueous phase was always more concentrated in these ions than its equilibrium organic phase.

Since no other source of chloride ion was present in this system, all the chloride ions resulted from the zirconyl and hafnyl chlorides. It is apparent from the data that relatively few chloride ions were transferred to any organic phase. Since all the material in the aqueous scrubbing section of the extractor must be introduced through the organic phase of stage 9 very few chloride ions would be expected in this aqueous scrubbing section. The ratio of the chloride concentration to the total hafnium plus zirconium concentration in the organic phase was less than 0.65 in every stage except in stage one and had a minimum value of 0.16. Consequently it is concluded that the hafnium and zirconium species extracted by the organic phase probably does not contain a chlorine atom.

The high concentration of the nitrate ion in the equilibrium organic phases relative to the total hafnium plus zirconium content indicate that the nitrate radical might possibly constitute part or all of the extracted zirconium and hafnium anion. An ion balance indicated that about 45 per cent of the total nitrate ion introduced into the extractor were delivered by the organic product phase. These ionic data indicate the importance of nitrate ions in the transfer and separation of zirconium from hafnium.

(e) Multistage extraction 5. Since the hafnium product from the multistage extraction 4 was very pure, it was requested that sufficient high purity hafnium salt equivalent to 100 pounds of elemental hafnium be produced. The conditions employed for this production extraction, or multistage stage extraction 5, were quite similar to those used in extraction 4. The aqueous scrub and aqueous feed solutions were each 5.8 molar in nitric acid with the latter containing 280 grams of oxide per liter. Two more stages were added to the extractor to insure a high purity hafnium product. These additional stages were used in the organic scrubbing section of the extractor.

The production of the required amount of purified hafnium salt required 1300 cycles of operation. Average analysis of every 100 to 200 cycles indicated that most of the aqueous

product phase contained hafnium with less than 20 ppm zirconium. The stagewise data at the completion of the extraction also substantiated this value. Since the spectrographic method of determining zirconium in high purity hafnium has appreciable error at zirconium contents below 20 ppm, the exact composition is unknown. The oxide recovered from the organic product phase was about 25 per cent zirconium oxide. A material balance indicated that about 90 per cent of the total hafnium was delivered by the aqueous phase product. It is believed that the aqueous phase product from this extraction contained the purest hafnium salt relative to zirconium that has ever been produced in quantity. Most of this high purity hafnium salt has been reduced to the metal in this Laboratory.

#### D. Conclusions

##### 1. Single stage extractions

a. A mixture composed of about 96 to 98 per cent hafnium and 2 to 4 per cent zirconium was dissolved in nitric acid. This aqueous solution was extracted with either pure tributyl phosphate or its dilutions with dibutyl ether. In all cases zirconium was preferentially extracted by the organic phase.

b. The addition of nitric acid to the aqueous solution up to a concentration of 8.0 molar acid decreased the solubility of hafnium and zirconium oxychlorides.

c. An increase in the amount of nitric acid in the system increased the mass transfer of hafnium and zirconium from the aqueous phase to the organic phase.

d. The dilution of tributyl phosphate with dibutyl ether decreased mass transfer to the organic phase.

e. Hafnium-zirconium separation factors as large as 57 were obtained by variations of this liquid-liquid system.

f. The addition of nitric acid decreased the hafnium-zirconium separation factors.

## 2. Multistage extractions.

a. A series of countercurrent multistage extractions was carried out to prepare hafnium free of zirconium. Variables such as nitric acid concentration, hafnium plus zirconium concentration, flow rates and number of stages were considered. The conditions selected were based on the single stage extraction data.

b. A nearly saturated solution of the hafnium-zirconium mixture dissolved in about 6 molar nitric was employed as the feed solution for operating a 17 stage extractor. A hafnium salt equivalent to about 100 pounds of hafnium metal containing less than 20 ppm zirconium was produced. The organic phase employed was a mixture of tributyl phosphate and dibutyl ether. About 90 per cent of the total hafnium was recovered in the pure form.



c. A 15 stage extraction of a low nitric acid solution which was saturated with the hafnium-zirconium oxychloride mixture gave an aqueous phase product containing 99.1 per cent hafnium and an organic phase product containing 99.93 per cent zirconium.

d. The stagewise chloride analysis indicated that a very small amount of chloride ion was extracted by the organic phase. It was concluded that the extracted species probably does not possess a chlorine atom.

## VI. SEPARATIONS OF YTTRIUM AND SOME RARE EARTHS BY LIQUID-LIQUID EXTRACTION

### A. General History of Rare Earth Separation

Yttrium because of its favorable nuclear properties offers materials of interest in connection with the development of atomic reactors. The preparation of yttrium concentrates was the objective of the present work. However, the association of yttrium in nature with rare earth elements requires that consideration be given to rare earth separations for yttrium purification studies.

The separation of rare earth salts into their pure components has puzzled chemists since 1839 when Mosander discovered that "ceria" in Cerite ore and "yttria" in Gadolinite ore were complex mixtures. Although there is still some disagreement, the term "rare earth" or "lanthanide" usually includes all the elements of atomic numbers 57 through 71 (lanthanum to lutetium). Although the position of yttrium in the periodic table is not within this range it is chemically closely related to the lanthanides. Rare earth ores ordinarily contain yttrium which cannot be readily removed from the lanthanides by simple chemical procedures. Consequently rare earth mixtures from ore treatments generally contain yttrium. The rare earths are generally classified into the heavy and light fractions. In the light fractions

the elements with atomic numbers 57 to 64 inclusive, or lanthanum to gadolinium, are generally included while the remaining rare earths usually constitute the heavy fraction. Separation of the lanthanides into these fractions can be accomplished with some overlapping by chemical means. Yttrium is chemically near the border line of the two fractions but generally follows the heavy fraction. Further separation of each fraction into its individual elements is much more difficult.

Since the lanthanides are very similar chemically, progress on their separation has been slow. In 1885 von Welsbach introduced the double ammonium nitrate fractional crystallization of the light group while in 1900 Demarcay proposed the double magnesium nitrate method of fractionation (146). Moeller and Kremers (147) employed a double sodium sulfate precipitation to divide a yttrium-rare earth mixture into the following three fractions: (a) lanthanum, cerium, praseodymium, neodymium and samarium, (b) europium, gadolinium and terbium and (c) dysprosium, yttrium, holmium, erbium and thulium. Marsh (146) has reviewed the method of rare earth separation up to 1946. They primarily consisted of fractional crystallization of the sulfates or nitrates. Since 1946 purification by partial precipitation or fractional crystallization employing Versene complex formation (148,149), amino acid complexes (150), ferricyanide precipitation (151),

oxalic acid precipitation (152), solubility of oxides in an ammonium acetate solution (153), precipitation with nitriloacetate (154), carbonate precipitation in a trichloroacetate solution (155) and solubility in potassium carbonate solution (156,157) have been reported. Separation of rare earths by these methods generally do not serve to readily isolate any individual pure rare earth salts. Some of the treatments show promise as a method for preparing concentrates which could be used in further processing by other techniques. Attempted separations of rare earth salts by employing paper chromatography (158-162), radiometric adsorption (163) and adsorption on aluminum oxide (164) have been reported. Distillation of rare earth chlorides as a possible means of separation was investigated by Vickery (165). Marsh (166) observed that some rare earth acetates have no amalgam forming power when treated with sodium amalgam. By this method he separated samarium from gadolinium and neodymium (167), and ytterbium from lutetium and thulium (168). As indicated for fractional crystallization none of these methods offer a means to effectively fractionate a complex rare earth salt mixture into its pure components.

In 1947 Spedding and co-workers (169-172) reported the use of ion-exchange resin columns for separating complex rare earth salts on a pilot plant scale. In the same year Ketelle and Boyd (173) and Tompkins, Kymn and Cohn (174)

employed ion-exchange resin columns for separation of selected mixtures of rare earth salts. Since then many other papers on rare earth separation by ion-exchange columns have been written (175-180). In general this technique entails elutriating the rare earth chloride mixture through an ion-exchange resin, such as amberlite, with citric acid. The order of lanthanide elution was found to be that of decreasing atomic number while yttrium appeared in the gadolinium-dysprosium region. Since some rare earth concentrates contain considerable yttrium the capacity of a resin column for the rare earth salts is reduced in these cases. The ion-exchange technique has aided rare earth salt separation greatly since it produces the salts in their pure form. However, the rate and cost of production of these salts by this process has to date limited its scale of operation to minor quantities. Consequently, a cheap method for large scale fractionation of yttrium and lanthanide mixtures is desired if relatively large quantities of the purified components are to become industrially important.

Since liquid-liquid extraction often permits low cost large scale production, it was considered as a possible method for separating these yttrium and lanthanide salt mixtures. The reviews of Bock (181), Quill (182) and Wylie (183) stressed the importance of continuous liquid-liquid extraction for lanthanide fractionation.

The first use of solvent extraction for rare earth salt separation was reported in 1937 by Fischer, Dietz and Juber-mann (47). They claimed a 50 per cent difference in the distribution coefficients of neighboring rare earths when extracting an aqueous lanthanide chloride solution with numerous organic compounds (ethers, alcohols and ketones). Unfortunately none of these data were published at that time or have they been substantiated by other investigators. An aqueous solution containing a mixture of lanthanum and neodymium thiocyanates was extracted with n-butyl alcohol by Appleton and Selwood (66). They reported low distribu-tion values and a lanthanum-neodymium separation factor of only 1.06 with the latter element favoring the organic phase. Templeton and Peterson (23) when distributing a lanthanum-neodymium nitrate mixture between water and hexanol obtained a separation factor of 1.5 with the latter element favoring the organic phase. A further investigation on a nitrate-alcohol system by Templeton (24) indicated a regular increase in extraction with atomic number for all the rare earths from lanthanum to samarium inclusive. Studies on the extraction of an aqueous solution of neodymium and erbium chlorides with n-butanol indicated little transfer to the organic phase and no detectable separation (25). However for a corresponding rare earth nitrate system four times more material was transferred to this alcohol organic phase

with increased separation factors. The presence of ammonium thiocyanate in the chloride or nitrate lanthanide system yielded slightly more transfer but with no appreciable change in their separation factors (25).

In 1952 Peppard, Faris, Gray and Mason (26) reported that the extractability of the lanthanides into tributyl phosphate from a hydrochloric acid solution or from an 8.0 to 15.6 molar nitric acid solution increased with increasing atomic number. The order was inverted for a 0.3 molar nitric acid aqueous phase. Yttrium was extracted between dysprosium and holmium, or the position predicted from consideration of atomic radii. Addition of sufficient aluminum nitrate or ammonium nitrate caused complete transfer of the lanthanides into the organic phase with no contamination from most other inorganic salts. Although these salting-out agents were useful in separating rare earths salts from accompanying impurities, a concentrated nitric acid system was superior to this mixed nitrate-nitric acid phase for separation of individual rare earths. For increasing nitric acid concentrations they showed that the logarithm of the distribution ratios for a given pair of lanthanides diverged, consequently the theoretical maximum separation factors required concentrated acid. A constant separation factor of 1.9 was observed between nearest rare earth neighbors in a 15.6 molar aqueous nitric acid medium when extracting the rare

earths whose atomic numbers were not greater than 67, the limit of their work. For a 12 molar nitric acid system the separation factors between nearest neighbors was 1.6. Since these separation factor relationships were obtained from single stage extractions of pure rare earths employing only radioactive tracers their application to high concentrations of mixed rare earth salts might not be valid. It was concluded that any rare earth nitrate-nitric acid aqueous solution could be divided into two fractions by extracting with tributyl phosphate. The compositions of these fractions are a function of variables such as acidity, flow rates, rare earth concentration and the amount of diluent for the organic phase. Separations of complex lanthanide mixtures into two overlapping groups were reported using a simulated counter-current extraction.

Weaver, Topp and Kappelman (27) used a Varsol-tributyl phosphate organic phase and a nitric acid-rare earth nitrate aqueous system to prepare about a kilogram of 95 per cent gadolinium oxide. The remaining five per cent was essentially samarium with a small amount of dysprosium and terbium. However, the lanthanide starting material contained in terms of oxides about 66 per cent gadolinium, 15 to 20 per cent dysprosium, 3.0 to 5.0 per cent erbium and 1.0 to 3.0 per cent yttrium plus the other heavy rare earths. Two separate experiments employing an 11 stage York-Scheibel extraction



column were required for this separation with 57 per cent of the total gadolinium recovered having a purity of 95 per cent. It was also reported that temperature increases resulted in a decrease in the total material transferred into the organic phase. The lanthanide distribution coefficients appeared to be nearly independent of rare earth concentration.

Investigation of the liquid-liquid extraction of a samarium and neodymium nitrate mixture dissolved in 12 molar nitric acid with various Varsol-tributyl phosphate compositions was reported by Topp (28). A nearly constant separation factor of 2.8 resulted between these two elements although the temperatures and lanthanide concentrations were varied. The distribution values for these two elements were dependent upon temperature and independent of rare earth concentrations.

In a report by Bochinski, Smutz and Spedding (11) the partial separation of the lanthanide nitrates obtained from a monazite sand was discussed. They employed tributyl phosphate in various dilutions as the organic phase. Very little nitric acid was present in the aqueous phase. The starting mixture based on the oxides analyzed approximately 15 per cent praseodymium, 75 per cent neodymium, 6 per cent samarium and 4 per cent gadolinium plus minor amounts of others. The aqueous product was 25 per cent praseodymium, 75 per cent neodymium while the organic phase product

contained 48 per cent samarium and 34 per cent gadolinium plus others as oxides. Separation factors at these low acid conditions were reported to increase with increasing rare earth concentration but were independent of the particular rare earths in the mixture. It was also observed that the mass transfer to the organic phase was a function of lanthanide concentration and virtually independent of lanthanide composition. At high rare earth concentrations the per cent mass transfer of lanthanides to the organic phase was decreased by nitric acid while an increase in per cent mass transfer was reported at low lanthanide concentrations. Aluminum nitrate increased the per cent mass transfer to the organic phase most at a low rare earth concentration. Diluents in the tributyl phosphate were found to decrease both mass transfer to the organic phase and the rare earth separation factors. They assumed that for a given nitric acid concentration the separation factors were a function of the total rare earth concentration and completely independent of the lanthanide components. Distillation calculations were then employed to determine equilibrium equations for predicting the product compositions when extracting this multicomponent rare earth mixture.

All of the reported liquid-liquid extraction studies on rare earth separations employing tributyl phosphate have been carried out on dilute lanthanide solutions (26) or on mixtures

consisting essentially of only the light rare earths (11, 27-29). Separation of rare earth salts containing relatively large amounts of yttrium, dysprosium, gadolinium and the heavy rare earths by liquid-liquid extraction have not been reported. The report of Peppard and co-workers (26) on experiments employing dilute solutions indicated that separation of these heavier rare earths in high concentrations might be possible. In the extraction studies reported here the separations of rare earths that were obtained from Fergusonite ore, from Gadolinite and from the tailings of an ion-exchange column are discussed. The concentration and separation of yttrium from the rare earths was the primary objective of this work. However, the close association of yttrium with gadolinium and dysprosium required a detailed study involving the separation of these three elements from one another.

#### B. Experimental Details

The techniques employed in this investigation for the separations of yttrium and rare earth salts dissolved in mineral acids involved liquid-liquid extractions. Various yttrium-lanthanide salt mixtures, salting-out agents, mineral acids and water immiscible organic liquids were tested. In some experiments the organic phase was first acidified with an equal volume of aqueous phase containing only the mineral

acid to be used in the extraction. The acid concentration in the aqueous phase used for this treatment equaled the initial acid concentration of the feed solution containing the yttrium-rare earth salt mixture. The acid in the organic solution however was not after this treatment at the equilibrium concentration to be attained in the extractor.

The aqueous feed solutions consisting of yttrium and rare earth salts were usually prepared by dissolving the oxides directly in the mineral acid. However for preparing low acidity feed solutions the hydroxides were first precipitated with ammonium hydroxide from a mineral acid solution. After this hydroxide precipitate was washed with water to remove the residual ammonium ions, it was dissolved in a minimum amount of the desired mineral acid. This technique was useful in obtaining stable concentrated yttrium-rare earth nitrate solutions having as little as 0.06 molar free nitric acid.

The acid concentration of the aqueous and organic phases containing no inorganic salt was determined by titration with sodium hydroxide using phenolphthalein as the indicator. However before analyzing the organic phase for its acid concentration, acetone and water were added. The former compound insures a homogeneous phase while the latter compound allows sufficient dissociation of the indicator to observe the titration end point.

In the presence of the yttrium-rare earth salts and certain salting-out agents phenolphthalein could not be used as the indicator for determination of the acid concentration. Because of their reaction with sodium hydroxide these rare earth salts start to precipitate at about a pH of 4. Consequently an alcoholic solution of bromphenol blue which changes from yellow to blue in the pH range of 3.0 to 4.6 was employed as the indicator. The indicating effect of bromphenol blue was destroyed (probably by adsorption) when the end point was reached if it were added to the aqueous solution at the beginning of the titration. Therefore the indicator was not added until sufficient sodium hydroxide was present to form the first permanent precipitate. The blue solution was then back-titrated with standard acid until the yellow color persisted for about 60 seconds. This titration was reproducible to within 5 per cent of an average value. It is believed that this technique indicated the free acid concentration within 10 per cent of its actual value. With several mixtures of known composition a pseudo-molecular weight, based on the relative proportions of each component, was calculated. This molecular weight permitted the determination of the number of acid equivalents required to react with the mixed oxides. Several comparisons of these two methods for obtaining the acid concentration indicated that the values obtained from the bromphenol blue titrations

were consistently 5 to 15 per cent lower than the values calculated from assuming an average molecular weight.

All single and multistage extractions were carried out at room temperature. In the single stage tests the organic and aqueous phases were placed in a separatory funnel and agitated vigorously by shaking for at least 60 seconds to insure equilibrium conditions. The equilibrium phases were allowed to separate and their volumes were then measured. Analytical data on the contents of each phase then permitted calculation of the yttrium and the rare earth distribution coefficients and their separation factors. The apparatus employed for the multistage extractions of the yttrium-rare earth mixtures appears in Figure 1.

After extraction of the aqueous solution with an organic phase the yttrium plus rare earth content of each phase was determined. The yttrium and rare earth oxalates were quantitatively precipitated directly from the low acidic aqueous phase by addition of a water solution of oxalic acid. For the highly acid systems ammonium hydroxide was first added to adjust the pH of the aqueous phase to about one. Addition of oxalic acid then insured quantitative and rapid precipitation. Asselin, Audrieth and Comings (25) concluded that either ammonium hydroxide or oxalic acid gives a quantitative precipitation of rare earths from aqueous acidic solutions. The oxalate precipitate is slightly granular and consequently

can be filtered and washed much easier than the gelatinous yttrium and rare earth hydroxides.

For recovering the yttrium and rare earths from the organic phase it was found that two separate equal volume water scrubs of the organic phase was usually sufficient to back-extract all of the material. However, three separate equal volume water scrubs were usually employed. Addition of oxalic acid to the composite aqueous scrub solutions resulted in the quantitative recovery of the oxalates. A direct oxalic acid precipitation of the yttrium and rare earths from the organic phase is possible although the addition of acetone is desirable to insure a homogeneous phase and ease of filtration. It is apparent that such a precipitation from the organic phase would probably make the recovery of the organic phase difficult. In preparation of analytical samples the oxalates were converted to oxides by calcining at 600 degrees Centigrade for at least two hours.

Analyses of the complex oxide mixtures required both spectrographic and spectrophotometric methods. All percentages are expressed on an oxide weight basis with the values referred to the total oxide weight of the sample. Some results were obtained from a series of analyses on similar samples and consequently represent an average value.

A spectrophotometric method similar to that proposed by Moeller and Brantley (184) was used to analyze the complex

rare earth mixtures for the oxide percentages of samarium, praseodymium, neodymium and dysprosium. This method required about 0.2 gram of the rare earth oxide mixture dissolved in 10.0 milliliters of a 10 per cent aqueous solution of hydrochloric acid. When employing a one centimeter spectrophotometric cell in the rare earth analyses the lower limits of detection were about 0.3 per cent for praseodymium, 0.5 per cent for neodymium and 1 per cent for samarium and dysprosium. This procedure is believed to be accurate to within  $\pm 5$  per cent of the total content of dysprosium, neodymium or praseodymium and  $\pm 10$  per cent of the samarium. The presence of minor amounts of other rare earths and common impurities should not alter these values (185) beyond these limits of error.

The spectrographic method of Fassel (186) was employed for analyzing the complex oxide mixtures for percentages of yttrium oxide and gadolinium oxide. This procedure required addition of ceric oxide as an internal standard to the complex yttrium-rare earth oxide mixture. A standard deviation of  $\pm 2.5$  per cent with a lower limit of detection of about 3.0 per cent for gadolinium oxide and for yttrium oxide was reported for this method. All qualitative analyses of the yttrium-rare earth mixtures were also done by spectrographic techniques.



### C. Results and Discussion

#### 1. Separation of the yttrium and rare earths obtained from the ion-exchange column tailings

(a) Introduction. In the ion-exchange method employed by Spedding (175-177) for producing pure rare earth salts an yttrium-lanthanide chloride mixture constitutes the charge for the resin columns. The rare earths and yttrium pass through the column as a series of separate bands which are collected individually with some overlapping. The heaviest of the rare earths emerge from the column first. After holmium and some of the dysprosium has been collected yttrium appears in the product. When the yttrium-lanthanide fraction from Gadolinite ore composed the initial mixture yttrium oxide constituted more than 50 per cent of the total weight. In many cases only the production of heavy rare earth salts was desired in the work of Spedding and co-workers. Consequently yttrium and the remaining light rare earth salts were stripped from the columns as a composite product. These column strippings, or tailings, were available and served as one rich source of yttrium for the present investigation. The partial composition of the column tailing yttrium-lanthanide mixture appears in Table 15 under the heading "initial percentage." The unaccounted for material in the

mixture is probably lanthanum, cerium, and perhaps a small amount of heavy rare earths.

A method was desired in which most of the yttrium could be cheaply and rapidly removed from this light rare earth fraction. The recovered light rare earth fraction low in yttrium could then be employed as a charge for another ion-exchange column process to prepare the individual light rare earths. Such an increase in the per cent of light rare earths per charge would at least double the production rate for pure light rare earth salts from a given column.

According to the report of Peppard and co-workers (26) and from the analysis of this mixture the separation of yttrium and dysprosium from gadolinium should result in a concentrated light rare earth fraction. Since maximum rare earth separation factors were reported at high nitric acid concentrations an aqueous nitrate solution of the column tailings containing 13 molar nitric acid was employed for the first extraction. Highly acidified tributyl phosphate constituted the organic phase.

In order to quickly estimate the nitric acid concentration in the acidified organic phase a series of extractions was carried out in which pure tributyl phosphate was contacted with an equal volume of aqueous phases containing various nitric acid concentrations. The equilibrium phases were titrated for nitric acid concentration. Figure 19 shows

the equilibrium nitric acid concentration in the two phases. From Figure 19 it is apparent that a 13 molar nitric acid aqueous phase is in equilibrium with tributyl phosphate containing a nitric acid concentration of about 5.0 molar.

Table 15

Analysis of the Mixtures from the Column Tailings Before and after the Multistage Extraction

Component	Initial percentage	Product phase percentage	
		Aq.	Org.
Pr <sub>6</sub> O <sub>11</sub>	2.0	3.4	N.D.
Nd <sub>2</sub> O <sub>3</sub>	7.6	22.	N.D.
Sm <sub>2</sub> O <sub>3</sub>	5.7	16.	N.D.
Gd <sub>2</sub> O <sub>3</sub>	8.4	22.	N.D.
Dy <sub>2</sub> O <sub>3</sub>	4.0	4.4	2.4
Y <sub>2</sub> O <sub>3</sub>	66.	24.	91.
Total	93.7	91.8	93.4

N.D. - Not detected.

