

SELECTIVE SOLVENT EXTRACTION OF TANTALUM
AND NIOBIUM FLUORIDES USING N-BENZOYL-
N-PHENYLHYDROXYLAMINE

By

JAMES SPENCER ERSKINE

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Northwestern State College

Alva, Oklahoma

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Thesis Approved:

Louis P. Varga

Thesis Adviser

Tom Elmore

JH Boyce

Dean of the Graduate College

621523

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CHAPTER I

INTRODUCTION

The extreme chemical similarity of tantalum and niobium has made the separation and determination of these two metals one of the most difficult operations in analytical chemistry. This chemical similarity, which results from the similarity in charge and radius of the ions, contributes to their ability to engage in isomorphism in the crystal lattice which, in turn, results in their coexistence in natural minerals. Combined with their useful properties as refractory alloys in electronics, space and other industries, the need for good commercial separation techniques and analytical separation methods was apparent.

Up until about the last decade, the standard separations and determinations of tantalum and niobium were slow, expensive and not particularly accurate. Better methods needed to be developed. Many methods have been studied but one of the best is solvent extraction.

Varga, Wakley and co-workers (70) have studied in some detail the extraction of tantalum with *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) in 3M perchloric acid containing varying amounts of fluoride. They reported very high distribution ratios and a very high extraction equilibrium constant for the tantalum-BPHA complex in this system. It was because of this ability to extract tantalum from highly acidic solutions and other desirable properties of BPHA, that studies were initiated to see if this reagent could selectively extract tantalum and

niobium under various aqueous phase conditions.

Therefore, the purpose of this work was to determine the individual distribution curves for tantalum and niobium as a function of the fluoride ion concentration using tracer amounts of the elements. Then, using these curves, studies were performed to determine if a separation of tracer amounts of the elements could be achieved from a synthetic mixture of these two. Lastly, experiments were performed to see if tantalum and niobium could be separated one from the other from a mixture of millimolar quantities of these two metals. The radioisotopes, tantalum-182 and niobium-95, were used in the analysis of the phases. Computer calculations were also performed to gain some idea as to the best model for each extracting system along with the equilibrium constant for this model and the formation constants for the species in solution.

CHAPTER II

HISTORICAL

General Information

Hatchett, an English chemist, discovered a new element in 1801 which he named Columbium in honor of America, the country where the columbium mineral was found (25). Rose, in 1844, announced the discovery of another new element which he named Niobium after Niobe, the mythological daughter of Tantalus in Grecian mythology (57). After much controversy, the chemists of the time decided that Hatchett's columbium and Rose's niobium were the same element.

In 1802, Ekberg, a Swedish chemist, studied two minerals, one from Finland and the other from Sweden (22). From these, he isolated a new metallic oxide which he named Tantalum because of the tantalizing difficulty in dissolving the new oxide in acids. Tantalum metal was not actually isolated from this oxide until 1824 by Berzelius.

Niobium and tantalum are the "earth acid" elements because of the slightly acidic nature of their pentoxides. They are almost never found free in nature but are found associated together. Niobates and tantalates are the most common minerals containing niobium and tantalum. Rarely, if ever, does niobium occur in its minerals without tantalum and conversely. Columbite and tantalite are varieties of the same species, orthorhombic iron manganese tantaloniobate $(\text{Fe}, \text{Mn})\text{O} \cdot (\text{Nb}, \text{Ta})_2\text{O}_5$, which forms an isomorphous series in which niobium and tantalum replace each

other in all proportions. The minerals containing excess niobium are called columbite, while the term tantalite is reserved for those containing over 50% of Ta_2O_5 . Many other ores of tantalum and niobium exist and these can be found in the literature (46, 65).

The analytical determination of niobium and tantalum and especially the determination of one in the presence of the other has long presented a challenge to the chemist that is matched in difficulty only by the rare earth and zirconium-hafnium separations. The association of tantalum and niobium in nature with many of the other less common elements adds to their analytical complexity.