(b) Single stage extractions of the ion-exchange column tailings. Several single stage extractions were carried out to aid in selecting the proper flow rates to use in the 20 stage extractor. The aqueous phase which was 13 molar in nitric acid contained the equivalent of 52 grams of the oxides from the tailings per liter. Various relative volumes of the tributyl phosphate which was 5.0 molar in nitric acid

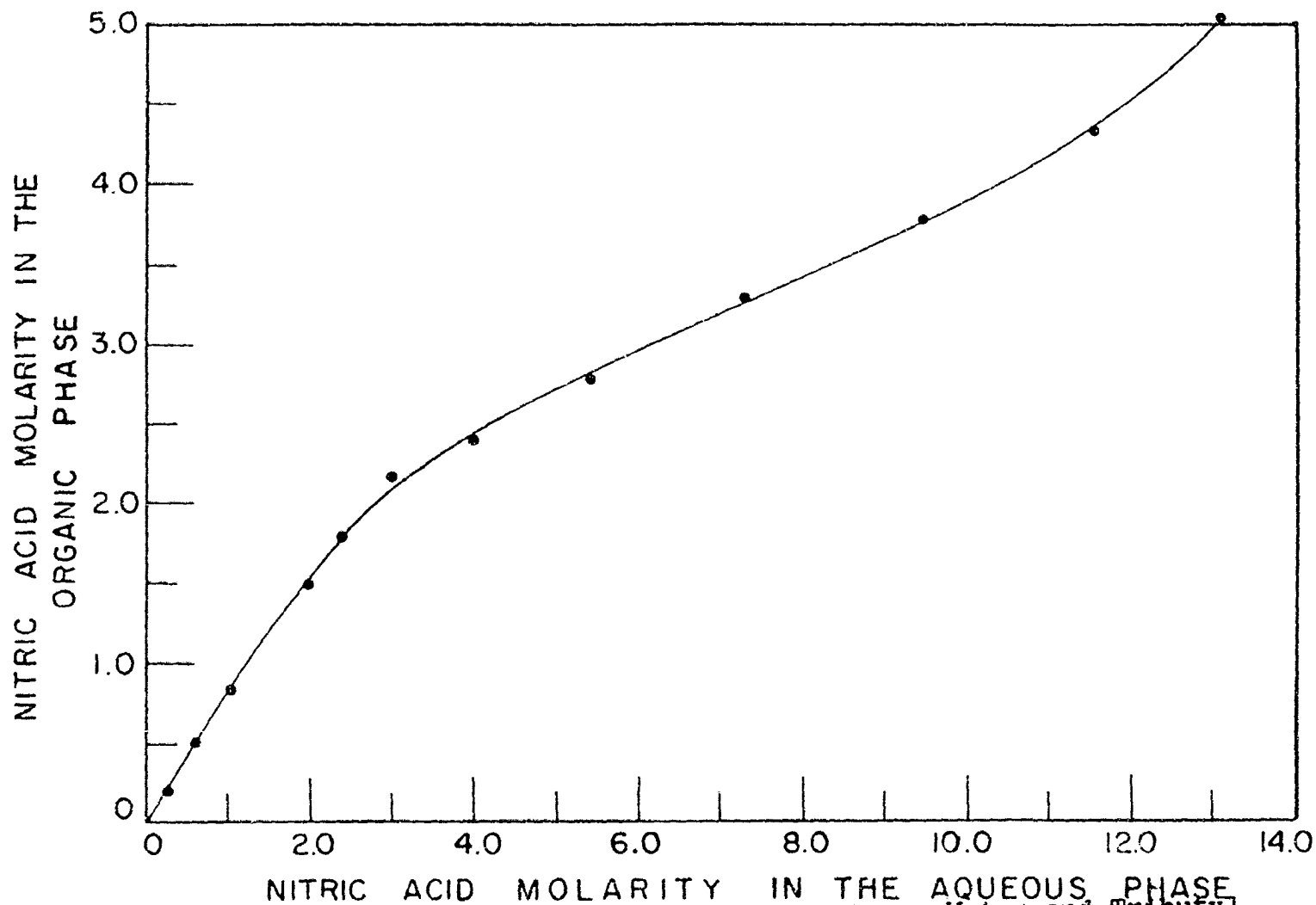


Figure 19 - Distribution of Nitric Acid between Water and Tributyl Phosphate.

was employed as the organic phase. Table 16 contains the results of these extractions.

Table 16

Single Stage Extraction Data for Separating the Yttrium-Rare Earth Nitrates Obtained from the Column Tailings

Org./ aq. vol.	% oxide weight in org.	Equil. anal.				Dist. coef.		Gd-Y sepn. factor
		% Gd <sub>2</sub> O <sub>3</sub>		% Y <sub>2</sub> O <sub>3</sub>		K <sub>Gd</sub>	K <sub>Y</sub>	
		Aq.	Org.	Aq.	Org.			
1	72.1	10.6	6.2	33	67	1.51	4.97	3.29
3	89.5	5.9	8.3	15	67	3.92	13.6	3.47
9.	97.4	3.6	8.6	5.9	64	9.87	44.7	4.53

It is apparent from Table 16 that the gadolinium-yttrium separation factors and the per cent mass transfers increased with the increased organic to aqueous phase volume ratio. According to Peppard and co-workers (26), who obtained distribution data on dilute solutions of the pure rare earth salts, the gadolinium-yttrium separation factor should be about 5.0 for a nitric acid concentration of 13 molar. This value is being approached as the concentrations of the rare earth salts in the equilibrium phases decrease.

(c) Multistage extraction of the ion-exchange column tailings. Since this original mixture contains 66 weight

per cent yttrium oxide and 4 per cent dysprosium oxide it is apparent from the mass transfer data in Table 16 that nearly equal volumes of the organic and aqueous phases are required for a desirable split of these two elements from the lighter rare earth portions. Consequently, a twenty stage counter-current extraction was carried out in which four volumes of organic, one volume of aqueous feed and four volumes of aqueous scrub were added for each cycle of operation. The aqueous feed contained the equivalent of 267 grams of the oxides per liter. It is apparent that when the one volume of aqueous feed mixed with the four volumes of aqueous scrub a concentration equivalent to about 53 grams of oxides per liter resulted. Both the aqueous feed, introduced at stage 11, and the aqueous scrub, introduced at stage 20, were 13 molar in nitric acid. The organic phase was tributyl phosphate which had been pre-equilibrated with 13 molar nitric acid. It was added to the extractor at stage 1. The relative flow rates from stages 1 to 11, or the organic scrubbing section, were five volumes of aqueous to four volumes of organic while from stages 12 to 20, or the aqueous scrubbing section, a one to one volume ratio existed.

This extraction was carried out for 176 cycles although steady state based on the gadolinium and yttrium analyses and total oxide concentration was reached at about the 150th cycle. About 65 cycles and 100 cycles, respectively, of

operation were necessary for gadolinium and yttrium to reach the aqueous outlet end of the extractor. Yttrium appeared in the organic product in the early stages of the extraction. Steady state analyses of the organic and aqueous product phases appear in Table 15.

The mass transfer of material to the organic product phase was about 60 per cent of the total weight as oxides. As indicated in Table 15 the organic product phase was primarily yttrium although a small amount of dysprosium was also present. On the other hand the aqueous product phase contained almost a quantitative recovery of the light rare earths. Consequently, this extraction based on oxides yielded a 90 per cent recovery of yttrium which was 91 per cent pure and about a threefold increase in the concentration of the light rare earths.

The results of this multistage extraction agree in general with the ideas presented by Peppard and co-workers (26). It is apparent that as the atomic number of the rare earths increase their preference to be extracted from a highly concentrated nitric acid solution by this organic phase also increase. For extracting a 13.0 molar nitric acid aqueous solution of rare earths and yttrium with a nearly equal volume of tributyl phosphate the rare earth phase preference should have reversed between element 61 and 62 according to Peppard and co-workers (26). However, the

change in phase preference appeared just above the element with atomic numbers 66, or dysprosium. This deviation from the ideal predicted position was probably caused by the increased salt concentration. Peppard's distribution coefficients were obtained by extracting very dilute solutions of pure individual rare earth nitrates. The presence of the large amount of yttrium with the rare earth mixture might also cause a shift in individual distribution coefficients.

The results from the stagewise analyses of the aqueous and organic phases for total oxide, gadolinium and yttrium concentrations at steady state conditions appear in Figures 20, 21 and 22. From Figure 20 it is apparent that in many stages the concentration expressed as oxide was greatest in the organic phase. This was expected since yttrium which prefers the organic phase constituted more than half the starting mixture. Little variation in concentration in either phase took place in stages 6 to 11 inclusive but at the ends of the extractor sharp decreases in concentrations appeared. This indicates that refluxing both the organic and aqueous product liquids would be useful in obtaining more highly concentrated products.

From Figure 21 it can be noted that gadolinium was not present in the organic phase beyond the feed stage, stage 11. Since this element was detected in the aqueous phase up to



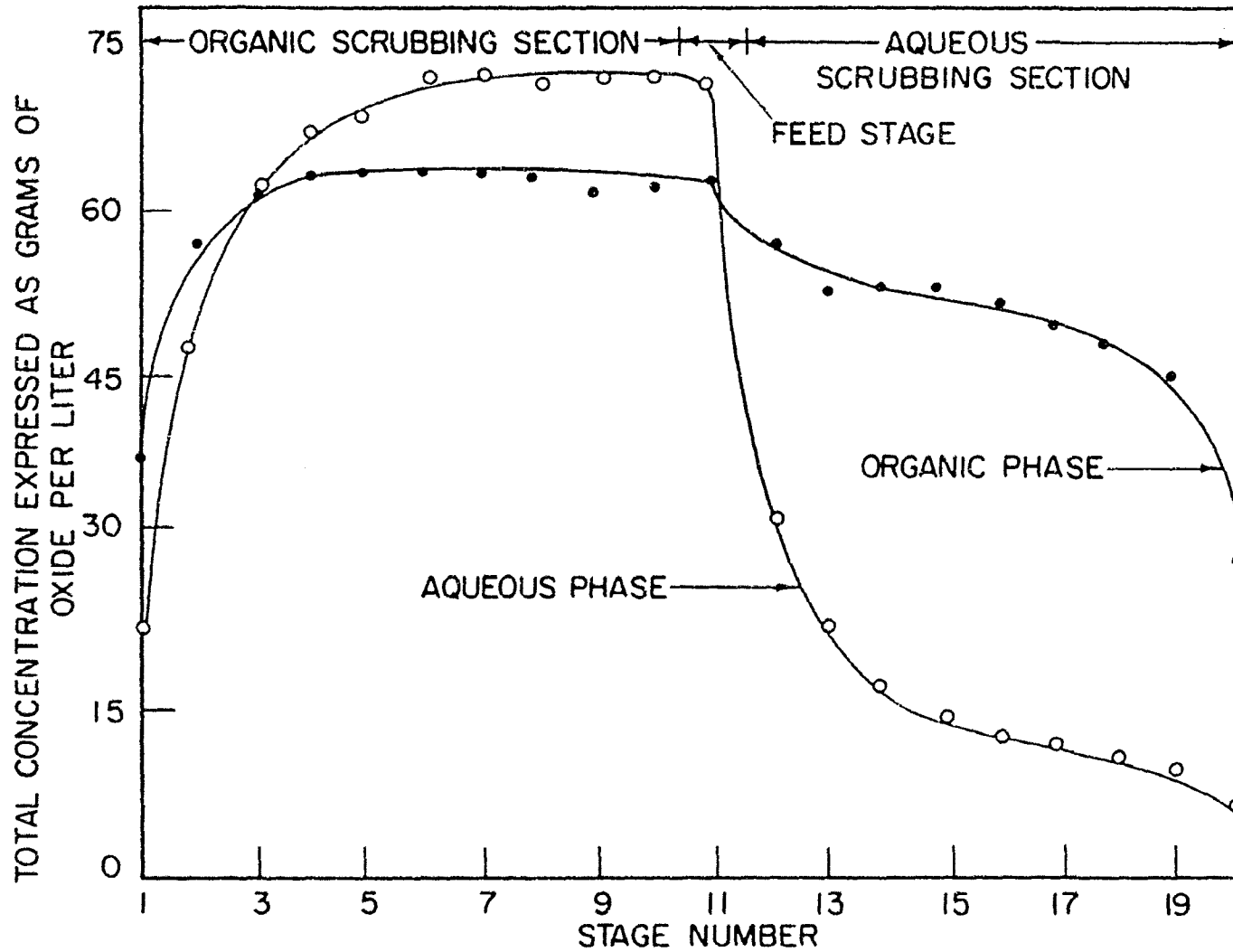


Figure 20 - Yttrium Plus Rare Earth Concentration in the Equilibrium Liquid Phases as a Function of Stage Number.

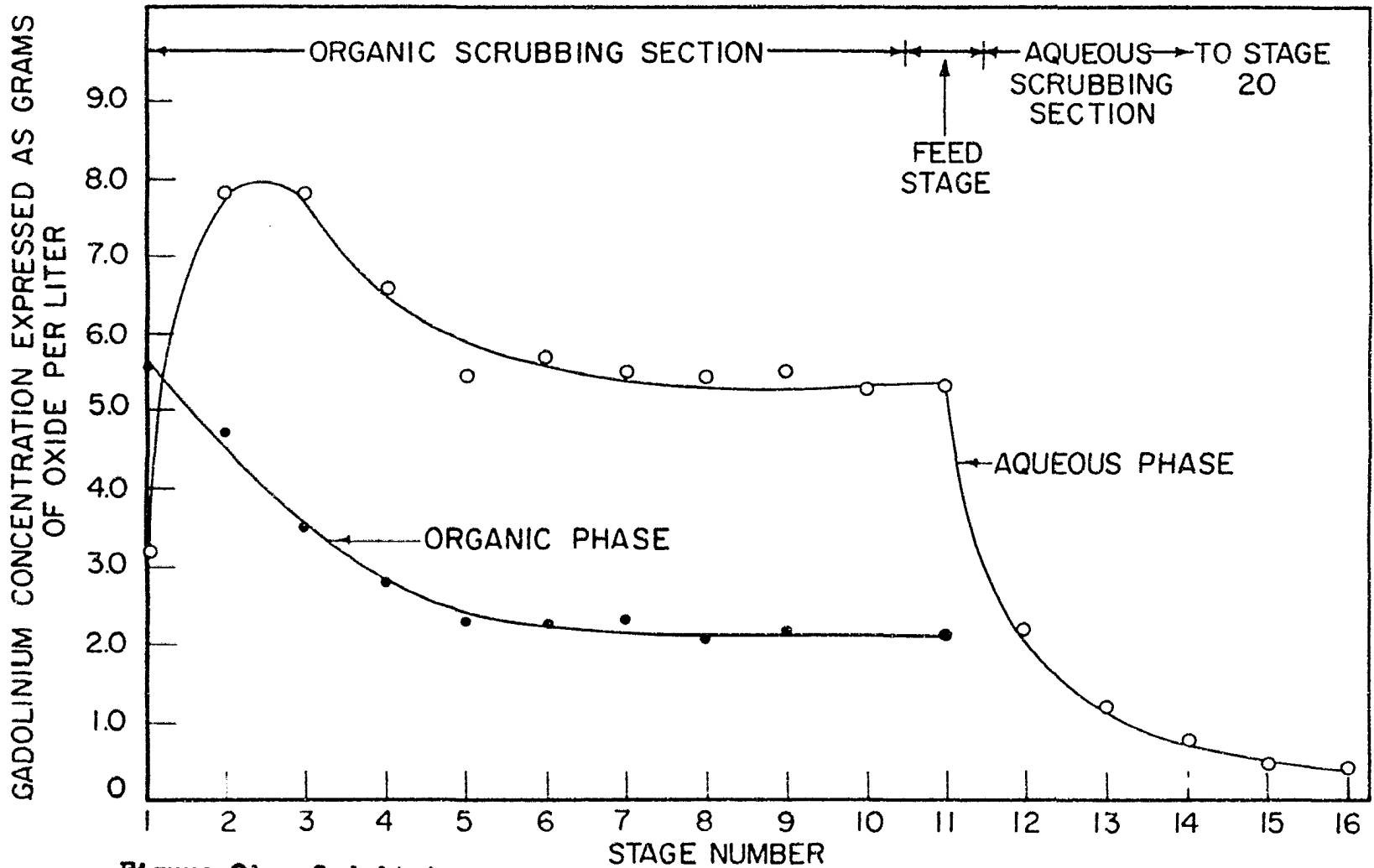


Figure 21 - Gadolinium Oxide Concentration in the Equilibrium Liquid Phases as a Function of Stage Number.

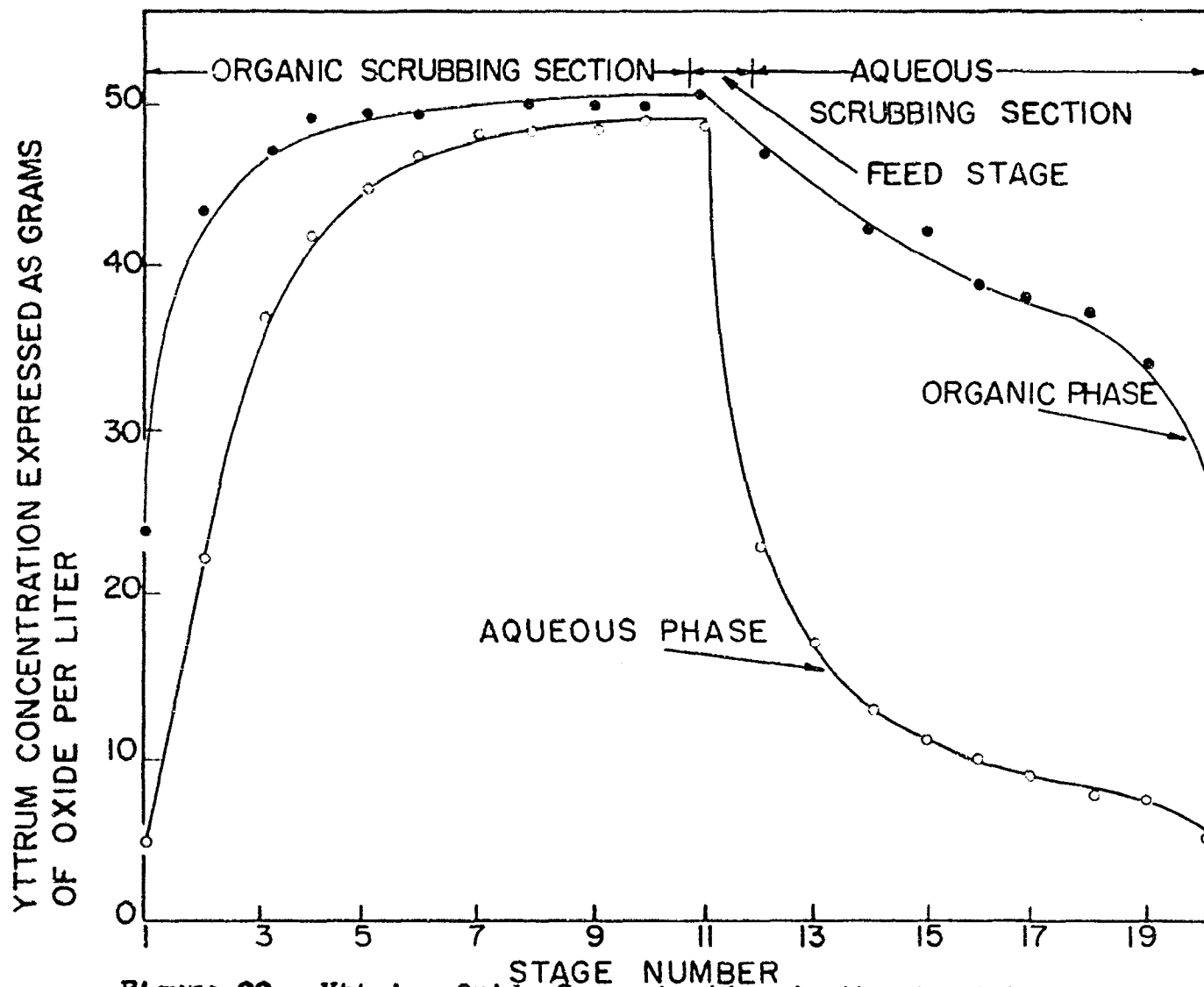


Figure 22 - Yttrium Oxide Concentration in the Equilibrium Liquid Phases as a Function of Stage Number.

stage 16 there must have been gadolinium in the equilibrium organic phase to at least this stage. Evidently the amount of gadolinium in the organic phase from stages 12 to 16 was below the limit of detection (less than 3.0 per cent) by the analytical method employed. As is indicated by Figure 22 this condition did not exist for yttrium. It is also evident from Figures 21 and 22 that on a concentration basis yttrium favored the organic phase in every stage while gadolinium favored the aqueous phase in every stage except in stage one. The sharp decrease in the yttrium and gadolinium concentration at the ends of the extractor could probably have been prevented by refluxing.

The distribution coefficients and separation factor for gadolinium and yttrium as a function of stage number were calculated from the data in Figures 21 and 22 and plotted in Figure 23. Since gadolinium was not detected in the organic phase beyond stage 11 a distribution value could not be calculated past this stage. It is apparent from Figure 23 that only a small deviation resulted for the distribution values and for the gadolinium-yttrium separation factor from stages six to 11 inclusive. Since the concentration data for total oxides, gadolinium oxide and yttrium oxide appearing in Figures 20, 21 and 22 also indicated little change in these stages it appears that the extractor might be shortened about six stages while obtaining the same results.

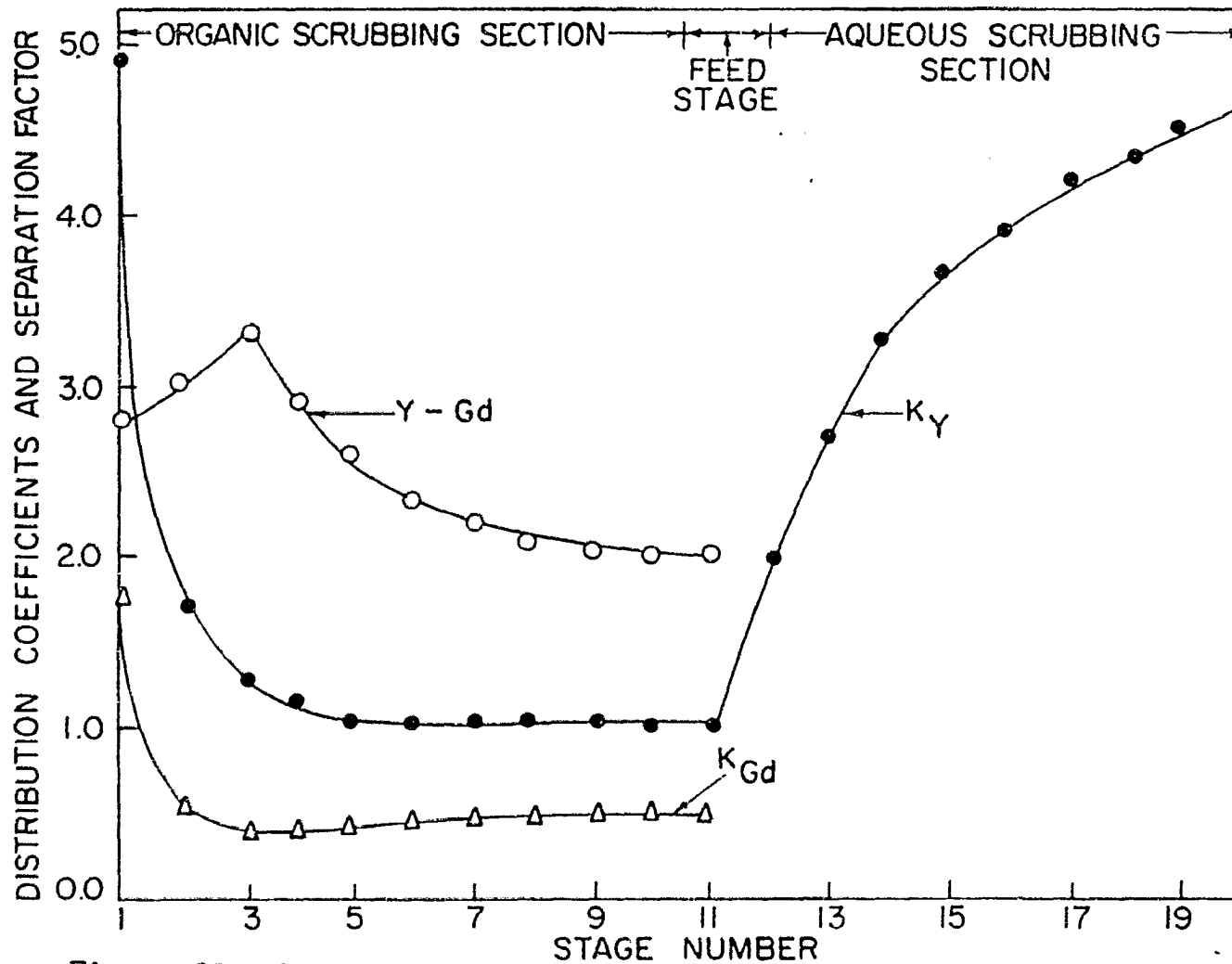


Figure 23 - Yttrium and Gadolinium Distribution Coefficients and their Separation Factor as a Function of Stage Number.

Figure 23 also indicates that the gadolinium-yttrium separation factor reaches a maximum value of about 3.3 when the gadolinium oxide concentration had a maximum value in the aqueous phase.