Treatment of Ores

Before isolating the metals tantalum and niobium, a preliminary separation from the bulk impurities is necessary. The first step is usually decomposition of the ore to render the components amenable to further treatment. The methods of procedure differ considerably but they may be grouped under five basic divisions. They are: fusion with alkaline fluxes, fusion with acid fluxes, digestion with acid solutions, digestion with alkaline solutions and chlorination.

Separation of Tantalum and Niobium

Classical Separations

Since their discovery, many methods have been proposed for the separation of tantalum and niobium. However, it was Marignac (43) who made the first major contribution in the separation of the metals by his discovery, in 1866, that these two metals could be separated by utilizing the marked differences in the solubilities of their double

fluorides of potassium. In this process, hydrofluoric acid was added to a slurry of the separated earth acids to form the fluorides. Hot potassium hydroxide was added to form K_2TaF_7 and K_2NbOF_5 . The solution was cooled and the K_2TaF_7 crystallized out leaving the K_2NbOF_5 in solution. This method of separation was employed for so many years, not only for analysis but also for production, that eventually it was regarded as the classical method of separation. This method, however, gave only approximate results and it had the fault that if titanium was present it remained tied to the niobium while the tantalum was free from titanium. Surprisingly enough, in spite of its cost and need for special corrosion-resistant equipment, only recently is it being replaced by newer methods.

For 17 years, starting in 1919, Schoeller and his workers made investigations into a better method for the separation of niobium and tantalum. (See the Analyst for this period.) A. R. Powell and W. R. Schoeller (55, 60) devised a method for this separation based on the fact that tantalic oxide was precipitated more readily by tannin from a slightly acid oxalate solution than was any other "earth", particularly niobic oxide. The order was tantalic oxide, titania and niobic oxide. A complete separation could not be quantitatively effected without appreciable coprecipitation of niobium, hence, a process of fractional precipitation was adopted. This can be controlled because the color of the precipitated tantalum-tannin complex is a reliable indicator of its purity. The pure tantalum complex is a light yellow, while the niobium complex is a bright vermilion-red. Titania should be either absent or present in very small amounts (<2%) since it is coprecipitated also thus masking the color changes. The fractionation

process furnished three products: a niobium-free tantalum fraction, a mixed or intermediate fraction (orange to red precipitates), and a tantalum-free niobium filtrate. The second fraction was re-treated, giving another three fractions, the intermediate one of which was again fractionated. Full details of this complicated method are given by W. R. Schoeller and A. R. Powell (59, 61) in their monographs.

During this period tartrate, oxalate and hydrogen peroxide were first used for the stabilization of solutions of the earth acids.

The Need for Better Methods of Separation and Analysis

In the last 30 years, numerous other methods for the separate determination of tantalum and niobium have been investigated. The last 10 years in particular have been very fruitful due to the increased importance of tantalum and niobium. High-temperature applications, missiles, nuclear, electronic and chemical corrosion applications are just a few general uses of tantalum and niobium (65, 49). It seems safe to predict that their use, which has increased several thousandfold since about 1940, will continue to grow and that they will provide qualities under many conditions that are unmatched by any other metal. It is for these reasons that better methods of separation and analysis of tantalum and niobium are needed.

Although the methods evolved by Schoeller, Powell and their co-workers during the period 1919 to 1936 became standard practice for the separation and analysis of tantalum and niobium, the complete analysis of a mineral was still highly complicated. The various separations were not well defined, filtrates and residues needed repeated treatment and several precipitates and solutions had to be handled at the same

time or kept in reserve for various periods; so that cumulative personal errors and various indeterminate losses were usually unavoidable. In addition, a complete analysis took 12-15 days. Better methods needed to be developed.

Recent Methods for the Separation of Tantalum and Niobium

Hydrolysis. Methods depending on hydrolysis have been a common means of separating tantalum and niobium from other metals but not from each other. Jaboulay (29) has used this principle, but complete separation of tantalum and niobium was difficult.

Precipitation. Precipitation methods for separating tantalum and niobium have been used quite extensively.

The method described by Schoeller and Powell based on fractional precipitation with tannin has already been described. Many modifications of the procedure have been used (26, 61, 76).

Many other precipitation methods and reagents have been reviewed by Moshier (49). Reagents included were benzenearsonic acid, 8-hydroxyquinoline, cinnamylhydroxamic acid, N-cinnamoyl-N-phenylhydroxylamine, n-propylarsonic acid, cupferron, sodium hypophosphite, quercetin, morin and hexamethylenetetramine.

Other precipitating reagents are selenous acid, (5) salicylhydroxamic acid (37), sodium diethyl- and sodium pyrrolidinedithiocarbamate (42), and 3:3':4':5:7-pentahydroxyflavanone (15). Moshier and Schwarberg (50) proposed the use of N-benzoyl-N-phenylhydroxylamine (BPHA) as a specific precipitant for tantalum from niobium. The sample was dissolved in hydrofluoric acid, acidified with H_2SO_4 to a pH of 1.0 and the tantalum precipitated by adding a hot aqueous solution of

BPHA. The resultant mixture was filtered, washed and ignited. Only two to three precipitations were needed even for high concentrations of niobium. The operating time was less than that of many other methods and the precipitate was uncontaminated by other metals. Majumdar and Mukherjee (40) also reported that at a pH of 3.5-6.5 BPHA precipitated niobium from tantalum. Majumdar and Mukherjee (38) later reported that BPHA formed a stable complex with niobium of definite composition that could be weighed directly after drying. This eliminated the ignition step. This reagent has been used by other workers using similar methods (35, 36, 39, 41).

The disadvantage of gravimetric methods has been that pre-separation of tantalum and niobium from other constituents of the sample was nearly always necessary. Some satisfactory gravimetric methods have been evolved specifically for alloys, but these have not been generally suitable for minerals.

Chlorination. Chlorination methods usually depend on the fact that tantalum and niobium halides have sufficient difference in volatility to be separated by distillation. Atkinson, Steizman and Hisky (8) developed a chlorination method which employed octachloropropane in large excess heated to about 300°C and then distillation separation of titanium and tin from oxide mixtures of niobium and tantalum. Schafer and Pietruck (58) used carbon tetrachloride to chlorinate an oxide mixture of niobium, tantalum, titanium and tin. The niobium and tantalum pentachlorides were distilled and weighed as such. They were then hydrolyzed and ignited to the mixed pentoxides. Each could be determined by the following:

Let a be the sum of the weights of $Nb_2O_5 + Ta_2O_5$

Let x be the weight of the Nb_2O_5

Let b be the sum of the weights of $\text{NbCl}_5 + \text{TaCl}_5$

$$\text{then } b = x \cdot \frac{2\text{NbCl}_5}{\text{Nb}_2\text{O}_5} + (a-x) \cdot \frac{2 \text{TaCl}_5}{\text{Ta}_2\text{O}_5} \quad \underline{1}$$

Chaigneau (14) separated niobium and tantalum by chlorinating a mixture of their oxides with anhydrous aluminum chloride. Tantalum pentachloride distilled off at 150°C and the niobium oxychloride at 230°C .

Column Chromatography. Chromatography has also been used to separate tantalum and niobium. Good reviews on this are available (18, 24, 49). The chief use of chromatographic techniques has been in the elution of the fluoride complexes from a cellulose column (12, 44, 45, 75).

In general this process has been based on the extraction of niobium and tantalum as the fluorides by ethyl methyl ketone in the presence of a cellulose absorbent. Tantalum was extracted first with ethyl methyl ketone saturated with water. Niobium was then extracted with the same organic solvent containing hydrofluoric acid. The separation was usually good, requiring very little apparatus, but preliminary separation from large amounts of other elements was usually necessary.

Paper Chromatography. A rapid paper strip chromatographic method separated tantalum and niobium from a hydrofluoric acid solution by upward diffusion on a strip of paper (28). Tannic acid was used for color development.

Electrophoresis. A study has been reported of the separation of niobium and tantalum on a micro-scale by paper electrophoresis, using

oxalic and citric complexes with different buffer solutions (11).