This multistage extraction was successful in concentrating an yttrium oxide fraction analyzing 66 per cent to one analyzing 91 per cent and at the same time concentrating the light rare earths of the initial fraction by almost threefold. Since only 60 per cent of the total oxide weight was delivered by the organic product phase better results would probably be obtained by increasing the organic phase volume by about 20 per cent per cycle. The conditions employed for this multistage extraction were approximately the same as those listed in the first single stage extraction reported in Table 16. However, the yttrium and gadolinium distribution coefficients as well as the over-all mass distribution were different while their separation factor was quite similar. This indicates that the single stage extraction data sometimes serve only as a means of estimating the conditions to be employed and results to be expected in a multistage extraction. Although the maximum separation of yttrium from these light rare earths was not expected in this first multistage extraction these results indicate that liquid-liquid extraction would certainly be

useful for concentrating both the yttrium and the light rare earths from their mixtures.

2. Concentration and separation of yttrium and rare earths obtained from Fergusonite ore

(a) Introduction. The results from extracting the yttrium-rare earth mixtures from the ion-exchange column tailings indicated that light and heavy rare earth fractions should easily be obtained by processing complex lanthanide mixtures. Further separation, assuming proper adjustment of such variables as acidity, concentration and flow rates, should also be possible by application of liquid-liquid extraction. Consequently the yttrium-rare earth concentrate from Fergusonite ore, which is mined near Kingman, Arizona, was separated into several fractions by this method.

Fergusonite ore, which is slightly radioactive, is an oxide composed essentially of yttrium, rare earths, niobium and tantalum. The yttrium-rare earth oxide mixture constitutes about 25 per cent by weight of the ore while the niobium and tantalum oxides constitute approximately 40 per cent. The rare earth fraction from this ore is relatively high in gadolinium. The yttrium-rare earth oxide mixture is composed of about 50 per cent yttrium and contains only small quantities of the heavy rare earths. It is shown here that a preliminary separation of yttrium plus the few heavy rare

earths from gadolinium and the other light rare earths could be accomplished by liquid-liquid extraction. The heavy and light lanthanide fractions which could also constitute charges for an ion-exchange column were separated further by other extractions.

(b) Processing of Fergusonite ore. The fusion of an alkali mixture in the presence of Fergusonite ore was used to render this mineral in a soluble form. A suitable charge consisted of 10.0 grams of finely ground ore, 8.0 grams of sodium hydroxide and 4.0 grams of sodium peroxide. Grinding the ore resulted in a smaller amount of unreacted material. This mixture was heated in a stainless steel crucible for about 30 minutes at approximately 650 degrees Centigrade. After allowing the fusion product to cool, a hot 1.0 molar sodium hydroxide leach was employed to remove much of the aluminum, tin and silicon. This basic liquid was filtered and the remaining solid mass leached with boiling 3.0 molar nitric acid for about ten minutes. When this acidic liquid was filtered, oxalic acid was added to the filtrate to precipitate the yttrium and rare earths as oxalates. The liquid obtained from filtering these yttrium and rare earth oxalates contained iron, aluminum, titanium, manganese, magnesium and calcium and a radioactive material. This radioactive substance is believed to be uranium. The material which did not dissolve in either the sodium hydroxide or the



nitric acid leaches was treated with concentrated hydrofluoric acid to dissolve the niobium and tantalum fraction. The unreacted ore remained and was recovered as a residue since it is relatively inert to these three leaches. Table 17 gives the relative weights as oxides in each fraction from the leaching treatments while Table 18 shows the quantitative and Table 19 the qualitative analysis of the yttrium-rare earth concentrate. The total minor impurities probably do not constitute more than three per cent of the entire weight.

Table 17

Weights of Various Fractions from a Caustic Fusion Treatment of 10.0 Grams of Fergusonite Ore

Operation	Oxide weight
1. Soluble in NaOH leach	0.89 g.
2. Soluble in HNO <sub>3</sub> leach	
(a) Oxalic acid precipitation	2.51 g.
(b) NH <sub>4</sub> OH precipitation of filtrate from (2a)	2.05 g.
3. Soluble in HF leach	3.99 g.
4. Insoluble (unreacted ore)	0.53 g.
Total	9.97 g.

(c) Single stage extractions of the yttrium-rare earth concentrate from Fergusonite ore. The multistage extractions

Table 18

Partial Analysis of the Yttrium-Rare Earth Oxide Concentrate  
from Fergusonite Ore

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Component	Analysis (wt. %)
$\text{Pr}_6\text{O}_{11}$	2.0%
$\text{Nd}_2\text{O}_3$	10.0%
$\text{Sm}_2\text{O}_3$	10.0%
$\text{Gd}_2\text{O}_3$	11.0%
$\text{Dy}_2\text{O}_3$	7.0%
$\text{Ho}_2\text{O}_3$	< 1.0%
$\text{Er}_2\text{O}_3$	< 2.0%
$\text{Yb}_2\text{O}_3$	< 2.0%
$\text{Y}_2\text{O}_3$	50.0%

---

Table 19

Qualitative Analysis for Common Impurities in the Yttrium-  
Rare Earth Concentrate from Fergusonite Ore

Element	Analysis	Element	Analysis
Ca	W	Nb	W
Cu	W	Si	VW
Cr	W	Sn	VW
Fe	W	Ti	--
Mg	VW	Ta	--
Mn	VW	Zr	W
Na	W		

W - Weak.

VW - Very weak.

-- - Not detected.

of the yttrium-rare earth mixture obtained from the ion-exchange column tailings showed that a concentrated nitric acid medium tended to concentrate the light rare earths and yttrium fractions in different phases. This was accomplished in a system having a gadolinium-yttrium separation factor of about three. Because of the excessive cost and corrosiveness of concentrated nitric acid, single stage extractions employing less acidic conditions were carried out and the results compared with those for the highly acid systems. Various mineral acid systems, effects of hexone and tributyl phosphate and additions of ammonium thiocyanate were investigated. The yttrium-rare earth fraction from Fergusonite ore was dissolved in the proper aqueous phase and then extracted with an equal volume of the organic phase in each case. Only the gadolinium-yttrium separation factor was determined as this value was assumed to give a good indication of the trends for the other components in the system.

In Table 20 the equilibrium data appear for single stage extractions employing tributyl phosphate which had been pre-equilibrated with an equal volume of 6.0 molar nitric acid. The initial aqueous feed phase was 6.0 molar in nitric acid and contained the equivalent of 100 grams of total oxides per liter. Various amounts of hydrochloric, acetic or sulfuric acid were added to the aqueous feed phase before the extraction.

Table 20

Effect of Acid Addition on the Single Stage Extraction Data  
for Yttrium and Rare Earths from their 6.0 M HNO<sub>3</sub> Solution

(Yttrium-Rare Earth Fraction from Fergusonite Ore)

Init. aq. phase Acid added	Conc. % of oxide acid added in (m.) org.		Equil. anal. % Gd <sub>2</sub> O <sub>3</sub> % Y <sub>2</sub> O <sub>3</sub>				Dist. coef. K <sub>Gd</sub> K <sub>Y</sub>		Gd-Y sepn. factor
	Aq.	Org.	Org.	Aq.	Org.				
----	0	35.1	13.3	9.9	51	51	0.38	0.52	1.37
HCl	0.50	34.9	15.4	10.5	52	58	0.34	0.55	1.62
HCl	1.0	33.3	13.7	9.4	50	61	0.32	0.57	1.78
HCl	2.0	37.3	13.6	8.8	48	57	0.34	0.64	1.88
HAc	0.50	37.1	13.6	9.7	48	58	0.39	0.67	1.72
HAc	1.0	35.8	13.4	9.1	49	58	0.36	0.61	1.70
HAc	2.0	39.1	13.6	9.3	49	55	0.40	0.66	1.65
HAc	4.0	44.7	13.8	10.0	48	59	0.52	0.74	1.42
H <sub>2</sub> SO <sub>4</sub>	0.25	33.3	15.3	9.5	50	57	0.29	0.55	1.90
H <sub>2</sub> SO <sub>4</sub>	0.50	32.0	15.3	9.4	49	58	0.27	0.53	1.97
H <sub>2</sub> SO <sub>4</sub>	1.0	32.0	16.4	8.0	53	61	0.21	0.50	2.38
H <sub>2</sub> SO <sub>4</sub>	2.0	22.0	12.8	7.6	49	61	0.15	0.33	2.20

From the data in Table 20 it is apparent that the gadolinium-yttrium separation factor for the 6.0 molar nitric acid system was 1.37. This value is less than one half of that obtained from an extraction employing a concentrated nitric acid system and the yttrium-rare earth mixture from the column tailings. These data indicate that decreases in the nitric acid concentration decreases the separation factor as reported by Peppard and co-workers (26). It is also apparent that for extracting this 6.0 molar nitric acid medium the mass transfer to the organic phase as well as the yttrium and gadolinium distribution coefficients were considerably lower than those for extracting the 13.0 molar nitric acid system. However, since these distribution coefficients and separation factors were obtained for slightly different mixtures and at a different total concentration only a qualitative comparison is possible.

Addition of hydrochloric acid to the initial aqueous phase resulted in a definite increase in the gadolinium-yttrium separation factors while not essentially affecting the mass transfers to the organic phase. This increase in separation factor is probably due somewhat to the increased acidity of the aqueous phase although the rapid increase up to about 1.0 molar hydrochloric acid indicates that the presence of small amounts of chloride ions may also be significant.

The addition of acetic acid to the initial aqueous phase resulted in some unexplainable effects on this nitric acid system. In general as the concentration of acetic acid increased the mass transfer to the organic phase also increased. Addition of a small amount of acetic acid to the initial aqueous phase resulted in a large increase in the gadolinium-yttrium separation factor. On further addition of this organic acid the value decreased until at 4.0 molar acetic acid the separation factor was nearly equal to that obtained for the pure 6.0 molar nitric acid system. No explanation can be given for these results although it is evident that the presence of excess acetic acid decreases the gadolinium-yttrium separation factor.

When sulfuric acid was added to the 6.0 molar nitric acid system the mass transfers to the organic phase definitely decreased while the gadolinium-yttrium separation factors generally increased. The holdback effect of sulfuric acid did not become appreciable until a concentration of 2 molar was reached. Although this sulfate-nitrate system yielded a gadolinium-yttrium separation factor as high as 2.4, the decrease in mass transfer indicates that a high relative organic solvent rate would be required in a multistage liquid-liquid extraction of such a system.

Table 21 contains the single stage data from extracting an all chloride system. The yttrium-rare earth fraction from Fergusonite ore was dissolved in varying amounts of hydrochloric acid to give a solution containing the equivalent of 95 grams of oxides per liter. Since very little hydrochloric acid will dissolve in tributyl phosphate the organic phase employed for these extractions was not pre-equilibrated with acid.

It is apparent from these data that as the concentration of hydrochloric acid increases the per cent mass transfer to the organic phase also increases while the gadolinium-yttrium separation factors remain essentially constant. Comparison of the data for the all nitrate and all chloride systems show that approximately six times more material was extracted by the organic phase from the corresponding nitrate system. The gadolinium-yttrium separation factor was also substantially higher for this nitrate system. It is apparent from these data that the nitrate system is much more effective than the chloride system for the separation of yttrium from gadolinium. This generality has been reported by other investigators (25,66) while employing alcohols, esters, ketones, ethers and hydrocarbons as the organic phase and extracting mixtures of lanthanum and neodymium (66) and neodymium and erbium (25).



A single stage extraction of the 6.0 molar hydrochloric acid solution of yttrium and rare earth chlorides was carried out with pure methyl isobutyl ketone (hexone) constituting the organic phase. Only 1.34 per cent of the

Table 21

Effect of HCl Addition on the Single Stage Extraction Data for the Yttrium-Rare Earth Chlorides Employing Tributyl Phosphate

(Yttrium-Rare Earth Concentrate from Fergusonite Ore)

HCl conc. in aq. phase (m.)	% oxide wt. in org.	Equil. anal.				Dist. coef.		Gd-Y sepn. factor
		% Gd <sub>2</sub> O <sub>3</sub> Aq.	Org.	% Y <sub>2</sub> O <sub>3</sub> Aq.	Org.	K <sub>Gd</sub>	K <sub>Y</sub>	
2	2.60	12.0	*	51	*	-----	-----	----
4	2.78	12.5	11.5	54	42	.0268	.0224	1.20
6	5.47	13.0	11.5	53	44	.0465	.0433	1.07
8	7.70	12.5	11.3	54	43	.0703	.0620	1.14
10	7.40	13.0	10.5	52	40	.0618	.0590	1.05

\*Insufficient sample for analysis.

material was transferred to the organic phase with a gadolinium-yttrium separation factor of only 1.02. When 3.0 molar ammonium thiocyanate was added to the initial aqueous yttrium-rare earth chloride solution a similar single stage extraction was carried out. At equilibrium

a mass transfer of 3.04 per cent of the total weight was detected in the organic phase with a gadolinium-yttrium separation factor of only 1.01. These extractions indicate that tributyl phosphate yields greater mass transfer to the organic phase with a higher gadolinium-yttrium separation factor than hexone under similar conditions. They also indicate that ammonium thiocyanate although increasing mass transfer to the organic does not affect the gadolinium-yttrium separation factor. These generalities were reported by other investigators (25,66) employing alcohols as the organic phase.

(d) Multistage extractions of the yttrium-rare earth fraction from Fergusonite ore. The single stage extractions with tributyl phosphate employing a concentrated nitric acid aqueous solution containing the yttrium-rare earth nitrates gave the most effective separation of yttrium from gadolinium. It is implied here that this system is also effective in separating the heavy rare earth fraction from the light rare earth fraction. Consequently, some of the multistage liquid-liquid extractions of this mixture from Fergusonite ore were carried out under conditions derived from these single stage extractions.

The 20 stage extractor illustrated in Figure 1 was used for all multistage extractions. The initial conditions and results of each extraction appear in Table 22. Stage 1

Table 22

Steady State Analyses for the Multistage Extractions of the Yttrium-Rare Earth Concentrate from Fergusonite Ore by Tributyl Phosphate

Ext. no.	Oxide conc. (g./l.)	HNO <sub>3</sub> conc. (m.)	Flow rate (ml./cycle)	Equil. anal. (wt. %)						% of product rep't.	% of oxide wt.	
				Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Dy <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>			
<u>Influents</u>												
	Aq. feed	195	13	10.0	2.0	10.0	10.0	11.0	7.0	50	90.0	
	Aq. scrub	0	13	15.0								
1	Org. scrub	0	5.0	30.0								
<u>Effluents</u>												
	Aq. prod.	35.5	---	24.0	4.3	19.7	17.2	19.0	6.8	21	88.0	44
	Org. prod.	40.7	---	27.0	N.D.	N.D.	N.D.	N.D.	7.2	80	87.2	56
-----												
<u>Influents</u>												
	Aq. feed	205	13	10.0	2.0	10.0	10.0	11.0	7.0	50	90.0	
	Aq. scrub	0	13	15.0								
2	Org. scrub	0	5.0	25.0								
<u>Effluents</u>												
	Aq. prod.	38.9	---	25.0	4.0	20.7	22.3	21.3	9.0	24	101.3	50
	Org. prod.	39.6	---	24.5	N.D.	N.D.	N.D.	N.D.	6.3	82	88.3	50

--- = Not determined.

N.D.= Not detected.

Table 22 (Continued)

Ext. no.	Oxide conc. (g./l.)	HNO <sub>3</sub> conc. (m.)	Flow rate (ml/cycle)	Equil. anal. (wt. %)						% of product rep't.	% of oxide wt.	
				Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Dy <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>			
<u>Influents</u>												
3	Aq. feed	100	8.0	10.0	2.0	10.0	10.0	11.0	7.0	50	90.0	
	Aq. scrub	0	8.0	15.0								
	Org. scrub	0	3.9	25.0								
<u>Effluents</u>												
	Aq. prod.	29.9	---	25.0	2.3*	12.6	12.5*	12.5	8.9	46	94.8	81
	Org. prod.	9.8	---	24.5	N.D.	N.D.	N.D.	N.D.	5.3	71	76.3	19
-----												
<u>Influents</u>												
4	Aq. feed	105	6.0	10.0	2.0	10.0	10.0	11.0	7.0	50	90.0	
	Aq. scrub	0	6.0	15.0								
	Org. scrub	0	3.0	20.0								
<u>Effluents</u>												
	Aq. prod.	38.4	---	23.8	2.0*	9.3	9.1	12.6	7.5	53	93.5	94
	Org. prod.	3.2	---	17.0	N.D.	N.D.	N.D.	N.D.	N.D.	35	35.0	5.6
-----												
<u>Influents</u>												
5	Aq. feed	100	2.0	10.0	N.D.	N.D.	N.D.	N.D.	7.2	80	87.2	
	Aq. scrub	0	2.0	15.0								
	Org. scrub	0	0.8	20.0								
<u>Effluents</u>												
	Aq. prod.	37.5	---	24.8	N.D.	N.D.	N.D.	N.D.	7.2	83	90.2	98
	Org. prod.	1.3	---	18.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0	2.4

\*Calculated value.

Table 22 (Continued)

Ext. no.	Oxide conc. (g./l.)	HNO <sub>3</sub> conc. (m.)	Flow rate (ml./cycle)	Equil. anal. (wt. %)						% of product rep't.	% of oxide wt.	
				Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Dy <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>			
<u>Influents</u>												
6	Aq. feed	112	6.0	10.0	N.D.	N.D.	N.D.	N.D.	7.2	83	90.2	
	Aq. scrub	0	6.0	15.0								
	Org. scrub	0	3.0	20.0								
<u>Effluents</u>												
	Aq. prod.	38.6	---	23.7	N.D.	N.D.	N.D.	N.D.	6.9	88	94.9	94
	Org. prod.	2.91	---	18.9	N.D.	N.D.	N.D.	N.D.	N.D.	53	53.0	5.7
-----												
<u>Influents</u>												
7	Aq. feed	90.0	7.0	10.0	N.D.	N.D.	N.D.	N.D.	6.3	82	88.3	
	Aq. scrub	0	7.0	15.0								
	Org. scrub	0	3.2	20.0								
<u>Effluents</u>												
	Aq. prod.	31.5	---	23.2	N.D.	N.D.	N.D.	N.D.	7.3	85	92.3	91
	Org. prod.	3.96	---	17.8	N.D.	N.D.	N.D.	N.D.	4.0	66	70.0	8.8
-----												
<u>Influents</u>												
8	Aq. feed	50.0	15.0	10.0	2.3*	12.6	12.5*	12.5	8.9	46	94.8	
	Aq. scrub	0	15.0	15.0								
	Org. scrub	0	5.0	20.0								
<u>Effluents</u>												
	Aq. prod.	4.37	---	24.3	10.4	67	1.6	N.D.	N.D.	N.D.	79.0	23
	Org. prod.	21.2	---	17.0	N.D.	1.0	11.8	17.9	9.3	55	95.0	77

was used in each extraction for introducing the organic phase and delivering the aqueous product phase. The aqueous scrub phase entered and the organic product phase left the extractor at stage 20. In all multistage extractions except the first one, the aqueous feed was added at stage 11. Stage 5 was used in this first extraction. Tributyl phosphate acidified with nitric acid was the organic phase in each case while a nitric acid solution of the yttrium-rare earth nitrates constituted the aqueous phase. The table gives for each extraction the analysis for yttrium and part of the rare earths as well as the total equivalent oxide concentrations, the acidities and the flow rates for all the influents. For the product phases, or effluents, the steady state yttrium and partial rare earth analyses, the total equivalent oxide concentrations and the volumes delivered are given. In operating the extractor there is a five to ten volume per cent carry-over of the organic phase by the aqueous product phase. Since this carry-over was not included in the material balance, a quantitative recovery of all material was not indicated by these data.

Multistage extractions one to four employed the nitric acid solution of the yttrium-rare earth concentrate from Fergusonite ore as the aqueous feed while three of the remaining four multistage extractions used the products from the first four extractions as their feed mixtures. The

first two extractions employed a nearly concentrated nitric acid system while for extractions three and four 8.0 and 6.0 molar nitric acid was used, respectively. For extractions five to eight, nitric acid systems varying from 2 to 15.0 molar were used.

The multistage extraction of the yttrium-rare earth mixture obtained from the ion-exchange column tailings indicated that insufficient mass was transferred to the organic phase when employing a flow ratio of 5 volumes of the aqueous phase to 4 volumes of the organic phase with the feed introduced at stage 11. Since the Fergusonite ore concentrate and the column tailings had somewhat the same composition similar separation relationships were presumed. Consequently, for the first multistage extraction of the yttrium-rare earth concentrate from Fergusonite ore the over-all flow ratio selected was five volumes of the aqueous phase to six volumes of the organic phase. Stage five was used as the feed stage in order to obtain a longer aqueous scrubbing section for separation of the last traces of gadolinium from yttrium. This extraction was carried out for 170 cycles.

As is apparent from Table 22 the general trends for multistage extraction one were similar to those observed for the extraction of the ion-exchange column tailings. All the light rare earths favored the aqueous product phase,

dysprosium was about equally divided between the two product phases and yttrium heavily favored the organic product phase. The light rare earth percentages in the product aqueous phase were approximately twice those in the original mixture. About 90 per cent of the total yttrium was delivered by the organic phase giving a product which analyzed 80 per cent yttrium oxide. The yttrium then on a percentage oxide basis was effectively concentrated from an initial mixture in which it constituted 50 per cent of the total weight. The analysis for holmium indicated that it composed about 1.2 per cent of the product from the organic phase while not being detected in the aqueous phase product. A qualitative analysis of the products showed very strong spectral lines for lanthanum in the aqueous phase while all the erbium (trace amounts) also appeared in the aqueous product phase. Ytterbium favored the organic phase while terbium was about equally distributed between the two product phases. Except for the trace amount of erbium, the heavy rare earths appeared to favor the organic phase while all the light rare earths definitely remained in the aqueous phase.

The results of stagewise analysis and calculations appear in Figures 24 to 27 inclusive. From Figure 24 it is apparent that on an equivalent oxide concentration basis a large salt build-up occurred in stages 3, 4 and 5 of the



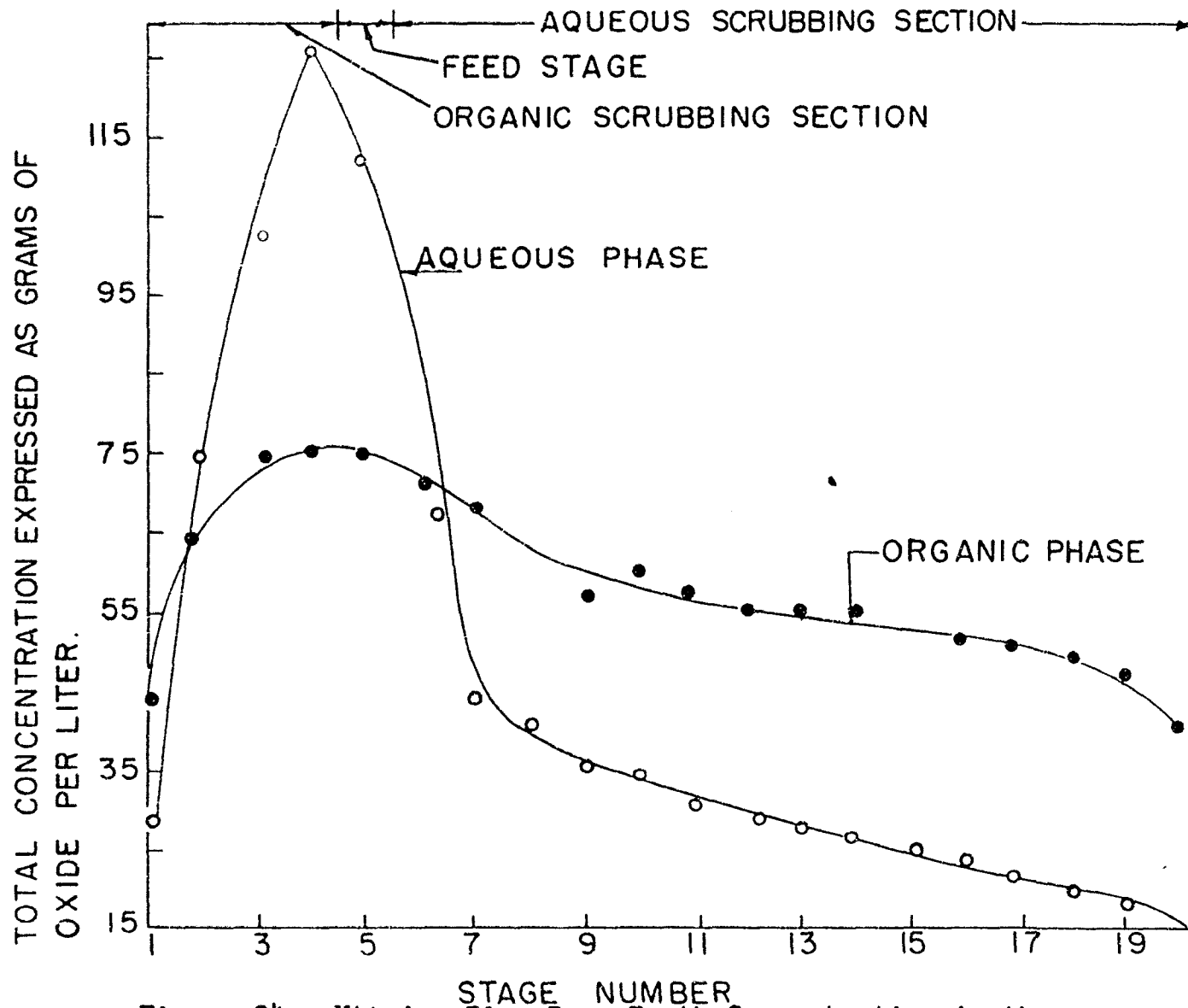


Figure 24 - Yttrium Plus Rare Earth Concentration in the Equilibrium Liquids as a Function of Stage Number.