Ion Exchange. Many studies have been made of separation and analysis by ion exchange. Reviews are given by Cockbill and Moshier (18, 49). Tantalum, niobium, protactinium and zirconium have been separated by Kraus and Moore (30, 31). The general procedure has been to use a column made from Dowex-1 in the chloride form. 9M HCl-.004M HF removed the zirconium and then Pa(V). 9M HCl-.18M HF removed the niobium and 4M NH_4Cl -1M HF removed the tantalum. The separation appeared good.

Solvent Extraction. At present, solvent extraction appears to offer the most practical means of separating tantalum and niobium. Commercial separation of niobium and tantalum has been described by Werning and workers (71, 72) and by Tews and May (68). One process uses the hydrofluoric-hydrochloric acid-methyl isobutyl ketone system. A second uses the hydrofluoric-sulfuric acid-methyl isobutyl ketone system. These are continuous operation processes, with advantages over the old batch process.

In 1952 Leddicotte and Moore (32) reported extracting niobium from tantalum in strong hydrochloric acid with a solution of methyl-diethylamine in xylene. Stevenson and Hicks (67) separated tantalum and niobium using diisopropyl ketone and various mineral acids. The hydrochloric-hydrofluoric acid system was one of the better ones. Ellenburg, Leddicotte and Moore report the niobium sulfate complex can be extracted from a tantalum sulfate complex with tribenzylamine in methylene chloride (23). Higbie and Werning (27) cite approximately 200 systems they have tried.

As can be seen, the solvent extraction systems are too numerous to discuss in detail here, but a good review by West (73) covers the

solvent extraction of tantalum and niobium. Other reviews are also available (18, 48, 49, 66, 74). Listed in these as extracting agents are diisobutylcarbinol, butyl phosphoric ester, tributyl phosphate and cyclohexanone.

Use of N-benzoyl-N-phenylhydroxylamine. As mentioned, cupferron has met with some success in the extraction of many metals. N-benzoyl-N-phenylhydroxylamine (BPHA), which is similar to cupferron, has also been used to extract several metals. Their structures are:

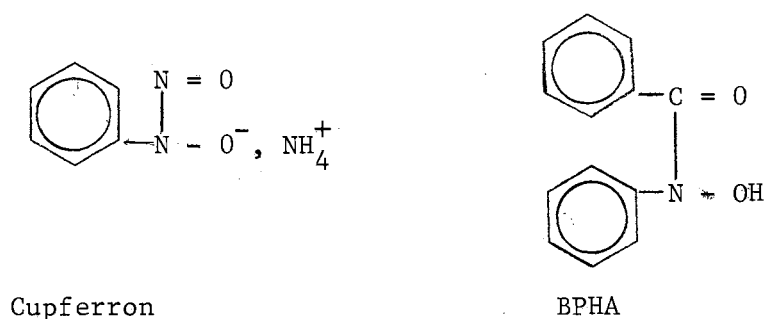


Figure 1. Structures of Cupferron and BPHA

BPHA has many desirable properties over cupferron. It is relatively stable toward heat, light and air. It is destroyed by alkali and by concentrated nitric acid but not by sulfuric acid and hydrochloric acid up to eight normal. It is only slightly soluble in water (0.002M) but is soluble in aqueous ammonia, alcohol, benzene, ether, ethyl acetate and chloroform (0.74M). The partition coefficient between chloroform and the aqueous phase is 214 at 25°C. An aqueous solution of BPHA is slightly acidic ($pK_{HA} = 8.5$ at 25°C). BPHA is commercially available from Eastman Organic Chemicals. These and other properties of BPHA are given by Morrison and Freiser (48), Stary (66) and Dyrssen (21).

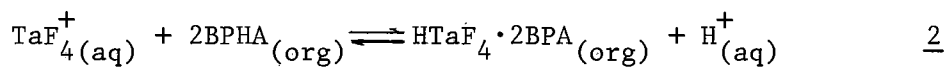
Shome (64) prepared BPHA by a slight modification of the Bamberger method (9), and used it in the gravimetric determination of copper,

iron, aluminum and titanium. Other ions are also listed that are precipitated with BPHA. This reagent has been used in the gravimetric determination of many other metals and ions as well as in the other determinations already mentioned.

BPHA has been used for the solvent extraction of the following: extraction of europium (III) and americium (III) (63); thallium (I) (62); tin (IV) and antimony (III) from indium (56); protactinium from niobium, titanium, zirconium and hafnium and others (17, 20, 51, 52); molybdenum (VI) (10); gallium (1); separation of gallium, indium, thallium, germanium, tin, and lead (33); lanthanum (III), thorium (IV) and uranium (VI) (21); plutonium (IV) from uranium (VI), americium, neptunium (V) and (IV), and most fission products (16); and scandium from zirconium, titanium and rare earths (7).

Alimarin and Petrukhin (2, 3, 4) have studied the extraction of tantalum and niobium from sulfuric acid solutions using BPHA in chloroform. Much of the Russian work has been reviewed by Alimarin, Sudakov and Golovkin (6).

Varga, Wakley, Nicholson, Madden and Patterson (70) carried out solvent extraction studies on tantalum fluoride complexes in 3M HClO₄, containing fluoride, with BPHA and other extracting agents. Chemical analysis of the BPHA-chloroform phase showed that TaF₄⁺ was the extracting species. Subsequent computer analyses were best explained on the basis that the species TaF₅, TaF₆⁻ and TaF₇⁻² were present in the aqueous phase. The model for the extraction system was:



K for this reaction was 1.25×10^8 . 3

$$\beta_5 = \frac{(\text{TaF}_5)}{(\text{TaF}_4^+)(\text{F}^-)} = 8.3 \times 10^5 \quad \underline{4}$$

$$\beta_6 = \frac{(\text{TaF}_6^-)}{(\text{TaF}_4^+)(\text{F}^-)^2} = 1.53 \times 10^{10} \quad \underline{5}$$

$$\beta_7 = \frac{(\text{TaF}_7^{-2})}{(\text{TaF}_4^+)(\text{F}^-)^3} = 1.93 \times 10^{14} \quad \underline{6}$$

In 1965, Lyle and Shendrikar (34) separated protactinium, niobium and tantalum, using BPHA, from hydrochloric acid solutions containing fluoride, but the data were insufficient to define the extracting species or the equilibrium constants.

Determination of Tantalum and Niobium

The preceding has dealt only with the separation of tantalum and niobium. For a complete analysis, each must, of course, be determined both qualitatively and quantitatively. There are many ways to determine these two after separation. Many of these are standard procedures and can be found in the literature (18, 46, 49, 65). These procedures include gravimetry, titrimetry, spectrophotometry, emission spectrography, X-ray spectrography, radio-activation, and polarography, to mention only a few.

CHAPTER III

THEORY

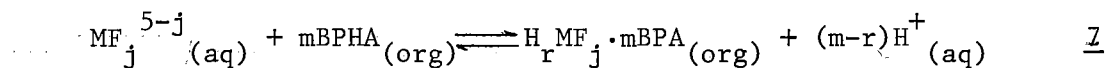
Extraction Model

Tantalum and niobium tend to form hydrolytic polymeric species at the lower acidities and higher metal concentrations. Very little specific information is available in the literature that gives the acidities or metal concentrations at which these species begin to form. However, information on similar elements is available. In 2M HClO_4 , zirconium begins to polymerize at zirconium concentrations of about 2×10^{-3} M (19). In 1M HClO_4 polymerization occurs at about 2×10^{-4} M. Paramonova and Koychev report that niobium in nitric acid solutions is not in the ionic state but is as niobium oxide particles (<1-3 μ) in the acidity range of 0.01 to 2N and concentrations of niobium from 10^{-14} to 10^{-5} grams per liter (53). The best information on tantalum is given by Varga and Freund (69). They report that non-hydrolyzed, monomeric species are present up to a tantalum concentration of two millimolar if C_H/C_M is greater than 150, where C_H is the stoichiometric sum of the perchloric and hydrofluoric acid concentrations and C_M is the total metal concentration.