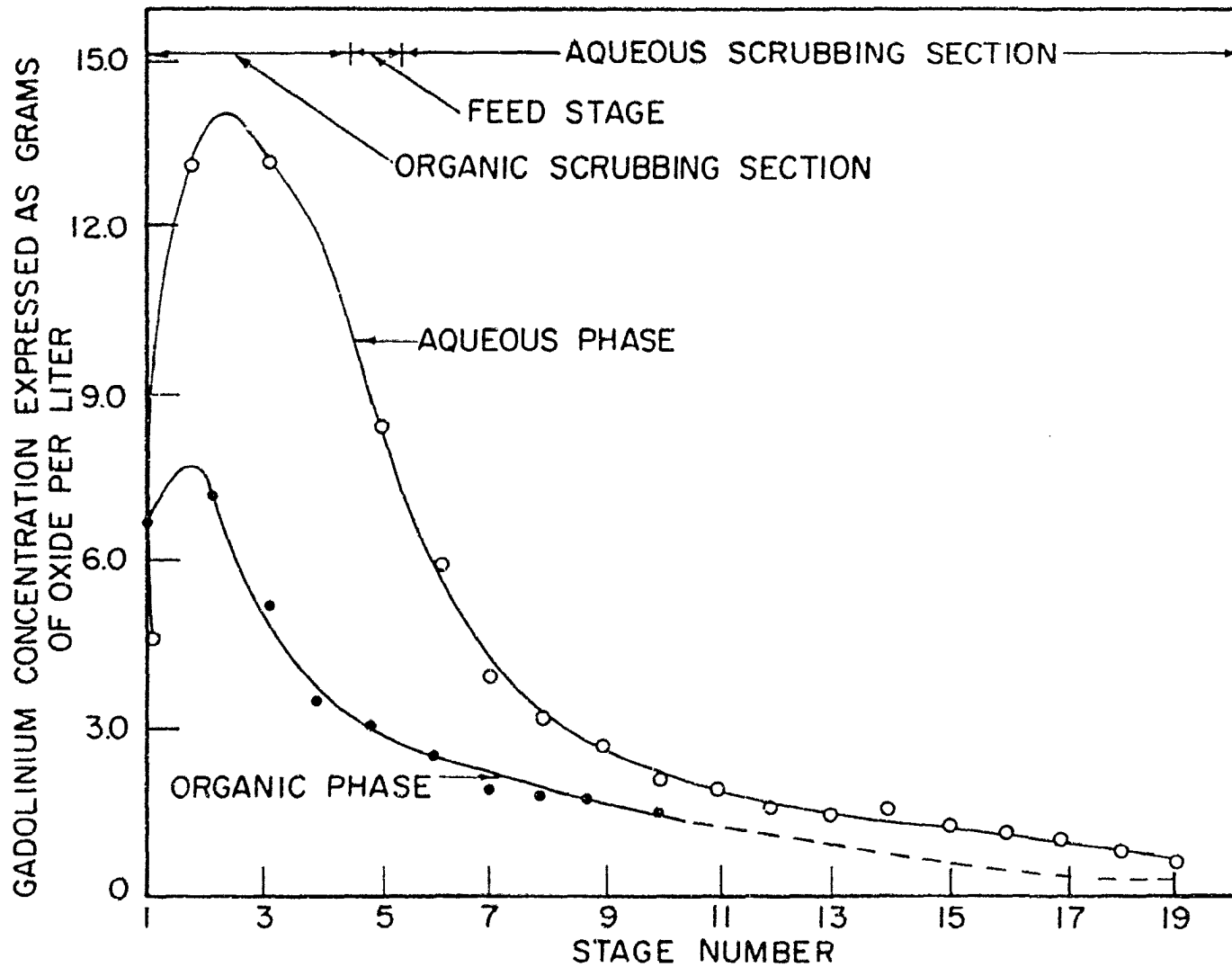


Figure 25 - Gadolinium Oxide Concentration in the Equilibrium Liquids as a Function of Stage Number.

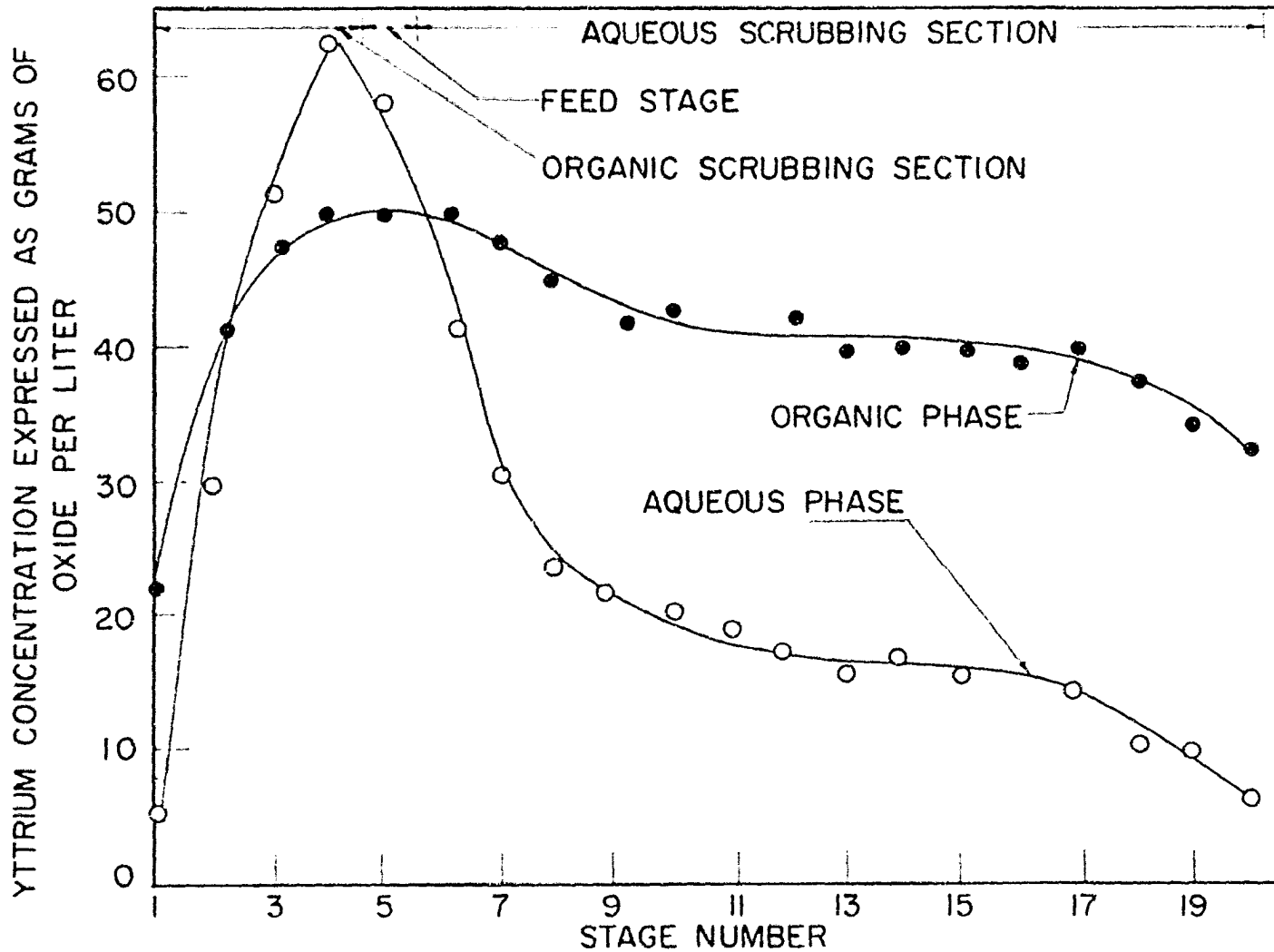


Figure 26 - Yttrium Oxide Concentration in the Equilibrium Liquids as a Function of Stage Number.

aqueous phase with stage 4 containing the highest salt concentration. A material build-up although smaller occurred for the organic phases in stages 3, 4 and 5. Figure 25 shows that a large gadolinium salt build-up occurred in both phases in stages 2 and 3 while from Figure 26 it is apparent that an yttrium salt concentration build-up occurred in stages 3, 4 and 5. This large increase in concentration of gadolinium in stage 2 was also noted for the multistage extraction of the yttrium-rare earth mixture obtained from the ion-exchange column tailings.

The high salt content in the equilibrium aqueous phase are probably related to the large volumes of rather concentrated aqueous feed added per cycle of operation. Since reflux was not used the total salt concentration of the aqueous phase decreased rapidly as it progressed toward stage one, the aqueous product outlet. As the organic scrubbing section was short rapid changes in concentration, as shown in Figures 24 to 26, resulted in this section of the extractor. The difference in shape for the curves appearing in Figures 20 to 22 and 24 to 26 are perhaps explained by the fact that the organic scrubbing section for the extraction shown in the latter figures contained five less stages.

In the stagewise analyses gadolinium was not detected in the organic phase past stage 10. Since it was detected

in the aqueous phase of stage 19 a certain amount must also have been present in the organic phase. Extrapolation of the gadolinium concentration curve beyond stage 10 as shown in Figure 25 allows estimation of the gadolinium distribution coefficients for this region. The distribution coefficients for gadolinium and yttrium and their separation factor as a function of stage number appear in Figure 27.

From this figure it can be noted that the lowest gadolinium-yttrium separation factor which was about 2.4 occurred in the vicinity of the feed stage of the extractor. This relationship was also noted in the multistage extraction of the ion-exchange column tailing mixture. As the salt concentration decreased throughout the extractor the gadolinium-yttrium separation factors increased. Since the distribution coefficient curves for gadolinium and yttrium diverge rapidly in the extrapolated region beyond stage 12 their separation factors increase considerably in this region.

The material expressed as oxide delivered by the organic product phase of this multistage extraction was about 56 per cent of the initial weight. Based on the analysis of the original mixture this should be about the optimum weight fraction for separating the heavy rare earths plus yttrium from dysprosium and the light rare earths. However, it is apparent from Table 22 that dysprosium although slightly

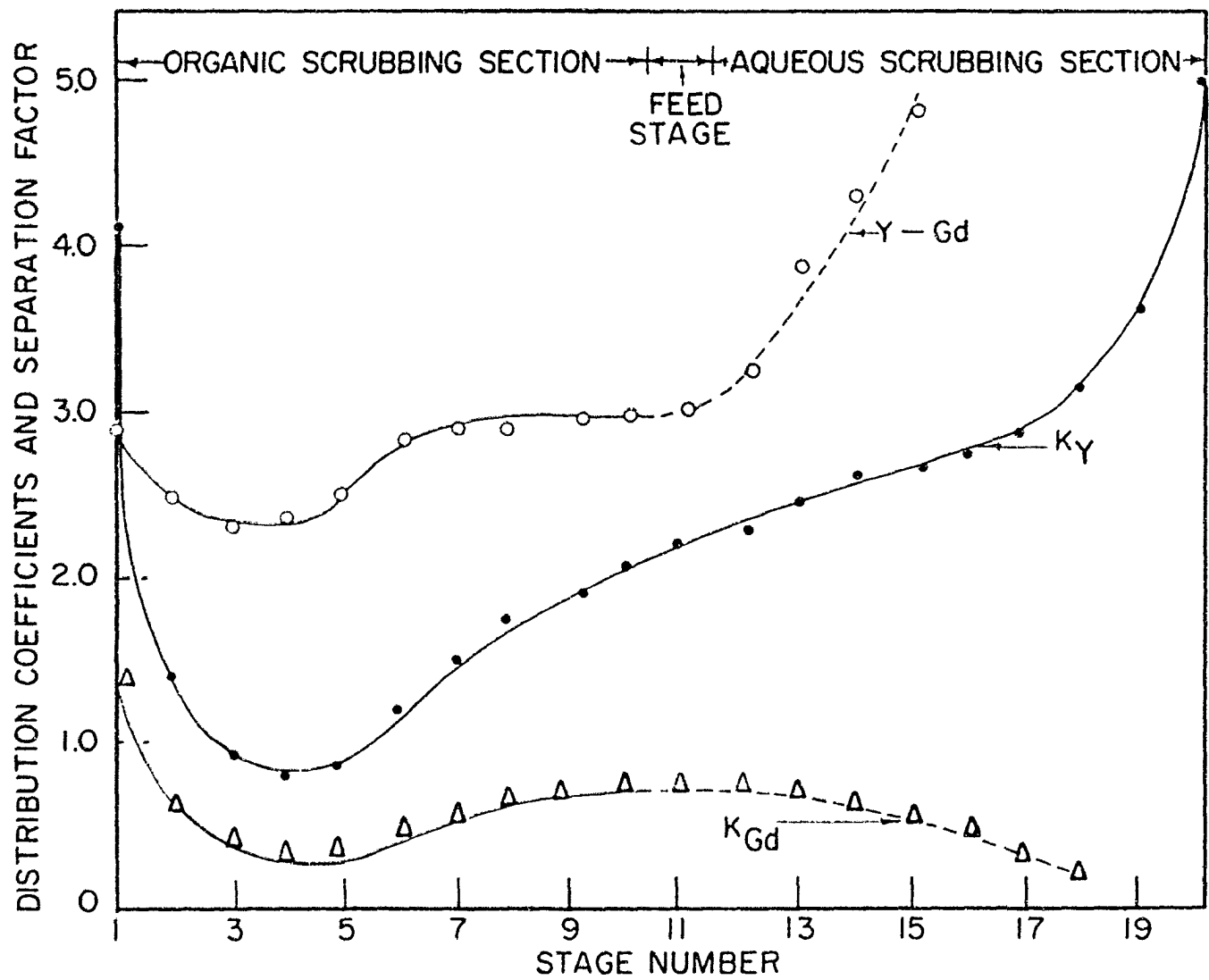


Figure 27 - Distribution Coefficients and Their Separation Factor as a Function of Stage Number.

favoring the organic phase failed to concentrate appreciably in either product phase. Peppard and co-workers (26) predicted that the separation of yttrium from dysprosium would be more difficult than the separation of yttrium from gadolinium or of dysprosium from gadolinium. In light of these data, this prediction appears to be correct.

In the second multistage extraction of the Fergusonite ore concentrate the feed stage was changed to stage 11 and the organic scrub was decreased to 25 milliliters per cycle. Since the other variables were similar to the first multistage extraction of this Fergusonite ore concentrate similar results were generally expected. Even though the aqueous scrubbing section consisted of 11 stages instead of five a smaller transfer to the organic phase was expected because of the decrease in the relative organic flow rate.

The steady state data in Table 22 which were obtained after 115 complete cycles of operation indicate that this second multistage extraction resulted in delivery of 50 per cent of the total weight as oxide by the organic product phase. The light rare earth fraction concentrated in the aqueous product phase while the fraction delivered by the organic product phase consisted of 82 per cent yttrium oxide. This also represented an 82 per cent recovery of the total yttrium oxide in the organic phase. Dysprosium favored the aqueous phase appreciably although a good

separation of it from yttrium was not obtained. It appears that when extracting a concentrated nitric acid solution of the Fergusonite ore yttrium-rare earth mixture with tributyl phosphate a complete separation of yttrium from dysprosium cannot be accomplished in 20 stages. However, proper adjustment of flow rates and over-all concentrations would probably improve their separation in the high nitric acid system.

In the third and fourth multistage extractions of the Fergusonite ore concentrate, the nitric acid concentrations of the influent aqueous scrub and feed phases were 8.0 and 6.0 molar respectively. The flow rate of the organic phase was decreased to 20 milliliters per cycle while the flow rates of the aqueous scrub and feed solutions were the same as employed in the two multistage extractions given just above. Multistage extractions three and four were carried out for 205 and 145 complete cycles of operation respectively. A separation of yttrium plus the light rare earths from the heavy rare earths was desired in extractions with these lower nitric acid systems.

The decrease of nitric acid concentration from 8.0 to 6.0 molar resulted in a decrease of mass transfer to the organic phase of from 19.3 per cent to 5.6 per cent. In multistage extraction three yttrium percentagewise favored the organic phase while dysprosium remained in the aqueous



phase. However, in extraction four both yttrium and dysprosium preferred the aqueous phase. All the light rare earths which were detected appeared in the equilibrium aqueous product phase in each extraction. In both extraction three and extraction four about 3.7 per cent of the total oxide processed and which occurred in the organic product was not accounted for by the individual element analyses. This unreported fraction probably constitutes the heavy rare earth components of the lanthanide mixture.

Multistage extractions three and four substantiate qualitatively the predictions of Peppard and co-workers (26) that variations in the nitric acid concentration would change the position of dividing the yttrium-rare earth mixture into two fractions. A direct comparison of the nitric acid concentration effects from the first four multistage extractions cannot be made because of varying flow ratios and feed concentrations. However, it appears from these data that the lower nitric acid conditions resulted in an enriched yttrium-light rare earth fraction. On this basis, a nitric acid concentration of about four to five molar might result in a more complete separation of the heavy rare earth salts from yttrium and the light rare earth fraction in about 20 stages.

Since further separations were desired the products from the above multistage extractions of the Fergusonite

concentrate were employed as the feed mixtures for other extraction studies. The yttrium-rare earth mixture in the organic phase products from multistage extraction one and two were used for multistage extractions five and seven, respectively. Extraction six used the yttrium-rare earth mixture in the aqueous phase product from multistage extraction five while extraction eight employed the yttrium-rare earth mixture in the aqueous phase product from extraction three.

Further separation of the organic phase products required essentially the separation of the heavy rare earths from yttrium. Consequently, a series of single stage extractions at varying nitric acid concentrations was carried out to determine favorable conditions. The yttrium-heavy rare earth mixture in the organic product phase of multiple extraction one was employed in preparing the initial aqueous feed. In each single stage extraction equal volumes of the aqueous feed and acidified tributyl phosphate were used. The initial aqueous phase contained the equivalent of 96 grams of the oxides per liter. Figure 28 shows the dependence of the yttrium distribution coefficient and the ratio of total oxide weight in the two equilibrium phases on the nitric acid concentration in the aqueous feed.

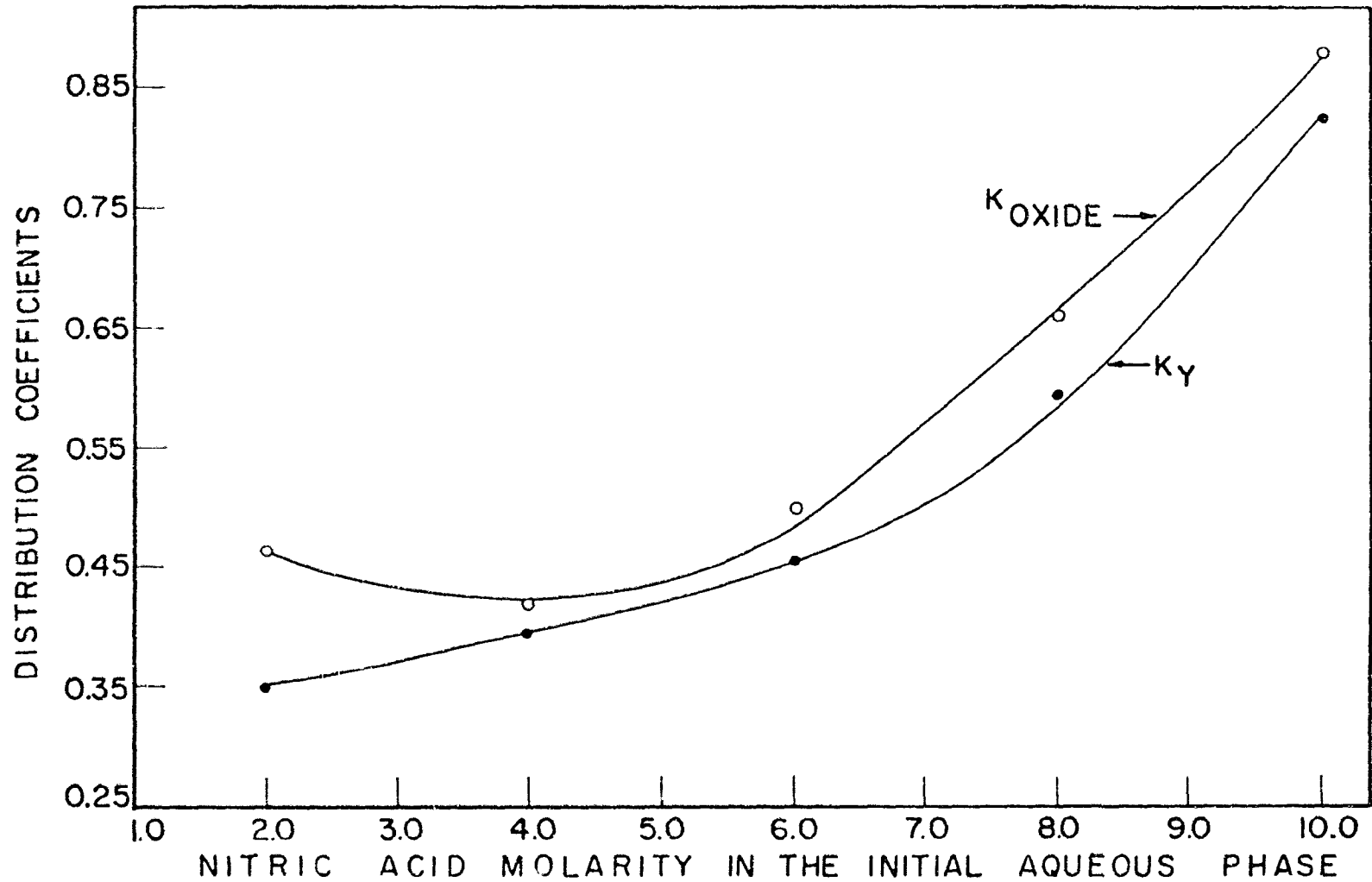


Figure 28 - Yttrium and Total Oxide Distribution Coefficients at Various Nitric Acid Concentrations.

It is apparent from Figure 28 that the mass transfer to the organic phase was a minimum between 3.0 and 4.0 molar nitric acid. The yttrium distribution factor decreases with decreasing nitric acid concentration although its variation becomes less pronounced for the low acid systems. The divergence of the two curves below three molar nitric acid indicates that a reverse in the trend for phase preference must have occurred for some of the components of the mixture. Inversion in extractability of rare earth nitrates at low nitric acid concentrations was observed by Peppard and co-workers (26).

Multistage extractions five, six and seven were carried out to observe the effects of lower nitric acid media on the separation of yttrium from the heavy rare earths. Multistage extraction five which consisted of 90 cycles employed a feed solution which was 2.0 molar in nitric acid and contained a mixture which consisted primarily of yttrium and heavy lanthanides. As the data in Table 22 indicate only 2.4 per cent of the total material as oxide which contained no yttrium or dysprosium was transferred to the organic phase. A qualitative spectrographic analysis of this organic phase product showed it was strong in cerium and contained no heavy rare earths. The resulting aqueous phase product which was initially 80 per cent yttrium oxide was concentrated to 83 per cent

yttrium oxide. The data indicated that an inversion of the light and heavy rare earth fractions had resulted when extracting the 2.0 molar nitric acid solution of these nitrates.

Since the transfer of the heavy rare earth fraction to the organic phase was desired for separating them from yttrium, multistage extraction six employed a 6.0 molar nitric acid aqueous feed. The aqueous feed solution contained the yttrium-rare earth fraction obtained from the aqueous phase product of multistage extraction five (see Table 22). After 47 complete cycles 5.7 per cent of the material as oxide had been delivered by the organic product phase. The product from this phase was about half yttrium oxide and contained no light rare earths. Spectrophotometric analyses indicated this product was concentrated in the heavy rare earth components. The aqueous phase product which analyzed 88 per cent yttrium oxide contained about 97 per cent of the total yttrium. Since only 47 cycles were used for this extraction essentially steady state was probably not reached, although the general separation trends should still apply.

Since multistage extraction six showed a favorable concentration of yttrium similar conditions were used in multistage extraction seven. However, in this multistage extraction the influent aqueous solutions were 7.0 molar

in nitric acid. The extraction was carried out for 165 complete cycles. As was expected the mass transfer to the organic product phase increased reaching a value of 8.7 per cent expressed as oxide of the total material processed. The yttrium oxide percentage which initially was 82 per cent was increased to 85 per cent in the aqueous phase product. This percentage change was small because the organic phase product contained substantial amounts of yttrium. Spectrophotometric analyses indicated that the heavy lanthanide components considerably favored the organic product phase although some were also detected in the aqueous phase product. It appears from these multistage extractions that the heavy rare earth fraction cannot be separated from yttrium as easily as yttrium can be separated from the light rare earth fraction. However, these data show that with a larger number of stages the separation of yttrium from the heavy rare earth fraction should be possible.