Experiments carried out in the present work to determine the optimum metal concentrations will be described in the section on results. However, the tantalum concentrations were always less than about 10^{-7} M and the niobium concentrations were less than about 10^{-14} M for the

tracer work. The acidity ranged between 2M and 5M HClO_4 . This would indicate, from the information just given, that only non-hydrolyzed, mononuclear species should be present or, if any hydrolyzed polymers were present, they should be at a minimum concentration. For this work it was assumed only non-hydrolyzed, mononuclear species were dealt with. The activity coefficients of the system were held constant by maintaining the perchlorate ion concentration at 5.0M.

The over-all reaction for the dissociation of the acidic hydrogen of BPHA to give the bidentate hydroxamate anion BPA, reaction of this with the metal fluoride and the extraction of the adduct into the organic phase may be represented by the equation:



where j is the fluoride ligand number of the extracting species, $m-r+j = 5$ and M represents either tantalum or niobium.

The equilibrium constant for this reaction is:

$$K = \frac{(\text{H}_r \text{MF}_j \cdot m\text{BPA})_{\text{org}} (\text{H}^+)_{\text{org}}^{(m-r)}}{(\text{MF}_j^{5-j})_{\text{aq}} (\text{BPHA})_{\text{org}}^m} \quad \underline{8}$$

Rearranging:

$$\frac{(\text{BPHA})_{\text{org}}^m}{(\text{H}^+)_{\text{aq}}^{(m-r)}} = \frac{1}{K} \frac{(\text{H}_r \text{MF}_j \cdot m\text{BPA})_{\text{org}}}{(\text{MF}_j^{5-j})_{\text{aq}}} \quad \underline{9}$$

The distribution coefficient, ϕ , is defined as:

$$\phi = \frac{\text{total metal concentration in organic phase}}{\text{total metal concentration in aqueous phase}} \quad \underline{10}$$

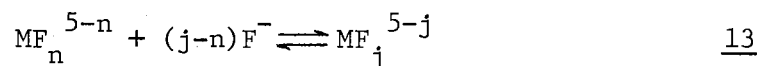
or

$$\phi = \frac{(H_r MF_j \cdot mBPA)_{org}}{N \sum_{i=n}^N (MF_i^{5-i})_{aq}} \quad \underline{11}$$

where n is the minimum and N is the maximum fluoride ligand number of the aqueous phase metal fluoride complex species which exist over the fluoride concentration range studied. Substituting equation 11 into 9 and rearranging:

$$\frac{(BPHA)_{org}^m}{(H^+)_{aq}^{(m-r)} \times \phi} = \frac{1}{K} \frac{\sum_{i=n}^N (MF_i^{5-i})_{aq}}{(MF_j^{5-j})_{aq}} \quad \underline{12}$$

But the formation of MF_j^{5-j} from the lowest metal species in solution is given by:



and the formation constant, β_j , is

$$\beta_j = \frac{(MF_j^{5-j})}{(MF_n^{5-n})(F^-)^{(j-n)}} \quad \underline{14}$$

Substituting equation 14 into 12:

$$\frac{(BPHA)_{org}^m}{(H^+)_{aq}^{(m-r)} \times \phi} = \frac{1}{K} \frac{\sum_{i=n}^N (MF_i^{5-i})_{aq}}{\beta_j (MF_n^{5-n})(F^-)^{(j-n)}} \quad \underline{15}$$

Rearranging:

$$\frac{(BPHA)_{org}^m (F^-)^{(j-n)}}{(H^+)_{aq}^{(m-r)} \times \phi} = \frac{1}{K} \times \frac{1}{\beta_j} \times \frac{\sum_{i=n}^N (MF_i^{5-i})_{aq}}{(MF_n^{5-n})} \quad \underline{16}$$

Making the substitution for the formation constant, β_i , for the formation of $MF_i^{5-i}(aq)$.

$$Y = \frac{(BPHA)_{org}^m (F^-)_{aq}^{(j-n)}}{(H^+)_{aq}^{(m-r)} \times \phi} = \frac{1}{K} \times \frac{1}{\beta_j} \times \sum_{i=n}^N \beta_i (F^-)^{(i-n)} \quad \underline{17}$$

This is the functional form of the equation used in the calculation of the extracting species and the formation constants.