In multistage extraction eight an attempt was made to separate the light rare earths obtained from the aqueous phase product of multistage extraction three. A concentrated (15 molar) nitric acid medium and a fairly dilute yttrium-rare earth concentration was employed in this 140 cycle extraction. From the data in Table 22 it is apparent that the mixture was divided between neodymium

and samarium with most of the samarium and essentially all of the gadolinium, dysprosium and yttrium delivered by the organic product phase. If a 13 molar nitric acid aqueous feed had been employed the mixture would probably have been separated between gadolinium and dysprosium. This again substantiates the predictions of Peppard and co-workers.

These eight 20 stage countercurrent extractions of yttrium-rare earth concentrates obtained from Fergusonite ore indicated that a series of such extractions should result in a number of highly enriched fractions. These fractions could be further purified by either additional extractions or by employing them as a feed for ion-exchange resin columns. Flow ratios, salt concentrations, acidities, numbers of stages and variation in yttrium-rare earth composition appear to be the important variables connected with the aqueous phase which must be controlled in order to obtain any particular separation. The data presented here indicates quite conclusively the potentiality of solvent extraction for separating the yttrium and rare earth fraction from Fergusonite ore. However, a great deal of work still remains to be done before a specific plan for the complete separation of such a mixture can be drawn.

### 3. Concentration and separation of yttrium and rare earths obtained from Gadolinite ore

(a) Introduction. The data for extracting the Fergusonite ore yttrium-rare earth mixture indicated that a series of extractions yielded a number of enriched fractions. Gadolinite ore is one of the sources of rare earth mixtures employed in this Laboratory for charging the ion-exchange columns. Various enriched fractions prepared by liquid-liquid extraction of the yttrium-rare earth concentrate from Gadolinite ore should be useful for increasing the production capacity for certain pure rare earth salts by the resin columns. Because of the similarities in the yttrium and rare earth compositions of the concentrates from Gadolinite ore and from Fergusonite ore it can be assumed that the solvent extraction data should apply about equally to both concentrates.

Gadolinite ore which is mined in the Scandanavian countries is essentially a silicate of iron, beryllium, yttrium and rare earths. Usually between 40 and 50 per cent of the total weight composes the yttrium-rare earth fraction. The chief advantage of this ore as a source of rare earth salts is its relatively high content of the heavy rare earth fraction. Analyses have indicated that about 15 to 20 per cent of the yttrium-rare earth mixture is composed of lanthanides having an atomic number of 66 or higher. The yttrium-rare earth fraction can be recovered from the ore either by several leaches with



concentrated nitric acid or by carrying out a caustic treatment of the ore with a subsequent acid leach. Generally the caustic treatment appears to recover from the ore slightly more yttrium plus rare earth salts.

(b) Processing of Gadolinite ore. The fusion of an alkali mixture in the presence of Gadolinite ore was used to render its yttrium-rare earth fraction in an easily soluble form. A suitable charge consisted of 10.0 grams of Gadolinite ore, 8.0 grams of sodium hydroxide and 4.0 grams of sodium peroxide. The mixture was heated in a stainless steel crucible at 650°C for 30 minutes. When the melt cooled it was transferred to a beaker and washed with water to dissolve sodium, beryllium, silicon, aluminum and tin. The residue was then treated with concentrated nitric acid. After boiling for about ten minutes the resulting mother liquor was filtered. Oxalic acid was added to the filtrate to precipitate the rare earth oxalates. After the rare earth oxalate slurry was filtered ammonium hydroxide was added to this filtrate to precipitate iron, titanium, manganese, and other soluble oxalates. A qualitative spectrographic analysis of the yttrium-rare earth fraction indicated weak amounts of iron and manganese, a very weak amount of calcium and trace amounts of chromium, magnesium and silicon. The material insoluble in the concentrated nitric acid leach was mainly silicic acid

with a little unreacted ore. It usually contained a few per cent yttrium. Table 23 gives the approximate weights of the various fractions after they were converted to oxides by calcining for at least two hours at 800 degrees Centigrade. Table 24 shows an average analysis of the yttrium-rare earth concentrate from Gadolinite ore.

Table 23

Weights of the Various Fractions from Processing 10.0 Grams of Gadolinite Ore

Operation	Weight
1. Soluble in $\text{HNO}_3$ leach	
a. Oxalic acid precipitation	4.55 g.
b. $\text{NH}_4\text{OH}$ precipitation of filtrate from 1(a)	2.00 g.
2. Acid insoluble fraction	2.86 g.

(c) Single stage extraction of the yttrium-rare earth concentrate from Gadolinite ore.

(1) Extractions employing tributyl phosphate. The extraction data for the Fergusonite ore concentrate showed that in a concentrated nitric acid system yttrium and the heavy rare earths could be separated from gadolinium and the other light rare earths by liquid-liquid extraction. However, yttrium and dysprosium were not easily separated

from each other. At low nitric acid concentrations an inversion was noted for the extractability of a number of the elements. It has been reported by Peppard and co-workers (26) that inorganic salting-out agents such as the nitrates

Table 24

Analyses of the Yttrium-Rare Earth Concentrate from Gadolinite Ore

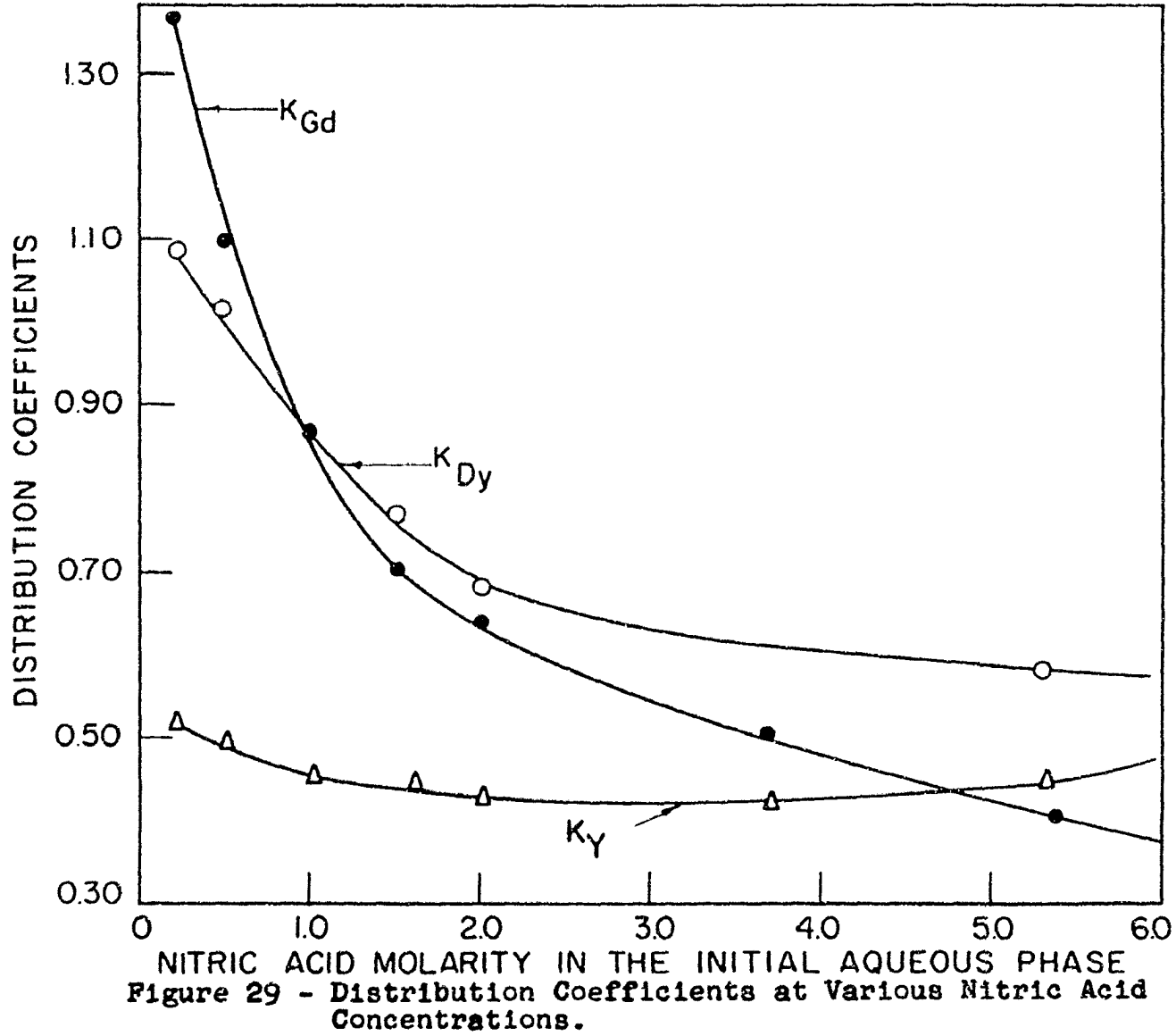
Component	Analysis (wt. %)
$\text{Pr}_6\text{O}_{11}$	2.0%
$\text{Nd}_2\text{O}_3$	5.0%
$\text{Sm}_2\text{O}_3$	5.0%
$\text{Eu}_2\text{O}_3$	4.7%
$\text{Gd}_2\text{O}_3$	5.2%
$\text{Dy}_2\text{O}_3$	7.6%
$\text{Ho}_2\text{O}_3$	1.1%
$\text{Yb}_2\text{O}_3$	4.6%
$\text{Lu}_2\text{O}_3$	2.7%
$\text{Y}_2\text{O}_3$	61.0%

of aluminum, magnesium, calcium and ammonium tended to increase the mass transfer of rare earths to the organic phase. These salting-out agents were extracted by the organic phase in only trace amounts. The fractionations of

the rare earths were reported to be little affected by the presence of these salting-out agents.

In light of these observations a series of single stage extractions employing low nitric acid conditions was carried out on the Gadolinite ore yttrium-rare earth concentrate. Various concentrations of aluminum nitrate, aluminum chloride, magnesium nitrate, magnesium chloride and sodium chloride were added to the initial aqueous phase. Equal volumes of the aqueous and organic phases were used for each extraction while unacidified tributyl phosphate constituted the organic phase. Appendix B contains the equilibrium data obtained from these extractions. Some of these data are represented graphically in Figures 29 to 38 inclusive.

The variations of the gadolinium, yttrium and dysprosium distribution coefficients with the nitric acid concentration of the initial aqueous phase appear in Figure 29. No salting-out agent was added to these systems. It is apparent that gadolinium prefers the organic phase to a greater degree than dysprosium up to nitric acid concentration of about 1.0 molar. However, the relative preference of these two elements for the organic phase is reversed at all higher nitric acid concentrations. Gadolinium prefers the organic phase to a greater degree than yttrium below about 4.7 molar nitric acid although this relative preference is also reversed at higher nitric acid concentrations. Up to at least 6.0 molar nitric



acid dysprosium prefers the organic phase more than yttrium. The data from extraction of the Fergusonite ore concentrate indicated that at higher nitric acid concentrations yttrium favored the organic phase slightly more than did dysprosium while gadolinium preferred the aqueous phase to a much greater extent than either dysprosium or yttrium. Evidently the distribution coefficient curves for yttrium and dysprosium cross at an acid concentration somewhere slightly above 6.0 molar nitric acid.

The data shown in Figure 29 indicate that separation of gadolinium and dysprosium from yttrium could be accomplished most efficiently at a very low nitric acid concentration. This is most effectively indicated in Figure 30 where the various separation factors are plotted as a function of the nitric acid concentration in the initial aqueous phase. The highest yttrium-dysprosium and yttrium-gadolinium separation factors occur in the very low nitric acid media. It was reported above that extracting the more concentrated nitric acid solutions yielded high gadolinium-yttrium and gadolinium-dysprosium separation factors. In the 3.0 to 6.0 molar nitric acid region all three separation factors were between 1.0 to 1.5. This shows why only little separation of these three elements was obtained in this range of acid concentration. The change in sign of the slope in the gadolinium-dysprosium and gadolinium-yttrium

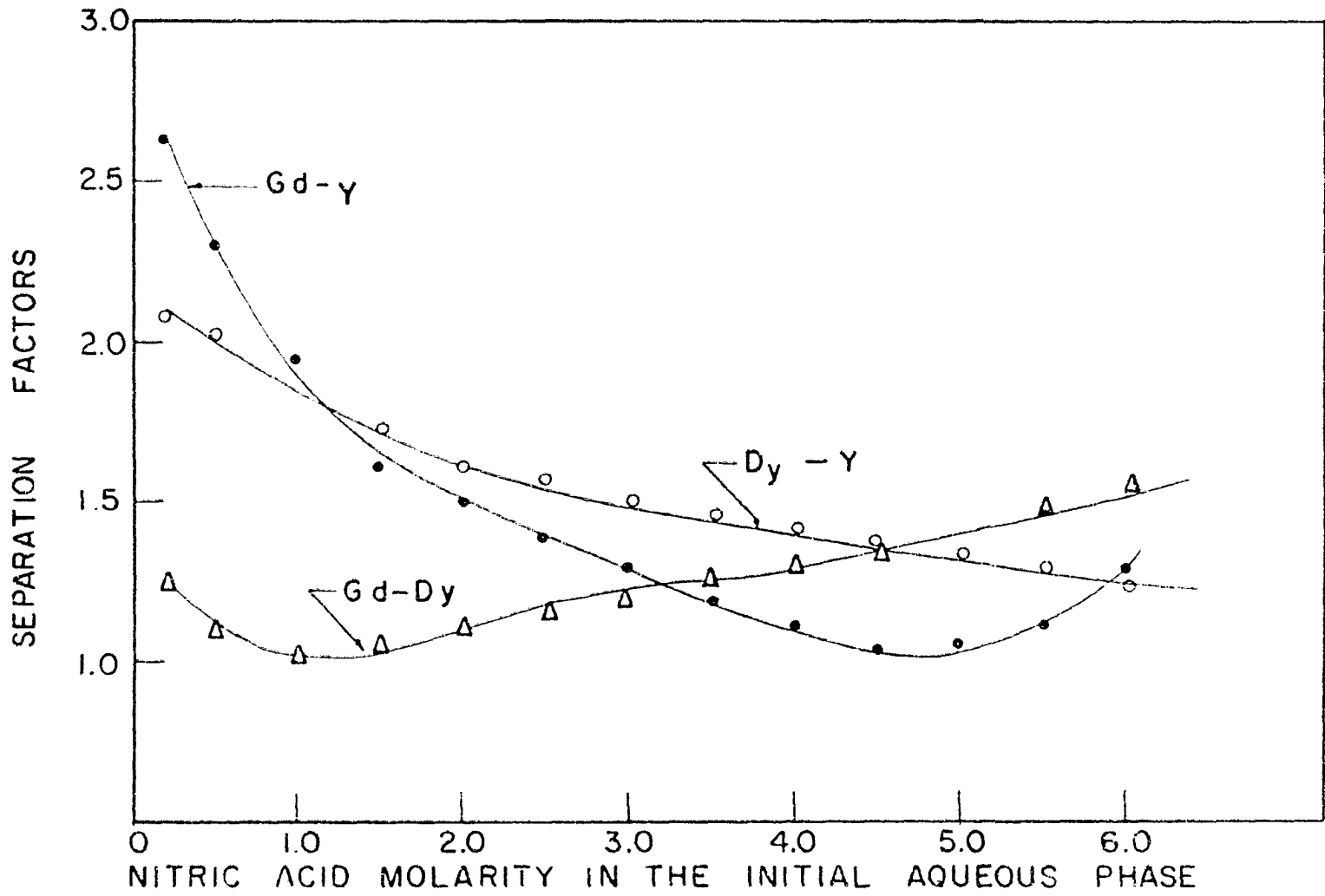


Figure 30 - Separation Factors at Various Nitric Acid Concentrations.

separation factor curves in Figure 30 occur where the distribution coefficient curves of Figure 29 cross each other. This reverse in relation phase preference causes a change in slope. These observations are directly related to the arbitrary definition employed here for the separation factor. These data together with other considerations definitely show that yttrium, gadolinium and dysprosium pass through an inversion in relative phase preferences within the range of 1.0 to 8.0 molar nitric acid.

Figure 31 shows the per cent mass transfer as oxide to the organic phase as a function of nitric acid concentration when various 1.0 molar salting-out agents were present in the initial aqueous phase. In general up to at least 5.3 molar nitric acid the amount of material transferred to the organic phase decreases with increasing acidity. The single stage extractions of the Fergusonite ore concentrate indicated the opposite trends at higher nitric acid concentrations. The presence of a salting-out agent definitely increased the mass transfer to the organic phase in the range up to 5.3 molar nitric acid. As is indicated by Figure 31 aluminum nitrate increased mass transfer more than a corresponding amount aluminum chloride while magnesium nitrate was more effective than magnesium chloride. In general, at constant cation concentration, the nitrates appear to effect transfer of the yttrium-rare earth salts



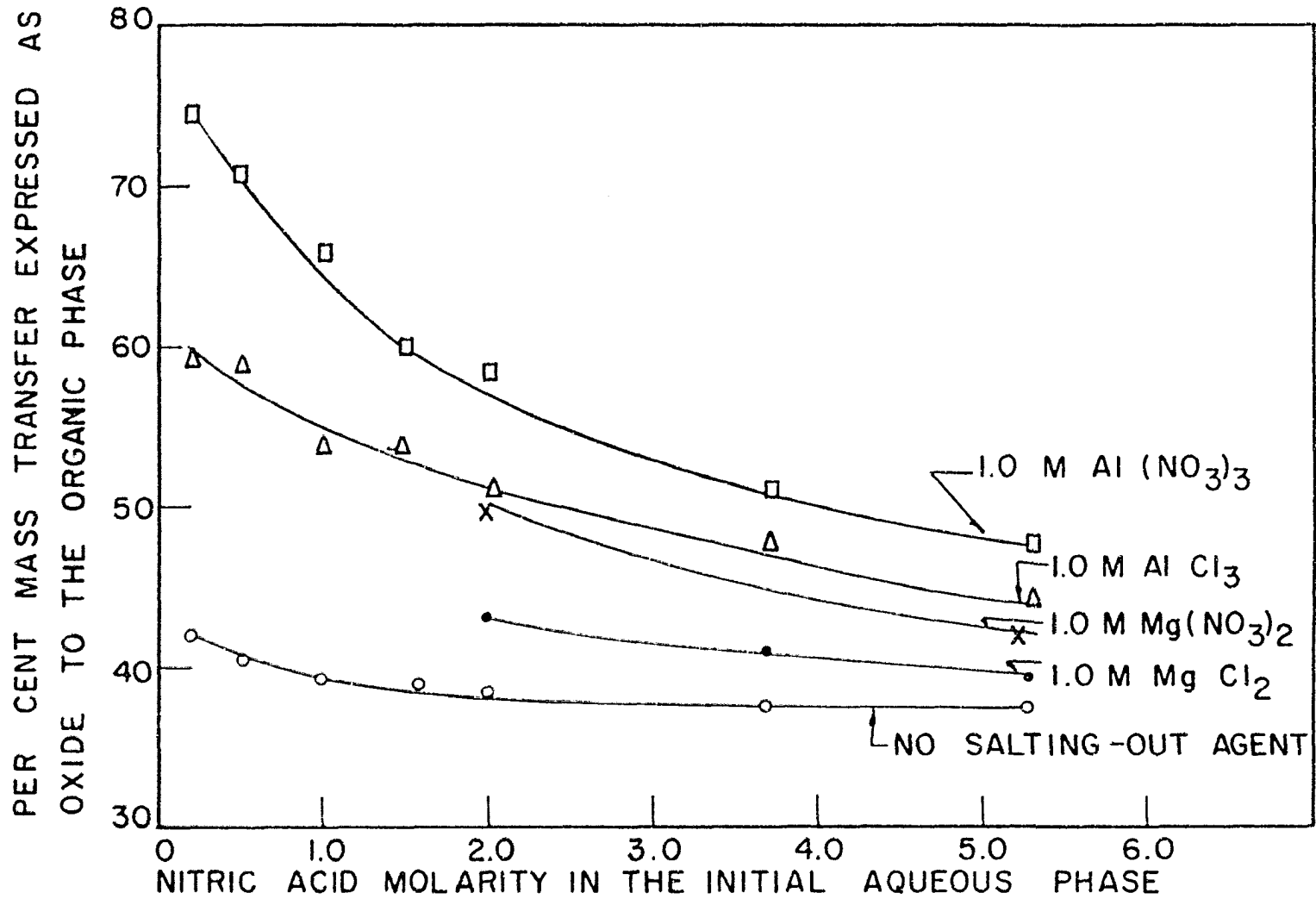


Figure 31 - Mass Distribution as a Function of Salting-Out Agents and Nitric Acid Concentrations.

to the organic phase more than the corresponding chlorides. The results also indicate that for similar anions and at a constant salting-out agent concentration the higher valence cations are most effective for increasing mass transfer to the organic phase.

Figure 32 shows the relationship between mass transfer in terms of oxide, and the aluminum chloride concentration in the aqueous phase at various nitric acid concentrations. It is apparent that the mass transfer increases as the concentration of this salting-out agent increases. However, the relative effect of the salting-out agent decreases as the nitric acid concentration increases. At very high nitric acid concentrations the effect of the salting-out agent on mass transfer would probably be negligible. Since in a highly concentrated nitric acid system the concentration of salting-out agent is negligible relative to the concentration of hydrogen and nitrate ions the behavior of the system would probably be controlled by these two ions.

The effects of the presence of 1.0 molar aluminum salts on the gadolinium, yttrium and dysprosium distribution coefficients at various nitric acid concentrations are illustrated in Figure 33 and 34. A comparison of these data with those in Figure 29 where no salting-out agent was employed indicates the same general trends. The distribution coefficients were considerably higher for the systems

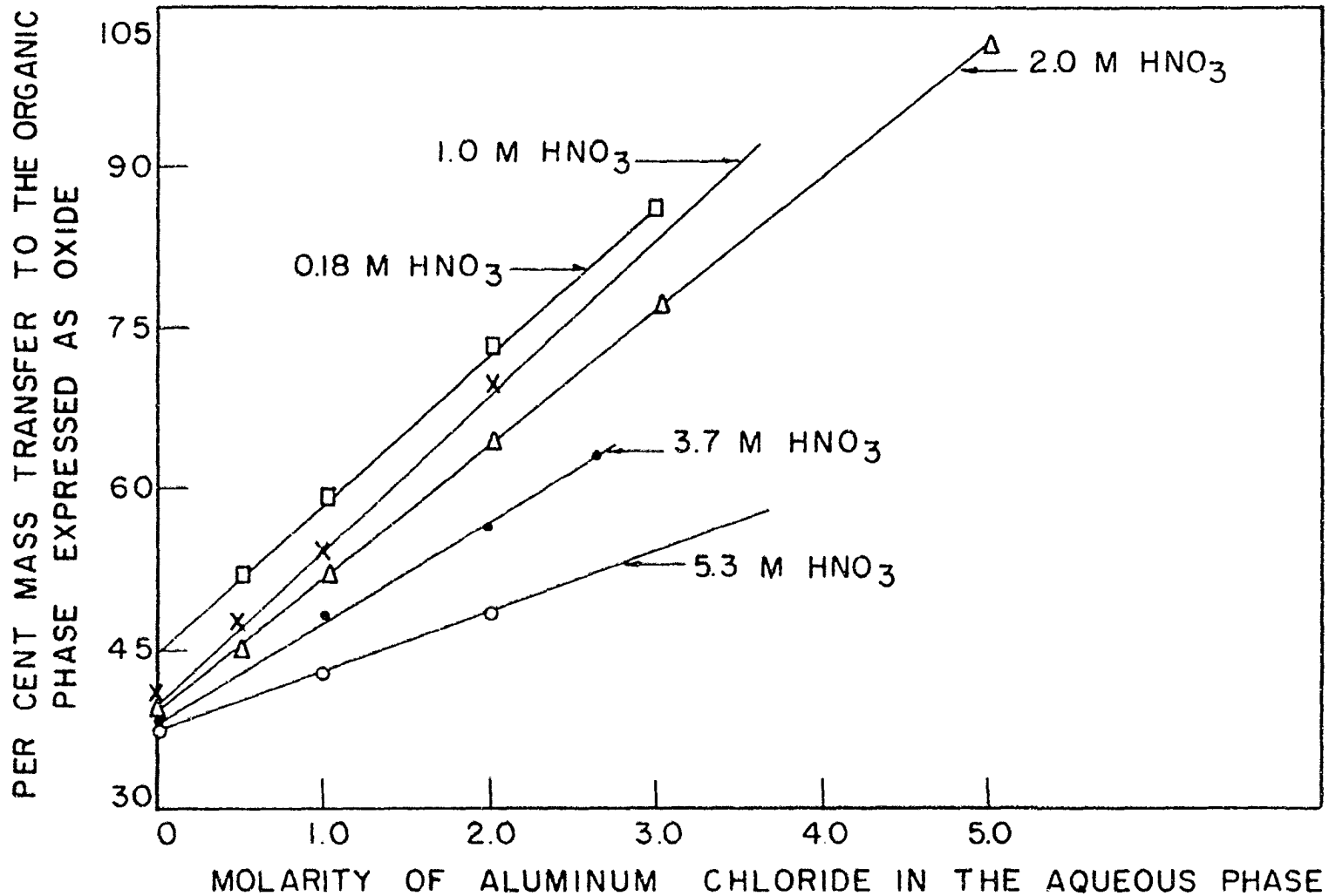


Figure 32 - Mass Distribution at Various Nitric Acid and Aluminum Chloride Concentrations.

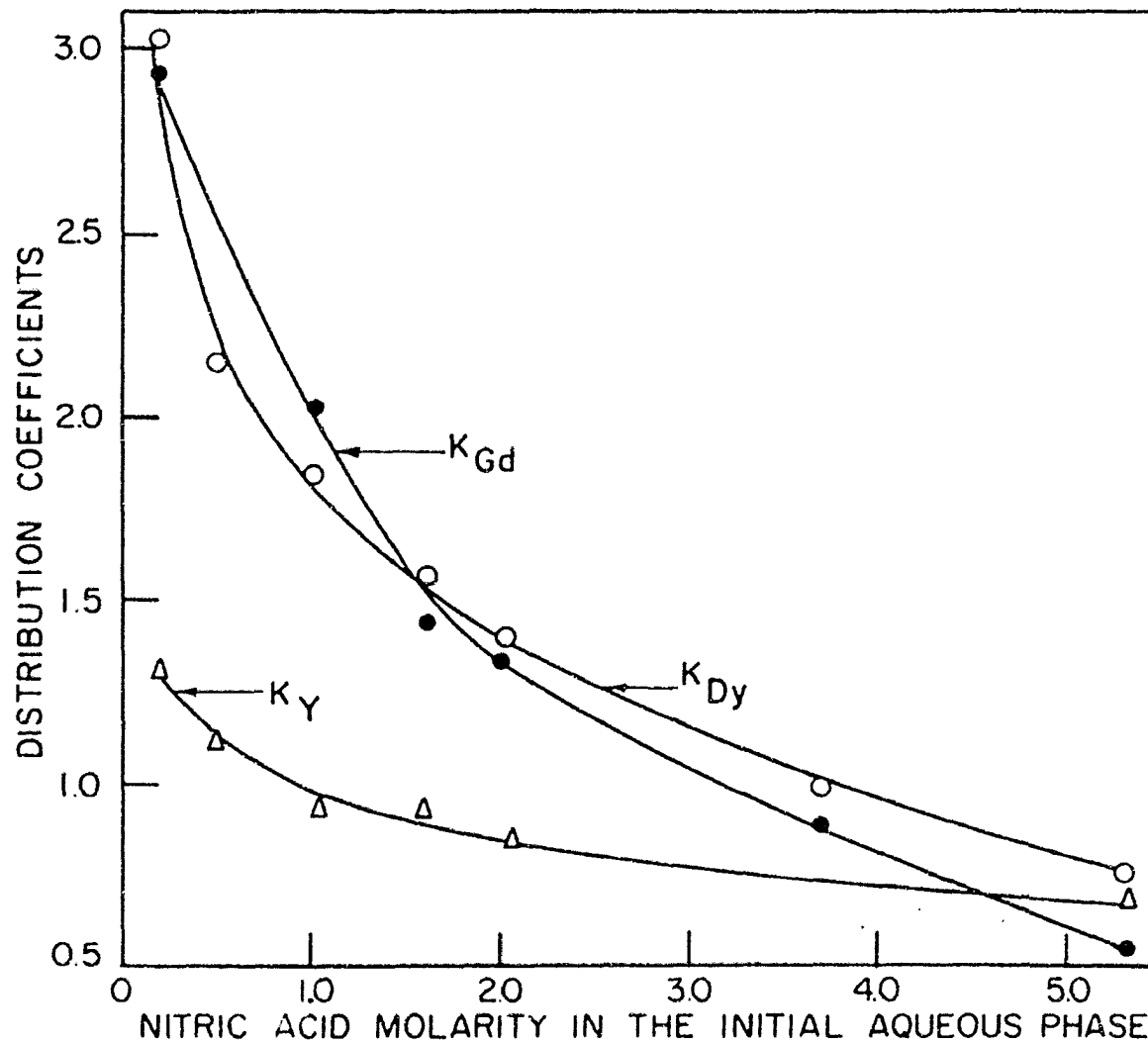
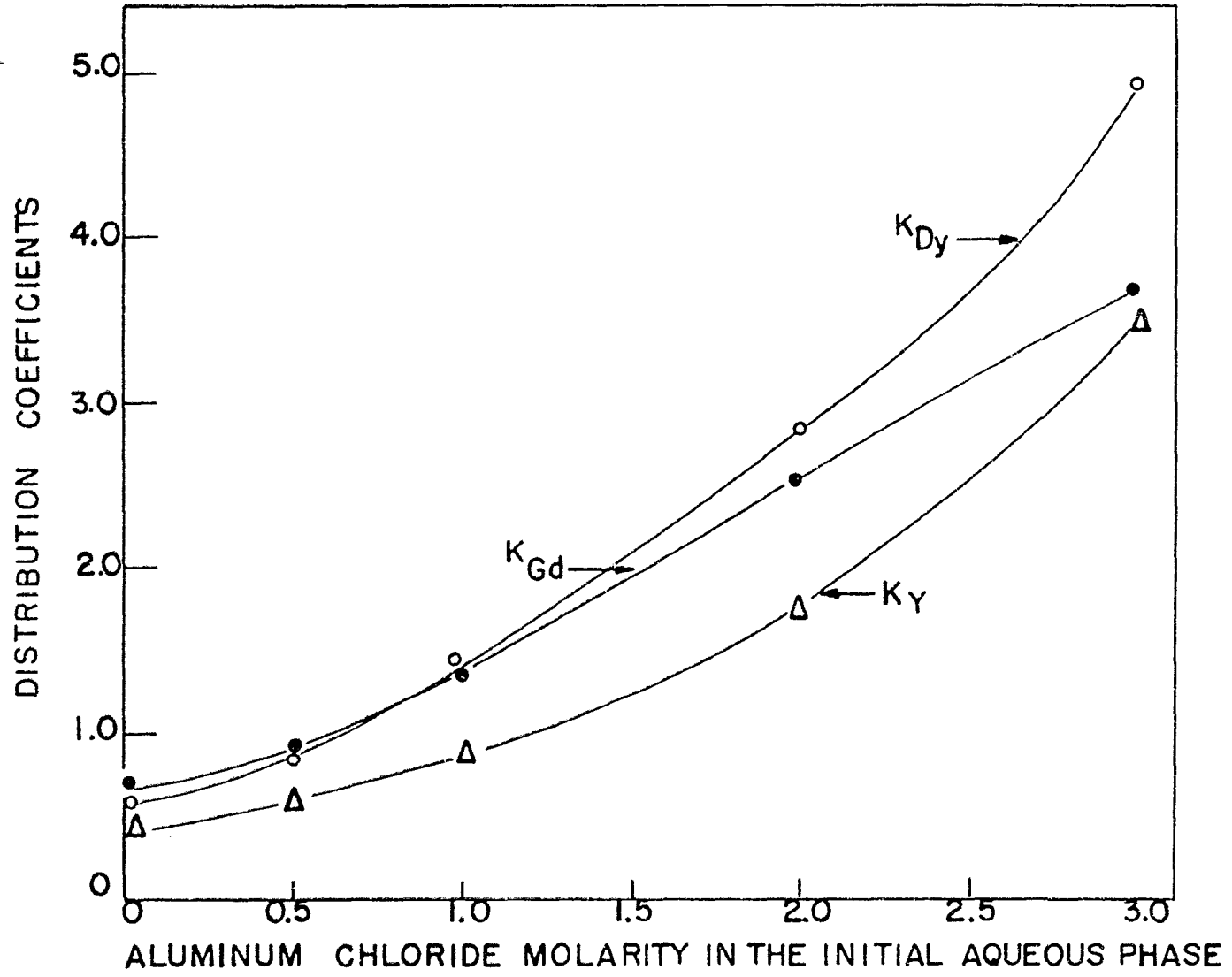


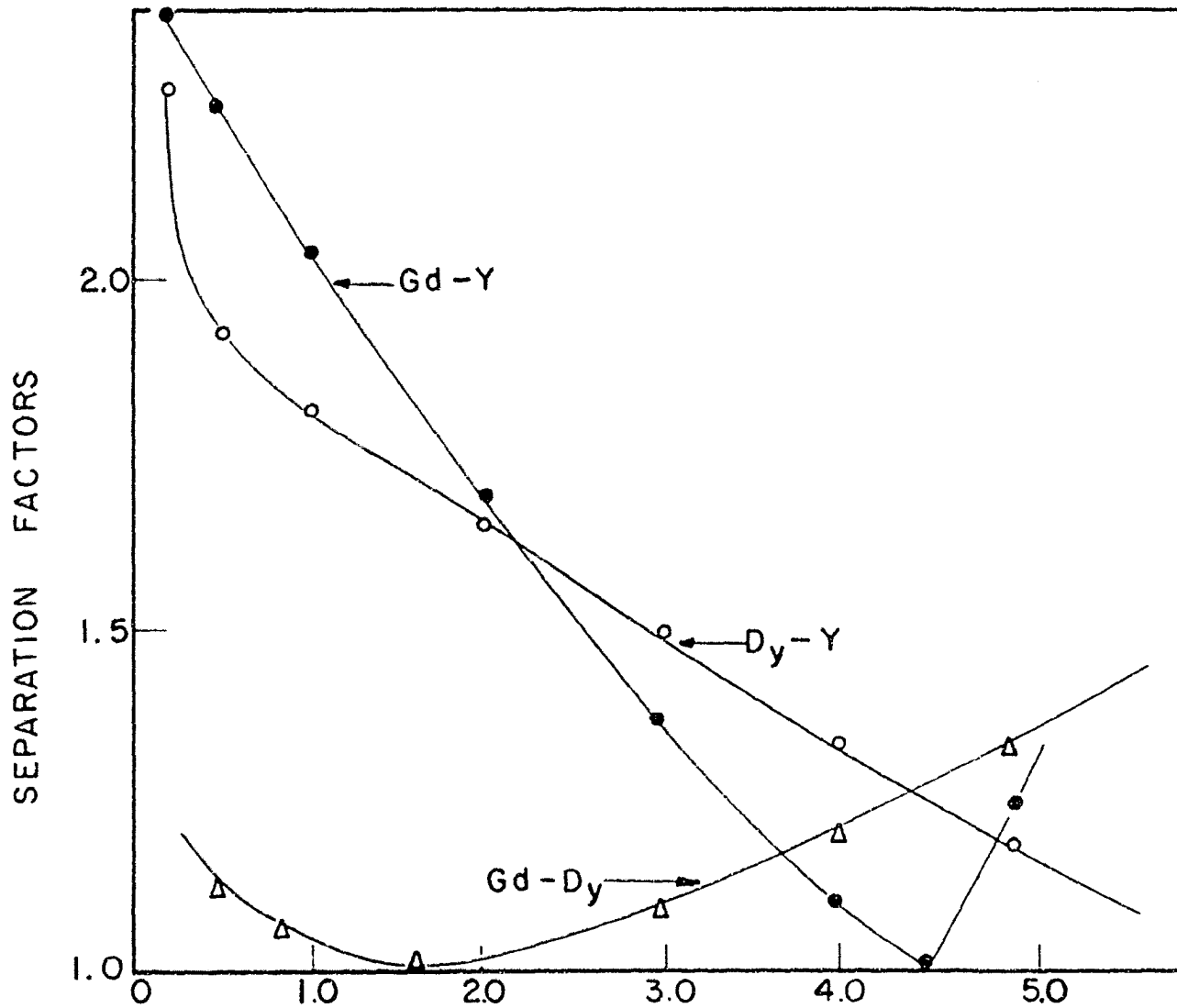
Figure 33 - Distribution Coefficients at Various Nitric Acid Concentrations in the Presence of 1.0 Molar Aluminum Chloride.



ALUMINUM CHLORIDE MOLARITY IN THE INITIAL AQUEOUS PHASE  
 Figure 34 - Distribution Coefficients at Various Nitric Acid Concentrations in the Presence of 1.0 Molar Aluminum Nitrate.

containing the salting-out agents.

From the distribution data appearing in Figure 33 and 34 the separation factors as the function of nitric acid concentration at constant salting-out agent concentration were calculated and then plotted in Figures 35 and 36. A comparison of the extraction data for the aluminum chloride system with the system containing no salting-out agent (see Figure 30) indicates similar relationships although the presence of this aluminum salt generally decreased the separation factors slightly. The gadolinium-yttrium separation factor in the aluminum nitrate system as shown in Figure 36 has the same general variation with acidity as indicated for the other two systems discussed above. However, the gadolinium-dysprosium and yttrium-dysprosium separation factors which were obtained in the presence of aluminum nitrate were considerably different. No reason is known for these behaviors. Partial data for the magnesium nitrate system indicates a behavior similar to that of the aluminum nitrate system while the magnesium chloride system appears to give results similar to the aluminum chloride system. However, both the chloride and nitrate salting-out agents maintained high separation factors for dysprosium and gadolinium relative to yttrium in the very low nitric acid concentration range. It is obvious from Figure 36 that a mixture of yttrium, dysprosium



NITRIC ACID MOLARITY IN THE INITIAL AQUEOUS PHASE  
 Figure 35 - Separation Factors at Various Nitric Acid Concentrations in the Presence of 1.0 Molar Aluminum Chloride.

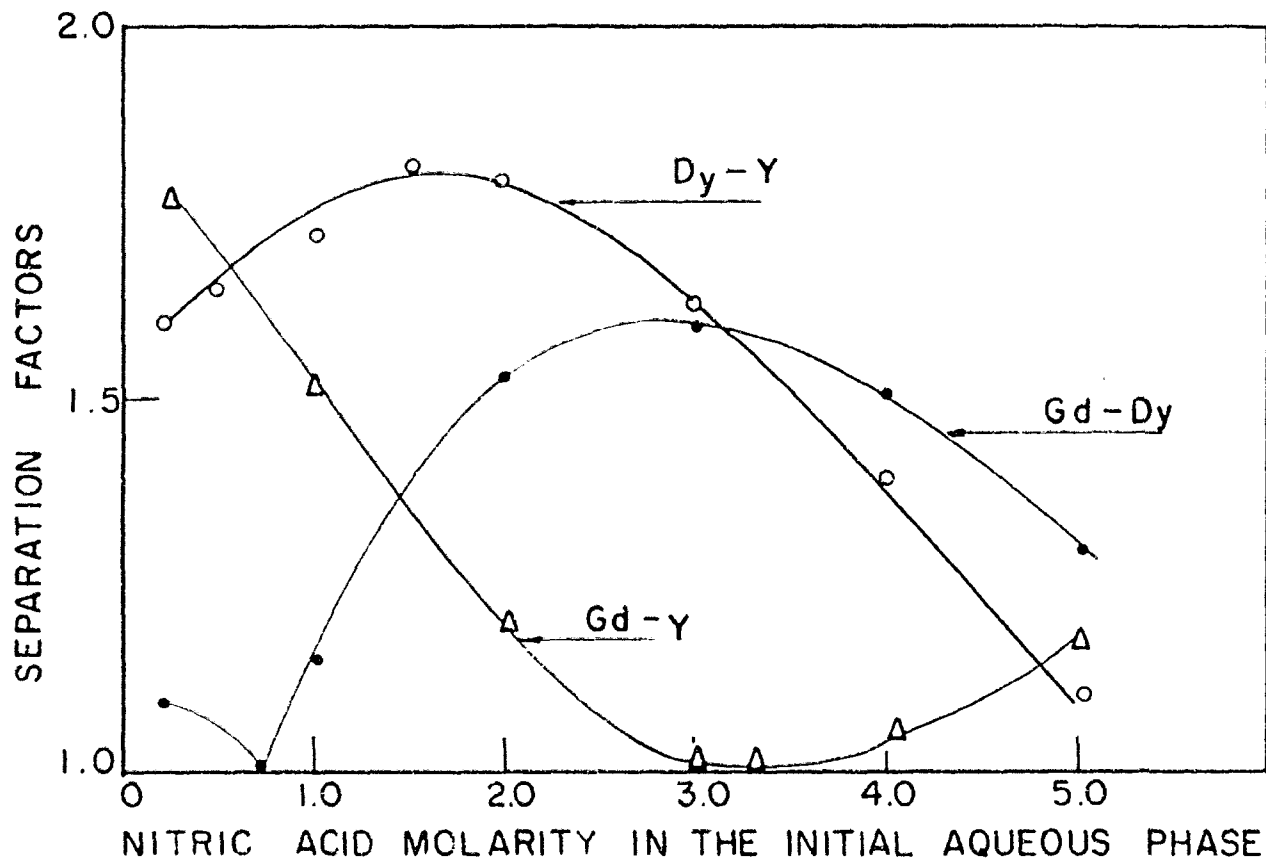


Figure 36 - Separation Factors at Various Nitric Acid Concentrations in the Presence of 1.0 Molar Aluminum Nitrate.



and gadolinium could be separated into three enriched fractions by two consecutive multistage extractions employing nitric acid concentrations of about 0.5 molar and about 3.0 molar.

The variations of the gadolinium, dysprosium, and yttrium distribution coefficients with aluminum chloride concentration in a 2.02 molar nitric acid aqueous solution appear in Figure 37. As the data plotted in Figure 32 indicated these distribution values increased with increasing concentration of the salting-out agent. From the data appearing in Figure 37 the separation factors were calculated and plotted in Figure 38 as a function of the aluminum chloride concentration. The data for the 4.0 molar salting-out agent, calculated from Appendix B, were employed here to determine the direction of the curves above the 3.0 molar concentrations. It is apparent from Figure 38 that the separation factor trends were similar to those obtained when the nitric acid concentration was varied at a constant concentration of aluminum chloride (see Figure 35). Evidently the addition of excess salting-out agent has the same effect as increasing the nitric acid concentration. This indicates that the ionic strength of the system might also be an important factor in controlling preferred extractibility of yttrium, dysprosium and gadolinium salts.

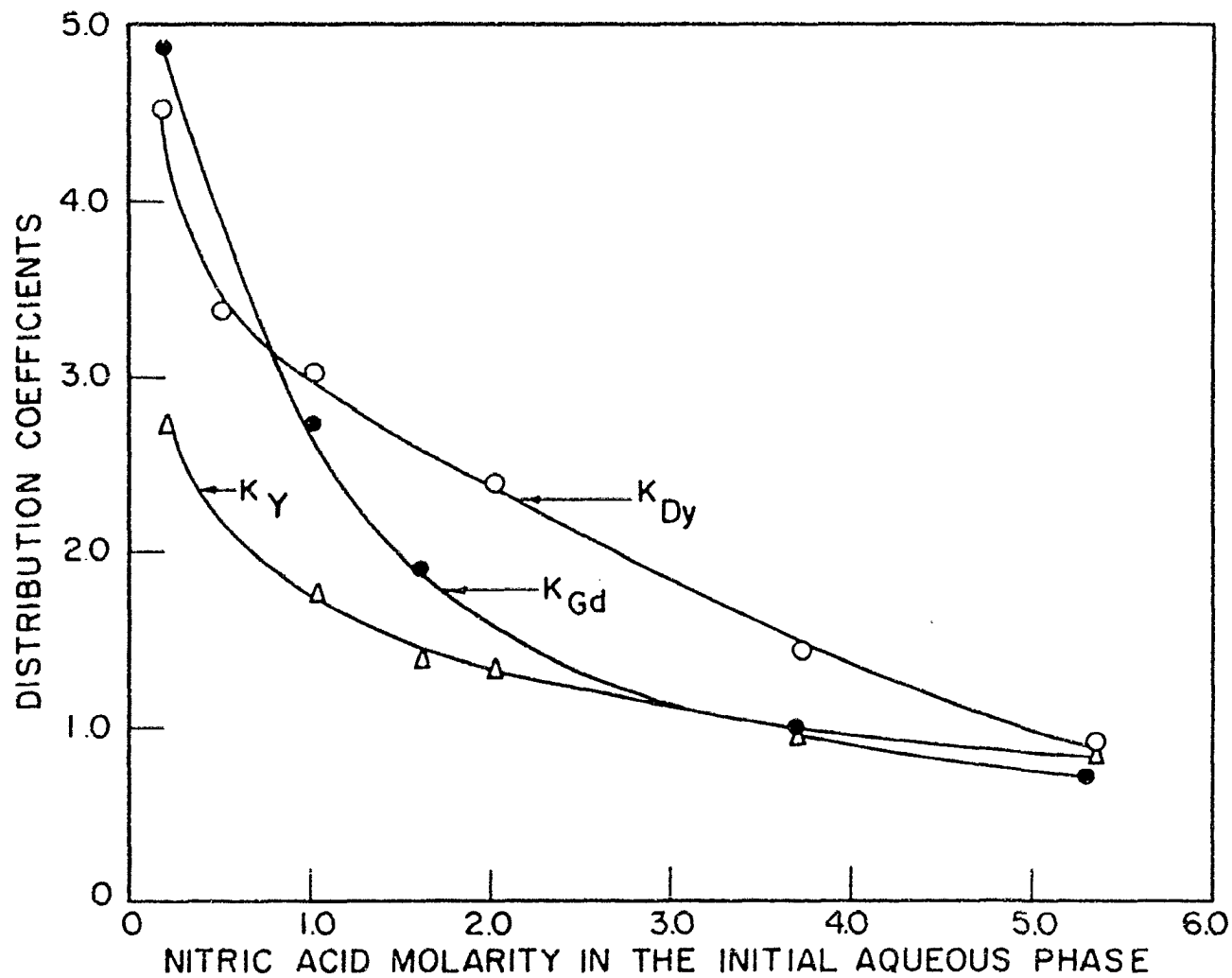


Figure 37 - Distribution Coefficients at Various Aluminum Chloride Concentrations in the Presence of 2.02 Molar Nitric Acid.

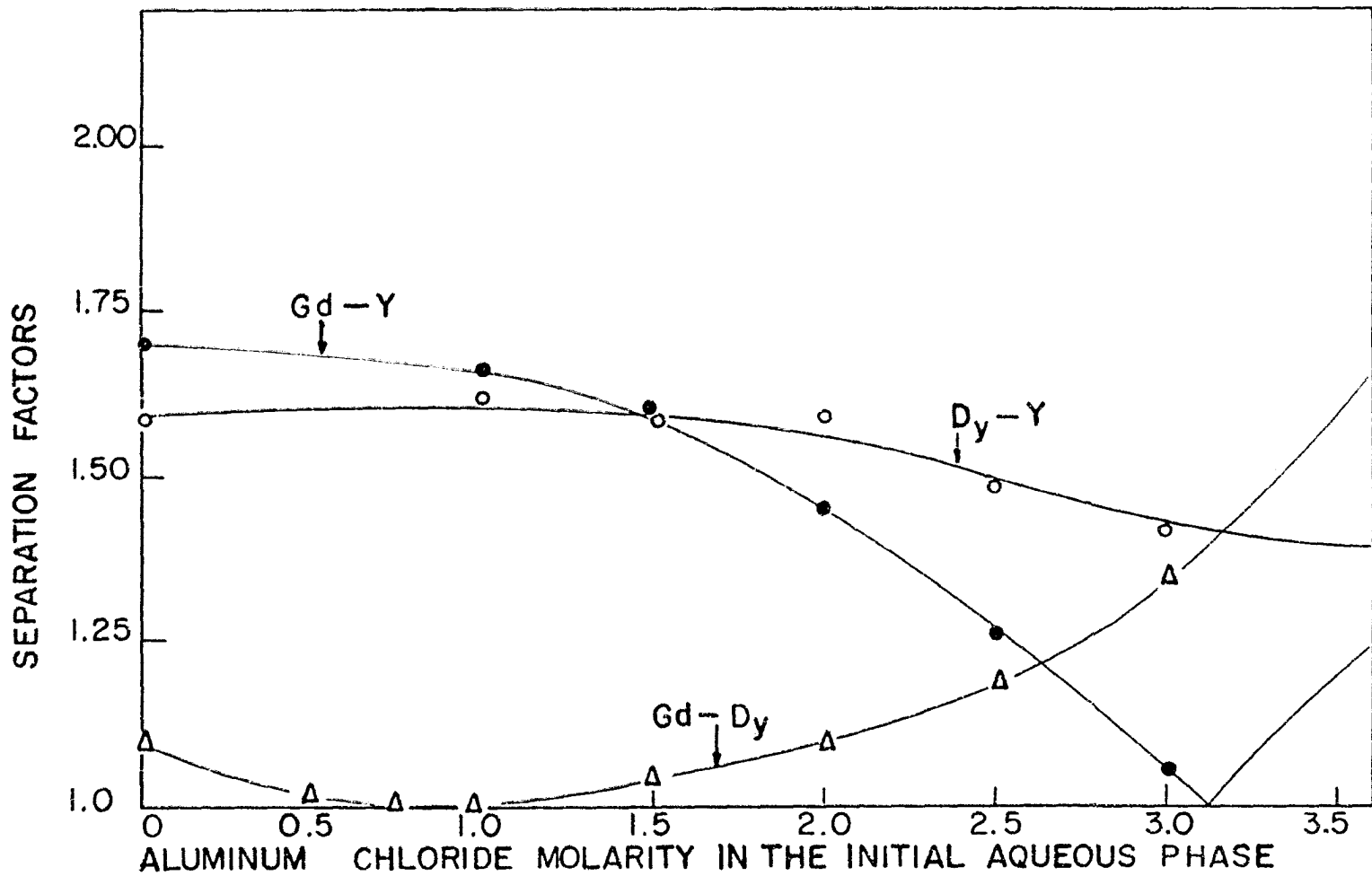


Figure 38 - Separation Factor at Various Aluminum Chloride Concentrations in the Presence of 2.02 Molar Nitric Acid.

In the operation of a multistage extraction process the time required for separation of the equilibrated phases is an important variable from the practical viewpoint. For extracting these yttrium-rare earth nitrate systems the phase separation time decreased as the acidity increased. In the 0.18 molar nitric acid system containing 2.0 molar aluminum chloride the phase separation time was about 20 minutes while for a similar system containing 5.3 molar nitric acid only about one minute was required. As the concentration of the salting-out agent increased the phase separation time also increased. In the 1.02 molar nitric acid medium free of any salting-out agent 50 seconds was needed for phase separation. When 2.0 molar aluminum chloride was added to this 1.02 molar nitric acid system the separation time was 9.0 minutes. Although factors other than the salting-out agent and nitric acid concentration are important in controlling phase separation times these variables must be carefully considered in selecting a system for the multistage extractions.

In general, extraction of the very low nitric acid yttrium-rare earth systems with tributyl phosphate gave a separation of gadolinium and dysprosium from yttrium. Although salting-out agents decrease these separation factors slightly, they increase the mass transfer of rare earth salts to the organic phase. Consequently, the required volume of organic solvent is decreased.

(2) Extractions employing various organic phosphates and phosphites. A number of single stage extractions were carried out employing various pure organic phosphates and phosphites as the organic phase. The nitric acid aqueous phase in each case contained the yttrium-rare earth concentrate from Gadolinite ore. The aqueous feed solution contained the equivalent of 280 grams of the combined oxides per liter. Equal volumes of the organic and aqueous phases were employed in each extraction.

Some generalities were evident from the observations made when employing organic phosphites. As their molecular weight increased less material was extracted by the organic phase with a decrease in the yttrium and gadolinium distribution coefficients. The gadolinium-yttrium separation factor increased almost linearly with per cent mass transfer to the organic phase. The values for di-2-ethylhexyl hydrogen phosphite did not follow these trends because of its low stability in the acid system. Partial hydrolysis of this organic phosphite resulted in the formation of complex phosphites and in subsequent inaccurate oxide weights. Diethyl hydrogen phosphite because of its rapid hydrolysis gave a completely miscible system. The distribution coefficient for the yttrium was larger than for the gadolinium in a corresponding system involving a phosphite extraction.

Upon comparison of similar organic phosphites and phosphates as solvents higher gadolinium-yttrium separation factor and distribution values were obtained in the phosphite systems. More material was extracted by the organic phosphite than by the corresponding organic phosphate. The assumptions were made in this work that the organic phosphite did not oxidize to the corresponding organic phosphate in this nitric acid system. Consequently, these extractions show that the doubly bonded oxygen of the phosphate radical is not an important factor in the yttrium-gadolinium separation. Fewer stages would probably be required for separation of yttrium from gadolinium when extracting with an organic phosphite rather than with the corresponding organic. The low stability of the organic phosphites, however, would probably decrease their utility for a continuous operation.

(d) Multistage extraction of the yttrium-rare earth concentrate from Gadolinite ore. Single stage extractions of the yttrium-rare earth nitrate mixture from Gadolinite ore showed that a low nitric acid system permitted separation of gadolinium and dysprosium from yttrium quite efficiently. Consequently, a 20 stage extraction employing this low acid condition was carried out in the counter-current extractor shown in Figure 1. The aqueous feed solution was 0.12 molar in nitric acid and contained the

equivalent of 230 grams of yttrium-rare earth oxides per liter. Five milliliters per cycle of this feed solution was introduced at stage 14. Tributyl phosphate which was 0.05 molar in nitric acid constituted the organic phase. It was added at stage one at a rate of 17.5 milliliters per cycle. Twenty-five milliliters per cycle of 0.12 molar nitric acid solution which was 0.50 molar aluminum chloride was added at stage 20. The nitric acid concentrations in the initial aqueous and organic phases constituted equilibrium values. In the aqueous phase the concentration of aluminum chloride was approximately 0.5 molar throughout the entire column. In addition to increasing the mass transfer to the organic phase this aluminum chloride gave a nearly constant ionic strength throughout the extractor.

After 100 cycles of operation, no rare earth or yttrium was detected in the organic product phase. However, stage-wise analyses of aliquots indicated that the organic phase of stage 19 contained the equivalent of 4.0 grams of oxide per liter. Since a complete separation of gadolinium and dysprosium from yttrium requires that approximately 25 per cent of the total material be transferred to the organic phase, a tap-off device (7) was added at stage 16 to deliver 7.0 milliliters of the organic phase for each cycle of operation. The remaining portion of the organic phase

which was delivered at stage 20 was added to the product phase delivered from the tap-off stream. The extraction was then continued for 100 more complete cycles.

Analyses of the product phase from the last 20 cycles indicated that 0.90 of a gram of oxide was delivered by the aqueous product phase while 0.28 of a gram was delivered by the organic product phase per cycle. This represented a 76-24 per cent split of the mixture by weight. Analyses of most of the major constituents of the initial feed mixture and product phases appear in Table 25.

It is apparent from these data that gadolinium and dysprosium preferred the organic phase and were separated from most of the yttrium which remained in the aqueous phase. It can also be noted that on an enrichment basis samarium and holmium to a great degree and neodymium to a lesser degree favored the organic phase. According to the analyses in Table 25 only yttrium on this same basis preferred the aqueous phase. However, a spectrographic qualitative analysis indicated that thulium and ytterbium also favored the aqueous phase.

From a material balance it was calculated that 89 per cent of the yttrium was delivered by the aqueous product phase. Approximately 80 per cent of the dysprosium and greater than 85 per cent of the gadolinium was delivered by the organic product phase. It is apparent therefore



that about 90 per cent of the yttrium was separated from about 80 to 85 per cent of the gadolinium and dysprosium in a continuous extractor. Further work on the improvement of this system and an increase in the number of stages should improve this separation of gadolinium and dysprosium from yttrium.

Table 25

Analyses of the Oxide Mixtures from the Multistage Extraction of the Yttrium-Rare Earth Concentrate from Gadolinite Ore

	Feed	Aqueous phase product	Organic phase product
$\text{Nd}_2\text{O}_3$	5.0%	4.1%	6.6%
$\text{Sm}_2\text{O}_3$	5.0%	1.0%	11.0%
$\text{Gd}_2\text{O}_3$	5.2%	< 3.0%	20.2%
$\text{Dy}_2\text{O}_3$	7.6%	2.0%	24.8%
$\text{Ho}_2\text{O}_3$	1.1%	1.0%	4.0%
$\text{Y}_2\text{O}_3$	61.0%	70.0%	26.4%

Figure 39 shows the total oxide concentration in the organic and aqueous phases as a function of stage number for this multistage extraction. It is apparent from this figure that no appreciable amount of material was detected in either phase past stage 17. Evidently all the rare

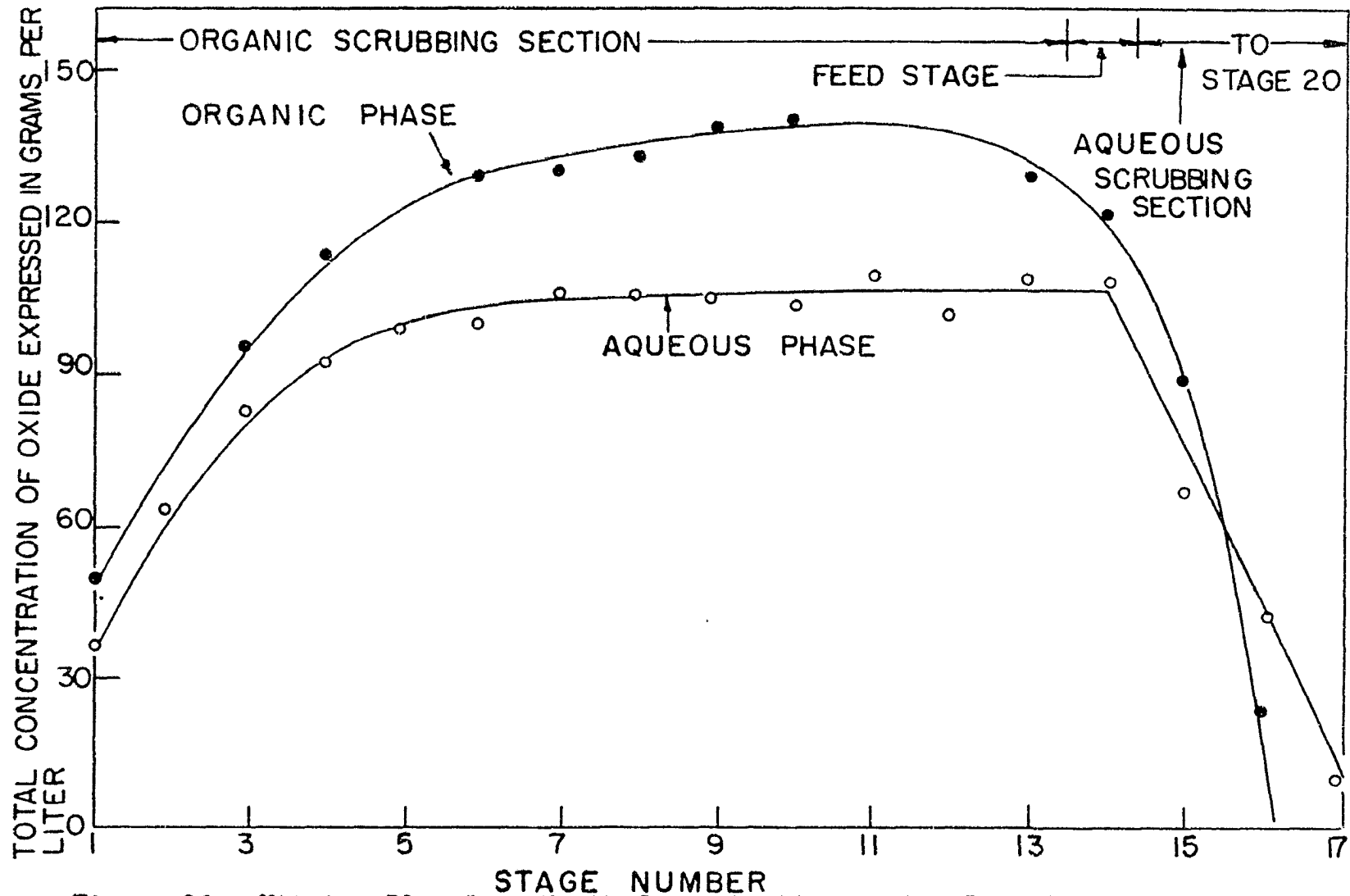


Figure 39 - Yttrium Plus Rare Earth Concentration in the Liquid Phases as a Function of Stage Number.

earths which were not delivered through the tap-off device in stage 16 were easily back-extracted by the aqueous phase. In almost all stages the rare earth salts preferred the organic phase on a concentration basis. The decrease in yttrium-rare earth concentration at the organic inlet end of the extractor as shown in Figures 20, 21, 22, 24, 25 and 26 was not as pronounced for this system. This was probably caused by the presence of the salting-out agent in the aqueous phase.

The results of this multistage extraction of the yttrium-rare earth concentrate from Gadolinite ore substantiate the single stage extraction data. This multistage extraction showed that dysprosium and gadolinium can be separated from yttrium quite readily on a continuous basis by extracting a low nitric acid feed solution of yttrium plus the rare earths with tributyl phosphate. The inversion of certain rare earth extractability as was also observed by Peppard and co-workers (26) was found useful in effecting separations. It is believed that for many separations the extraction of this dilute nitric acid solution of yttrium and rare earths would prove more economical than extractions employing the highly concentrated nitric acid.

## D. Conclusions

### 1. Ore processing

a. A Gadolinite ore was leached several times with hot concentrated nitric acid to obtain its yttrium-rare earth content. An ion-exchange resin treatment was employed to remove a certain fraction of the heavy rare earths. The remaining mixture, referred to as tailings, analyzed in terms of oxide about 65 per cent yttrium, about five per cent heavy rare earths and about 30 per cent light rare earths.

b. The yttrium-rare earth fraction of a Fergusonite ore was rendered soluble by treatment of the ore with fused alkali followed by an acid leach. This yttrium-rare earth concentrate in terms of oxides consisted of about 50 per cent yttrium, 10 per cent heavy rare earths and 40 per cent light rare earths.

c. The yttrium-rare earth fraction of a Gadolinite ore was recovered also by an alkali fusion followed by an acid leach. The resulting yttrium-rare earth concentrate in terms of oxide was about 60 per cent yttrium, 15 per cent heavy rare earths and 25 per cent light rare earths.

### 2. Single stage extractions

a. Tributyl phosphate in general preferentially extracts the rare earths from a concentrated nitric acid

solution according to their increasing atomic number. For low nitric acid systems some inversions in their relative extractability occurs. The mass transfers from the aqueous phase to the organic phase were a minimum for about a 6.0 molar nitric acid aqueous phase. Yttrium has an anomalous behavior since it resembles the low atomic numbered rare earths in a low nitric acid system, is similar to gadolinium in a 4.5 molar nitric acid system, resembles dysprosium in about the 6.0 to 8.0 molar nitric acid medium and acts like holmium in the concentrated nitric acid systems. Consequently, the control of nitric acid concentration permits the separation of yttrium from the rare earth salts.

b. The yttrium-rare earth mixture obtained from the ion-exchange column tailings was dissolved in 13 molar aqueous nitric acid and extracted with various volumes of tributyl phosphate. The mass transfers from the aqueous to the organic phase and the gadolinium-yttrium separation factors increased as the volume ratio of the organic to the aqueous phase increased. A mass transfer of 72.1 per cent in terms of oxides and a gadolinium-yttrium separation factor of about 3.3 was obtained from an extraction employing equal volumes of the organic and aqueous phases.

Extraction of a 6.0 molar nitric acid solution of the yttrium-rare earth concentrate obtained from Fergusonite ore with an equal volume of tributyl phosphate resulted in

a mass transfer to the organic phase of 35.1 per cent on an oxide basis and a gadolinium-yttrium separation factor of 1.37.

Addition of hydrochloric acid to this 6.0 molar nitric acid system before extraction resulted in a somewhat higher gadolinium-yttrium separation factor with little change in mass transfer.

The addition of acetic acid to the 6.0 molar nitric acid system increased the mass transfer from the aqueous to the organic phase. Small amounts of acetic acid increased the gadolinium-yttrium separation factor while large amounts decreased it.

Sulfuric acid when added to this nitric acid medium before extraction increased the gadolinium-yttrium separation factor while decreasing the mass transfer to the organic phase.

d. Extractions of the Fergusonite ore yttrium-rare earth concentrate dissolved in from 2 to 10 molar hydrochloric acid with equal volumes of tributyl phosphate indicated that an increase in acidity resulted in an increase in mass transfer to the organic phase. However, in no case was more than 7.7 per cent of the total yttrium-rare earth content expressed as oxide extracted by this organic phase. The gadolinium-yttrium separation factor remained approximately 1.1 over the entire hydrochloric

acid range. Consequently, the nitric acid system appeared to be superior to the hydrochloric acid system for separating yttrium-rare earth salts by liquid-liquid extraction.

e. The extraction of the Fergusonite ore yttrium-rare earth concentrate dissolved in 6.0 molar hydrochloric acid with an equal volume of hexone gave a mass transfer to the organic phase of only about one per cent and a gadolinium-yttrium separation factor of only 1.02. The addition of 3.0 molar ammonium thiocyanate to this aqueous phase before extraction caused slightly more extraction but no change in the gadolinium-yttrium separation factor. Tributyl phosphate appeared to be superior to hexone in a hydrochloric acid medium for yttrium-rare earth separations by liquid-liquid extraction.

f. Extractions of a nitric acid solution of the Gadolinite ore yttrium-rare earth concentrate with tributyl phosphate indicated that the presence of aluminum nitrate, aluminum chloride, magnesium nitrate, magnesium chloride or sodium chloride in the initial aqueous phase increased the mass transfer of rare earths to the organic phase. The higher the concentration of the salting-out agent in the initial aqueous phase the greater was the mass transfer to the organic phase. Likewise there was a corresponding increase in the yttrium, dysprosium, and gadolinium distribution coefficients. The effect of these

salting-out agents was most pronounced in the low nitric acid systems. For a given anion the higher valence cations effected the greatest mass transfer. The nitrate ion was more effective in increasing yttrium-rare earth transfer than the chloride ion for a given cation at equal concentrations.

The use of the chloride salts as a salting-out agent in general slightly decreased the gadolinium-yttrium, yttrium-dysprosium and gadolinium-dysprosium separation factors. The same general variation in the values of the separation factors with nitric acid concentration resulted with or without the presence of any salting-out agent. In the presence of the nitrate salting-out agents this gadolinium-yttrium separation factor trend was unchanged. However, in this case, a large variation in the yttrium-dysprosium and gadolinium-dysprosium separation factors resulted. In the presence of both the nitrate and chloride salting-out agents the dysprosium and the gadolinium separation factors with respect to yttrium were relatively high at low nitric acid concentrations.

The extraction of an aqueous phase containing increasing amounts of aluminum chloride at constant nitric acid concentration yielded the same general trends as increasing the nitric acid concentration at constant aluminum chloride concentration. The ionic strength of the solution might be



an important factor in controlling preferred yttrium-rare earth extractability.

g. The Gadolinite ore yttrium-rare earth mixture dissolved in nitric acid concentrations ranging from 0.17 to about 6.0 molar was extracted with tributyl phosphate. Gadolinium and dysprosium could best be separated from yttrium at low nitric acid concentration while yttrium and dysprosium can be separated most efficiently from gadolinium at high nitric acid concentrations. Dysprosium and gadolinium had similar distribution coefficients at about 1.0 molar nitric acid while the gadolinium and yttrium distribution coefficients were the same at about 4.5 molar nitric acid.

h. Extractions of a nitric acid solution of the Gadolinite ore yttrium-rare earth concentrate with a series of organic phosphites indicated an increase in mass transfer to the organic phase as the molecular weight of the organic phosphite decreased. The gadolinium-yttrium separation factor was inversely proportional to the percent transfer to the organic phase.

Comparison of extractions with corresponding organic phosphites and phosphates indicated that the phosphites yielded the highest gadolinium-yttrium separation factors and mass transfers to the organic phase. This indicated

that the doubly bonded oxygen in organic phosphate is not required for yttrium-rare earth extraction and separation.

### 3. Multistage extractions

a. The more promising conditions obtained from the single stage extractions were employed in a series of 20 stage countercurrent liquid-liquid extraction processes. The same general trends observed in the single stage extractions were observed in the multistage experiments although the separations were more pronounced.

b. The yttrium-rare earth nitrate mixture from the ion-exchange column tailings was divided into a fraction analyzing on an oxide basis greater than 90 per cent yttrium with about a 90 per cent recovery of the total yttrium present. The other fraction, or the aqueous phase product, contained the light rare earths and the remaining 10 per cent of the yttrium. A 13 molar nitric acid medium constituted the aqueous phase.

c. The Fergusonite ore yttrium-rare earth concentrate was separated into a fraction containing 85 per cent yttrium on the oxide basis by two separate countercurrent extractions. The nitric acid concentrations in the aqueous phases for the extraction processes were 13 molar and 7.0 molar respectively. Tributyl phosphate was the organic phase in both cases. The yttrium depleted fraction, or

the aqueous phase product from the first extraction process, was further separated into two fractions. One contained essentially only praseodymium and neodymium while the other was composed chiefly of samarium, gadolinium, dysprosium and yttrium.

d. Extraction of a 0.12 molar nitric acid solution of the yttrium-rare earth mixture from Gadolinite ore with tributyl phosphate gave an aqueous product which was enriched in yttrium and an organic product containing relatively large amounts of samarium, gadolinium and dysprosium. Consequently, this extraction indicated a method of separating yttrium from gadolinium and dysprosium.

## VII. SUMMARY

The use of liquid-liquid extraction for the separation of some inorganic compounds was demonstrated in this study. The inorganic compounds separated included those of niobium and tantalum, of vanadium and tantalum, of zirconium and hafnium and of yttrium and some of the rare earths. Tantalum and niobium spectrographically free of each other and hafnium spectrographically free of zirconium were prepared in quantity on a continuous basis. High purity fractions of zirconium, yttrium and vanadium were effected while the rare earth mixtures were divided into several highly enriched fractions.

In several cases these inorganic mixtures were obtained from naturally occurring ores by a caustic fusion followed by a series of basic and acid leaches. An aqueous liquid containing the compounds to be separated was in each single stage test extracted by an immiscible organic solvent. Analyses of the equilibrium phases allowed calculation of the distribution coefficients and separation factors. Modifications of such aqueous phase variables as solute concentration, mineral acid, acidity, complexing agent, salting-out agent and volume usually affected the values for the distribution coefficients and separation factors. The nature, composition and volume of the organic phase

also affected these values. A series of single stage extractions was required to establish the apparent optimum range of conditions for a particular separation. These conditions were employed in a multistage countercurrent extraction to produce the purified inorganic compounds on a continuous basis.

The tantalum and niobium mixture which contained about equal weights of each element was obtained by processing a columbite-tantalite ore. A stable aqueous solution, or stock solution, containing the equivalent of 517 grams of tantalum and niobium pentoxides per liter was obtained by dissolving the mixed earth acids in concentrated excess hydrofluoric acid. About six moles of hydrofluoric acid per mole of this niobium-tantalum mixture were required to obtain a stable aqueous solution. Single stage extractions of this stock solution and its various water dilutions with many organic solvents indicated that tantalum was always preferentially extracted. As a general organic class the ketones were most effective in obtaining the niobium-tantalum separation. However, many alcohols, amines, aldehydes, ethers, esters, organic phosphates, organic phosphites and mixed organic solvents also extracted appreciable quantities of high purity tantalum. Several of the organic solvents in a single stage extraction of a 22 per cent aqueous stock solution employing equal volumes of

the two phases extracted greater than 50 per cent of the tantalum which analyzed less than one per cent niobium. Included in this group were triethyl citrate, diethyl ketone, heptanone-2, isophorone, mesityl oxide, methyl-n-hexyl ketone, methyl isobutyl ketone, methyl isopropyl ketone, tri-2-ethylhexyl phosphite and a 5.0 volume per cent solution of Primene JM-T in diethyl ketone. Tantalum-niobium separation factors as high as 4180 were obtained from these single stage extractions.

As the water dilution of the stock solution was increased the tantalum-niobium separation factors and purity of the separated tantalum also increased while the mass transfer of niobium and tantalum to the organic phase decreased. A series of extractions was carried out in which diethyl ketone was the organic phase while the aqueous phase contained various ratios of hydrofluoric acid concentration to niobium plus tantalum concentration. It was observed that a decrease in the amount of excess hydrofluoric acid decreased the mass transfer to the organic phase and gave increased tantalum-niobium separation factors. Very little preference in the extractability of tantalum was evident when a large excess of hydrofluoric acid was present. It was proposed that in the presence of small amounts of free hydrofluoric acid the niobium and tantalum

species in the aqueous solution are different while they approach similarity as the excess acid is increased.

A series of multiple-contact batch extraction tests was carried out on the 22 per cent stock solution. Three successive equal volume extractions of this aqueous solution with pure diethyl ketone resulted in a recovery of 99 per cent of the niobium spectrographically free of tantalum and a 96 per cent recovery of the tantalum containing 0.15 per cent niobium oxide. The intermediate fraction which was mainly tantalum constituted 2.3 per cent of the initial total oxide weight. It was necessary to add a small amount of hydrofluoric acid to the system before making this third extraction with diethyl ketone. If isophorone were used in place of diethyl ketone for this third extraction the same results were obtained without this latter addition of hydrofluoric acid. It is believed that this multiple-contact extraction process could be readily developed to afford convenient analytical and commercial methods for separating tantalum from niobium.

Because of the highly corrosive nature of acid fluoride solutions toward glass equipment other liquid-liquid systems were investigated for separating niobium and tantalum.

A potassium hydroxide solution of the niobium and tantalum earth acids was neutralized with citric acid and extracted with an organic. The results indicated that niobium in this case was preferentially extracted by the organic phase.

Although this system was not fully investigated the lower values of the mass transfer to the organic phase and of the tantalum-niobium separation factor indicated that this solution was decidedly less favorable for effecting a separation of niobium from tantalum.

Aliphatic and aromatic hydroxyamines neutralized and formed a stable solution with the hydrofluoric acid solutions of niobium and tantalum. Corrosion tests indicated relatively little attack on glass by these hydrofluoric acid systems which had been neutralized with amines to a pH of 4 or more. A number of single stage extractions of these amine-neutralized solutions with various organic solvents was carried out. Tantalum was preferentially extracted by the organic phase. In general the tantalum-niobium separation factors obtained by extracting these amine-neutralized solutions were lower than those obtained by extracting the hydrofluoric acid solutions of niobium and tantalum. The hydrofluoric acid solutions which had been neutralized by the aromatic hydroxyamines yielded much greater transfers to the organic phase and greater tantalum-niobium separation factors than the corresponding aliphatic hydroxyamine neutralized systems. In the former systems tantalum-niobium separation factors as high as 657 were obtained.



Three countercurrent multistage extractions were carried out employing diethyl ketone as the organic phase and these aromatic hydroxyamine neutralized hydrofluoric acid solutions of niobium and tantalum as the aqueous feeds. The feed solution in the first extraction was neutralized with phenyl ethyl ethanalamine and contained the equivalent of 95 grams of combined niobium and tantalum pentoxides per liter. In 10 stages tantalum containing 100 ppm niobium and niobium spectrographically free of tantalum were delivered by the organic and aqueous product phases respectively.

The feed solutions for the second and third multistage extractions of this series were neutralized with phenyl diethanolamine and contained the equivalent of 260 grams and 300 grams respectively of the combined niobium and tantalum pentoxides per liter. Fifteen stages were employed for these extractions. In the second extraction tantalum containing 200 ppm niobium and niobium spectrographically free of tantalum were obtained. The organic phase product of the third multistage extraction contained tantalum spectrographically free of niobium while the aqueous phase product was 98.7 per cent niobium oxide and 1.3 per cent tantalum oxide. These multistage extractions indicated the practicability of countercurrent liquid-liquid extraction as a method for separating tantalum and niobium in quantity on a continuous basis.

Tantalum and vanadium dissolved in hydrofluoric acid were partially separated by extraction with various organic solvents. In all cases tantalum was preferentially extracted by the organic phase. For a single stage extraction with tributyl phosphate greater than 90 per cent of the tantalum containing less than 2.0 per cent vanadium was recovered from the equilibrium organic phase. Tantalum-vanadium separation factors as large as 736 were obtained with favorable mass distribution. It was evident that vanadium closely resembles niobium when extracting an acid fluoride solution. A three or four stage extraction would probably yield a quantitative separation of tantalum from vanadium.

The separation of hafnium and zirconium was accomplished by liquid-liquid extraction. Portions of a salt mixture which analyzed about 3 per cent zirconium and 97 per cent hafnium relative to their total were dissolved in varying concentrations of nitric acid. These aqueous solutions were extracted with either pure or diluted tributyl phosphate. The organic diluent employed was dibutyl ether.

In all the single stage extractions zirconium was preferentially extracted by the organic phase. Hafnium-zirconium separation factors and mass transfers as large as 57 and 51.2 per cent respectively were obtained when employing equal volumes of the aqueous and organic phases

in single stage extractions. The use of an organic diluent decreased the mass transfer from the aqueous to the organic phase as well as the hafnium-zirconium separation factor. The presence of nitric acid increased the mass transfers to the organic phase and decreased the hafnium-zirconium separation factors.

The apparent optimum conditions for hafnium-zirconium separation obtained from these single stage extractions were employed for estimating the operating conditions for multistage countercurrent extractions. In one 15 stage extraction the hafnium and zirconium were separated into a fraction containing 99.93 per cent zirconium and a fraction containing 99.1 per cent hafnium relative to their sum. In another 15 stage extraction the product from the organic phase contained 35 per cent zirconium oxide and 65 per cent hafnium oxide while the hafnium from the aqueous phase contained only 20 ppm zirconium.

A small scale production extraction was carried out in which the equivalent of about 100 pounds of pure hafnium spectrographically free of zirconium was recovered. The aqueous feed solution for this 17 stage extraction was 5.8 molar nitric acid which contained the equivalent of 280 grams of the combined zirconium and hafnium oxides per liter. A 40 volume per cent solution of dibutyl ether in tributyl phosphate constituted the organic phase while a

5.8 molar nitric acid solution was the aqueous scrub. The organic product phase from this extraction contained 25 per cent zirconium oxide relative to hafnium oxide while the hafnium in the organic product phase contained less than 20 ppm zirconium. Since this amount of zirconium was below the limit of accurate detection by the spectrographic method employed, the hafnium product was considered to be spectrographically free of zirconium. A material balance indicated that 90 per cent of the total hafnium was delivered by the aqueous product phase. As stated above the starting material on a hafnium plus zirconium basis analyzed about three per cent zirconium and 97 per cent hafnium. It is believed that the aqueous product phase from this production extraction contained the purest hafnium relative to zirconium that has ever been produced in quantity.

The yttrium-rare earth mixtures which were investigated were obtained from Fergusonite ore, Gadolinite ore and tailings from a process employing an ion-exchange resin column. In each case the mixture in terms of oxide was composed of from 50 to 60 per cent yttrium and 5 to 15 per cent heavy rare earths with the light rare earth fraction constituting the remaining material. In general tributyl phosphate was employed for extracting the nitric acid solutions of these rare earth mixtures although the use of other organic liquids was briefly investigated.

Single stage extraction data indicated that the preferential extractability of the rare earths from an aqueous system greater than 3.0 molar in nitric acid increase with atomic number. At lower nitric acid concentrations some deviations from this trend appeared. The mass transfers of yttrium and rare earths increased with nitric acid concentrations above about 6.0 molar. The reverse mass transfer trend resulted for the range below about 6.0 molar nitric acid. Yttrium extracts in combination with holmium in a highly concentrated nitric acid system. However, in the 6 to 12 molar nitric acid system it extracts essentially with dysprosium while in a 3.0 to 4.5 molar nitric acid system it resembles gadolinium. In lower nitric acid systems yttrium extracts with the lower atomic number rare earths.

The use of salting-out agents such as aluminum nitrate and chloride, magnesium nitrate and chloride and sodium chloride was investigated. These salting-out agents caused an increase in the mass transfer to the organic phase although in most cases not affecting the yttrium-rare earth separation factors to any appreciable extent. As the nitric acid concentration in the system increased the effect of these salting-out agents on mass transfer became less pronounced. The nitrate salting-out agents were more effective in increasing mass transfer than corresponding chloride salts. The high valence cations also caused the

greatest mass transfer of yttrium and rare earths from the aqueous to the organic phase.

The extractions of the nitric acid solutions of yttrium and the rare earths containing various amounts of hydrochloric, acetic and sulfuric acids were carried out. In general the presence of these acids increased the gadolinium-yttrium separation factor slightly. Tributyl phosphate extracted a very small amount of yttrium and the rare earths from their hydrochloric acid solutions. The gadolinium-yttrium separation factors were close to unity for this system. The use of hexone as the organic phase and addition of ammonium thiocyanate to this chloride solution resulted in no appreciable yttrium or rare earth transfer or separation of gadolinium from yttrium. Since the gadolinium-yttrium, yttrium-dysprosium and the gadolinium-dysprosium separation factors seldom exceeded a value of 3.0 many stages were required for their separation.

A number of 20 stage countercurrent extractions employing a nitric acid yttrium-rare earth solution as the aqueous phase and tributyl phosphate as the organic phase was carried out. For a concentrated nitric acid system the organic product phase generally contained yttrium and the heavy rare earths while the aqueous product phase contained the light rare earth fraction plus a small amount of yttrium and dysprosium. In one multistage extraction the

organic product phase delivered 90 per cent of the total yttrium which analyzed to be 91 per cent pure on an oxide basis. The heavy and light fractions of the yttrium-rare earth concentrate from Fergusonite ore was easily separated by liquid-liquid extraction. An additional extraction of the light fraction resulted in a fraction enriched in praseodymium and neodymium. Gadolinium and dysprosium were separated from yttrium to a great extent on a continuous basis by a multistage extraction employing a 0.12 molar nitric acid aqueous solution of the yttrium-rare earth mixture. The extractions of these yttrium-rare earth concentrates showed the possibility of separating yttrium from any particular rare earth and the rare earths themselves on a continuous basis by combinations of liquid-liquid extractions.

The liquid-liquid systems presented here indicate further the applicability of solvent extraction for separating inorganic compounds. Since the general approach was of a practical nature rather than theoretical, many questions regarding the extraction mechanisms and solution thermodynamics remained unanswered. Such a theoretical approach would probably initially require such data as presented here. It is believed that an accurate and detailed theoretical treatment of liquid-liquid extraction principles will be necessary before much of the time consuming and laborious

work as indicated here can be eliminated. However, until such studies have been made and more working principles evolved the development of conditions for practical liquid-liquid extraction separations will have to be determined by a systematic trial and error approach.



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X. APPENDICES

Table 26

## Appendix A

Sources of Some of the Organic Compounds Employed in the  
Liquid-Liquid Extraction Studies

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Organic Compound	Source
<b>A. Alcohols</b>	
1. Di-isobutyl carbinol	Carbide and Carbon Chem. Div.
2. Heptanol-3	Carbide and Carbon Chem. Div.
3. Methyl amyl carbinol	Carbide and Carbon Chem. Div.
4. Methyl n-hexyl carbinol	The Matheson Co., Inc.
5. Methyl propyl carbinol	Sharples Chemicals, Inc.
6. Octyl alcohol (iso)	Enjoy Company, Inc.
7. Oleyl alcohol	E. I. DuPont Chem. Co.
8. Pentasol-27	Sharples Chemicals, Inc.
<b>B. Aldehydes</b>	
1. Butyraldehyde	Eastman Org. Chem. Dist. Prod.
2. Crotonaldehyde	Eastman Kodak Co.
3. Heptaldehyde	Eastman Org. Chem. Dist. Prod.
4. Paraldehyde	Merck and Co., Inc.
<b>C. Amines</b>	
1. Aminoethyl ethanolamine	Carbide and Carbon Chem. Div.

Table 26 (Continued)

Organic Compound	Source
<b>C. Amines (Continued)</b>	
2. Aminohydroquinone diethyl ether	Tennessee Eastman Co.
3. Aminohydroquinone dimethyl ether	Tennessee Eastman Co.
4. 3-Aminopropanol	American Cyanamide Co.
5. Dibutyl amine	Sharples Chemicals, Inc.
6. Diethanolamine	Carbide and Carbon Chem. Div.
7. Diethylethanolamine	Jefferson Chemical Co.
8. Monoethanolamine	Carbide and Carbon Chem. Div.
9. Phenyl diethanolamine	Tennessee Eastman Co.
10. Phenyl ethyl ethanolamine	Tennessee Eastman Co.
11. Primene 81-T	Rohm and Haas Co.
12. Primene JM-T	Rohm and Haas Co.
13. Tertiaryoctylamine	Rohm and Haas Co.
14. m-Tolyl diethanolamine	Tennessee Eastman Co.
15. o-Tolyl propanolamine	Tennessee Eastman Co.
16. Tributyl amine	Sharples Chemical Co.
17. Triethanolamine	Eastman Kodak Co.
<b>D. Esters</b>	
1. Benzyl acetate	Eastman Kodak Co.
2. n-Butyl d-tartrate	Eastman Kodak Co.

Table 26 (Continued)

Organic Compound	Source
D. Esters (Continued)	
3. Diethyl carbonate	U. S. Industrial Chem., Inc.
4. Diethyl oxalate	U. S. Industrial Chem., Inc.
5. Diethyl phthalate	U. S. Industrial Chem., Inc.
6. Ethyl acetoacetate	Eastman Kodak Co.
7. Ethyl salicylate	Eastman Kodak Co.
8. Methyl benzoate	Eastman Org. Chem. Dist. Prod.
9. Tributyl citrate	Chas. Pfizer and Co., Inc.
10. Triethyl citrate	Chas. Pfizer and Co., Inc.
11. Tripropyl citrate	Chas. Pfizer and Co., Inc.
E. Ketones	
1. Cyclohexanone	Eastman Org. Chem. Dist. Prod.
2. Diethyl ketone	Carbide and Carbon Chem. Div.
3. Di-isobutyl ketone	Carbide and Carbon Chem. Div.
4. Di-isopropyl ketone	Eastman Org. Chem. Dist. Prod.
5. Heptanone-2	Eastman Org. Chem. Dist. Prod.
6. Heptanone-3	Eastman Org. Chem. Dist. Prod.



Table 26 (Continued)

Organic Compound	Source
<b>E. Ketones (Continued)</b>	
7. Heptanone-4	Eastman Org. Chem. Dist. Prod.
8. Isophorone	Carbide and Carbon Chem. Div.
9. Mesityl oxide	Eastman Kodak Co.
10. Methyl ethyl ketone	The Matheson Co., Inc.
11. Methyl n-hexyl ketone	The Matheson Co., Inc.
12. Methyl isobutyl ketone	The Matheson Co., Inc.
13. Methyl isopropyl ketone	Cliffs Dow Chemical Co.
14. Methyl phenyl ketone	The Matheson Co., Inc.
15. 2,4 Pentanedione	Carbide and Carbon Chem. Div.
<b>F. Phosphates</b>	
1. Tributoxyethyl phosphate	Ohio Apex Inc.
2. Tributyl phosphate	Commercial Solvents Corp.
3. Tri-2-ethylhexyl phosphate	Carbide and Carbon Chem. Div.
<b>G. Phosphites</b>	
1. Dibutyl hydrogen phosphite	Virginia-Carolina Chem. Corp.
2. Tri-2-propyl phosphite	Virginia-Carolina Chem. Corp.
3. Tributyl phosphite	Virginia-Carolina Chem. Corp.
4. Di-2-ethylhexyl hydrogen phosphite	Virginia-Carolina Chem. Corp.

Table 26 (Continued)

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Organic Compound	Source
<hr/> <b>G. Phosphites (Continued)</b>	
5. Trihexyl phosphite	Virginia-Carolina Chem. Corp.
6. Tri-2-ethyl hexyl phosphite	Virginia-Carolina Chem. Corp.
7. Tri-isooctyl phosphite	Virginia-Carolina Chem. Corp.

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Table 27

## Appendix B

## Single Stage Extractions of the Gadolinite Ore Yttrium-Rare Earth Concentrate

Organic Phase = Pure Tributyl Phosphate

Aqueous Phase = HNO<sub>3</sub> Solution Containing the Equivalent of 150 Grams of the Yttrium-Rare Earth Oxides Per Liter

Aq. phase		Equilibrium analysis								Dist. coef.		
HNO <sub>3</sub> conc. (M.)	Salt conc. (M.)	% oxide wt. in org.	% Gd <sub>2</sub> O <sub>3</sub>		% Y <sub>2</sub> O <sub>3</sub>		% Dy <sub>2</sub> O <sub>3</sub>		K <sub>Gd</sub>	K <sub>Y</sub>	K <sub>Dy</sub>	
			Aq.	Org.	Aq.	Org.	Aq.	Org.				
A. Addition of AlCl <sub>3</sub>												
0.18	0	42.0	3.4	7.2	67	54	6.0	10.0	1.36	0.52	1.08	
0.18	0.5	52.9	3.1	7.1	65	57	3.9	9.2	2.24	0.86	2.31	
0.18	1.0	59.0	< 3.0	6.4	63	60	4.0	8.8	----	1.32	3.04	
0.18	2.0	72.7	< 3.0	5.8	61	61	5.2	8.4	----	3.30	5.30	
0.18	3.0	85.1	< 3.0	5.5	65	62	4.8	8.0	----	5.78	10.2	
0.52	0	40.6	3.8	7.2	65	58	5.6	10.0	1.09	0.51	1.02	
0.52	0.5	50.5	3.3	6.9	65	57	5.2	9.2	1.92	0.77	1.55	
0.52	1.0	58.9	3.4	6.6	65	57	5.9	10.0	2.58	1.12	2.15	
0.52	2.0	73.5	3.3	5.6	65	58	5.6	8.8	4.63	2.44	4.30	
0.52	3.0	84.6	< 3.0	5.2	62	58	5.2	8.3	----	5.47	9.21	
1.03	0	39.0	3.9	6.5	66	52	6.0	10.0	0.87	0.44	0.88	
1.03	0.5	47.7	3.2	6.7	65	55	6.0	9.4	1.59	0.65	1.20	
1.03	1.0	53.7	3.4	6.5	65	57	5.2	9.2	2.02	0.92	1.85	
1.03	2.0	69.8	3.2	5.9	65	57	7.2	8.3	4.25	2.03	2.69	
1.03	3.0	83.1	3.9	5.7	63	60	5.6	7.8	7.62	5.02	7.35	
1.60	0	39.4	4.0	7.1	68	61	5.7	8.8	0.90	0.45	0.79	
1.60	1.0	54.1	4.0	5.7	67	63	5.5	8.6	1.43	0.94	1.56	
1.60	2.0	71.5	3.8	6.3	61	64	4.4	7.8	3.69	2.35	4.14	

Table 27 (Continued)

Aq. phase		Equilibrium analysis							Dist. coef.		
HNO <sub>3</sub> conc.	Salt conc.	% oxide wt. in org.	% Gd <sub>2</sub> O <sub>3</sub>		% Y <sub>2</sub> O <sub>3</sub>		% Dy <sub>2</sub> O <sub>3</sub>		K <sub>Gd</sub>	K <sub>Y</sub>	K <sub>Dy</sub>
(M.)	(M.)		Aq.	Org.	Aq.	Org.	Aq.	Org.			
1.60	3.0	79.8	3.8	5.1	63	62	4.5	7.1	5.48	4.04	6.24
2.02	0	38.3	4.9	6.9	70	62	6.6	9.5	0.68	0.43	0.65
2.02	0.5	43.8	4.3	6.0	69	62	6.1	8.7	0.89	0.58	0.92
2.02	1.0	51.3	4.4	6.9	63	60	6.2	9.2	1.41	0.85	1.33
2.02	2.0	64.8	4.3	6.1	63	64	5.2	8.3	2.47	1.77	2.80
2.02	3.0	76.9	4.6	5.1	62	65	5.1	7.7	3.65	3.46	4.90
2.02	4.0	94.5	5.3	5.3	54	66	4.6	7.6	16.8	23.6	31.8
2.02	5.0	100	0	5.3	0	63	0	7.7	----	----	----
3.70	0	37.9	4.9	6.0	66	61	6.6	9.0	0.56	0.42	0.63
3.70	1.0	47.6	5.0	5.9	60	63	6.1	7.9	0.90	0.79	0.98
3.70	2.0	54.3	5.2	5.6	62	66	6.8	8.6	1.21	1.19	1.41
5.30	0	37.5	5.3	5.5	63	65	6.5	8.5	0.45	0.45	0.58
5.30	1.0	42.9	6.1	5.3	60	63	7.0	8.3	0.54	0.65	0.74
5.30	2.0	48.2	6.3	4.5	59	63	7.0	7.4	0.59	0.89	0.89
B. Addition of Al(NO <sub>3</sub> ) <sub>3</sub>											
0.18	0.50	60.6	3.0	6.8	65	59	5.6	9.2	3.12	1.26	2.48
0.18	1.0	74.3	3.5	5.7	65	60	5.6	8.3	4.87	2.78	4.48
0.18	2.0	89.2	4.0	5.2	59	59	5.9	7.5	12.8	9.64	13.1
0.18	3.0	96.5	4.3	5.5	51	60	4.8	7.9	46.4	42.7	60.5
0.52	0.50	56.4	3.5	6.1	65	56	5.9	9.6	2.01	0.99	1.88
0.52	1.0	70.5	3.6	5.5	62	58	6.0	8.3	3.63	2.23	3.32
0.52	2.0	86.3	4.5	5.3	64	61	5.9	8.8	6.38	5.17	8.02
0.52	3.0	94.0	5.1	4.8	55	63	5.8	8.4	19.9	24.2	30.6
1.02	0.5	54.0	4.0	6.3	64	59	5.2	10.0	1.66	0.98	2.03
1.02	1.0	65.9	3.9	5.7	63	59	5.6	9.2	2.74	1.75	3.08
1.02	2.0	80.7	4.5	5.7	60	61	4.8	8.0	1.00	4.86	7.97
1.02	3.0	88.2	4.6	5.2	51	60	4.8	8.0	11.3	11.8	16.7

Table 27 (Continued)

Aq. phase		Equilibrium analysis							Dist. coef.		
HNO <sub>3</sub> conc.	Salt conc.	% oxide wt. in org.	% Gd <sub>2</sub> O <sub>3</sub>		% Y <sub>2</sub> O <sub>3</sub>		% Dy <sub>2</sub> O <sub>3</sub>		K <sub>Gd</sub>	K <sub>Y</sub>	K <sub>Dy</sub>
(M.)	(M.)		Aq.	Org.	Aq.	Org.	Aq.	Org.			
1.60	1.0	60.3	4.1	5.7	64	63	4.8	8.4	1.92	1.36	2.54
1.60	2.0	76.3	4.6	5.8	60	67	4.6	7.6	4.17	3.70	5.46
1.60	3.0	82.6	5.7	5.0	59	67	5.2	7.9	3.82	4.50	5.74
2.02	0.5	49.7	4.6	5.8	70	73	6.4	8.8	1.06	0.78	1.19
2.02	1.0	58.9	5.2	5.5	64	62	4.7	8.1	1.46	1.34	2.40
2.02	2.0	71.0	5.4	5.5	63	61	5.3	8.3	2.79	2.66	4.35
2.02	3.0	73.6	5.3	4.7	62	69	5.6	7.6	3.19	4.00	4.86
2.02	4.0	77.9	6.6	5.0	61	70	6.5	8.3	3.92	5.90	5.98
2.02	5.0	100	0	5.1	0	62	0	7.8	----	----	----
3.70	1.0	51.7	5.5	5.4	63	62	6.3	9.0	0.97	0.97	1.41
3.70	2.0	59.6	6.0	5.3	65	72	6.6	8.1	1.42	1.77	1.96
5.30	1.0	47.4	5.7	4.9	64	68	7.2	8.0	0.70	0.86	0.89
5.30	2.0	55.5	6.9	4.6	62	67	6.7	7.5	0.89	1.44	1.49
C. Addition of MgCl <sub>2</sub>											
2.02	0.5	43.1	4.2	6.2	68	57	6.3	8.7	0.91	0.57	0.86
2.02	1.0	46.2	4.5	6.2	70	61	6.3	9.3	1.06	0.67	1.14
2.02	2.0	51.5	3.8	5.9	63	65	6.2	9.5	1.67	1.10	1.65
3.70	1.0	42.1	4.6	6.1	66	66	6.5	6.8	0.84	0.63	0.66
3.70	2.0	47.1	5.0	5.3	62	65	6.4	8.3	0.94	0.93	1.16
5.30	1.0	39.1	5.3	4.6	65	69	6.1	8.4	0.46	0.56	0.73
5.30	2.0	41.8	5.7	4.9	59	71	6.6	8.0	0.61	0.85	0.86
D. Addition of Mg(NO <sub>3</sub> ) <sub>2</sub>											
2.02	1.0	50.5	3.9	6.1	64	67	5.6	8.8	1.46	0.98	1.46
2.02	2.0	57.6	3.9	5.8	56	64	5.5	4.5	1.85	1.66	1.16

Table 27 (Continued)

Aq. phase		Equilibrium analysis							Dist. coef.		
HNO <sub>3</sub> conc. (M.)	Salt conc. (M.)	% oxide wt. in org.	% Gd <sub>2</sub> O <sub>3</sub>		% Y <sub>2</sub> O <sub>3</sub>		% Dy <sub>2</sub> O <sub>3</sub>		K <sub>Gd</sub>	K <sub>Y</sub>	K <sub>Dy</sub>
			Aq.	Org.	Aq.	Org.	Aq.	Org.			
3.70	1.0	45.0	5.0	5.6	64	63	6.3	9.2	0.83	0.74	1.18
3.70	2.0	53.3	4.9	5.2	59	68	6.3	8.7	1.16	1.25	1.50
5.30	1.0	44.1	6.1	4.5	63	67	7.3	8.4	0.52	0.76	0.82
5.30	2.0	46.0	5.5	3.9	57	68	7.2	8.2	0.59	1.00	0.95