Least Squares Curve-Fitting

A Fortran listing of the computer program may be obtained from the Oklahoma State University Computer Center, Stillwater, Oklahoma, OSU 7.5.001, "Polynomial Curve Fitting," L. P. Varga and E. L. Butler, October 9, 1964 (70).

Evaluation of Y in equation 17 at various values for m, j, n and r gave a set of experimental Y values. Values of Y calculated by the least squares computer program were compared with the experimental Y values and a goodness of fit obtained. The goodness of fit is given as:

$$\frac{\sum_{i=1}^N W_i (Y_i - \text{Calc. } Y_i)^2}{DF-1} \quad \underline{18}$$

where DF is the number of degrees of freedom and W_i is the weight value assigned to each Y_i .

A set of values for m, j, n and r that gave a goodness fit between 0.5 and 1.5 indicated this set was compatible with the assumed model within the 70% confidence level. The set that gave the lowest goodness of fit in this range was taken as the best set of values for

the model.

Each value of Y was weighted according to the equation:

$$W_i = \frac{1}{(Y_i^2 \times P_i^2)} \quad \underline{19}$$

where P_i is the fractional error in ϕ . Values of 0.30, 0.25, and 0.20 were used for P_i using the tantalum data and 0.40 for the niobium data.

If $W_i (Y_i - \text{Calc. } Y_i)^2$ was large, the data point was either omitted or the value of P_i increased. When this situation occurred, the points were at the tails of the distribution curves where counting errors were greater or where chemical reactions could be occurring that were not in line with the original assumptions for the model.

CHAPTER IV

EXPERIMENTAL

Tracer Concentrations of Metals

Stock Solutions

Water. All water used was passed through a column containing Rexyn RG-501 (Fisher Scientific Company). This was a mixture of an anion and cation exchange resin in the OH^- and H^+ forms respectively.

Perchloric Acid. The stock perchloric acid was made by dilution of concentrated perchloric acid (Baker Analyzed reagent grade). This solution was standardized with Baker Analyzed reagent grade sodium carbonate using a Beckman Zeromatic pH meter.

Sodium Perchlorate. The sodium perchlorate solution was prepared by neutralizing Baker Analyzed reagent grade perchloric acid with Baker Analyzed reagent grade sodium carbonate. A pH of 7 was taken as the end point. The solution was boiled to expel the carbon dioxide and the solids were filtered off. The resulting sodium perchlorate solution was analyzed gravimetrically by evaporating a small aliquot to a constant weight in an oven at about 115°C .

Hydrofluoric Acid. The hydrofluoric acid stock solution was prepared by dilution of more concentrated hydrofluoric acid (Baker Analyzed reagent grade). It was standardized with carbonate free, Fisher Certified reagent grade sodium hydroxide solution using phenolphthalein as the indicator. A polystyrene buret (Fisher Scientific Company) was

used in the titration and all other equipment in contact with the hydrofluoric acid solutions was polyethylene or other fluoride-resistant plastics.

Phase Compositions

Organic Phase. The Eastman White Label N-phenyl benzohydroxamic acid (N-benzoyl-N-phenylhydroxylamine or BPHA) and its solutions were stored in the dark as a precautionary measure against any possible decomposition. BPHA was always dried in a desiccator over Drierite before use.

The organic phase composition was held constant at 1×10^{-3} M BPHA in chloroform. This solution was prepared by dissolving 0.2131 g of dry BPHA (M. W. = 213.24 g) in 1000 ml. of Baker Analyzed reagent grade chloroform.

Higher concentrations of BPHA gave higher distribution ratios but these ratios were too high to measure conveniently on the counting equipment. 1×10^{-3} M BPHA was chosen because the distribution ratios obtained were as high as possible and still be measured without extremely long counting times.

Aqueous Phase. The aqueous phase was composed of perchloric acid, sodium perchlorate and sodium fluoride or hydrofluoric acid. Four series of solutions were prepared. See Tables I, II, III and IV. The first series contained 2M HClO_4 , the second 3M HClO_4 , the third, 4M HClO_4 , and the fourth, 5M HClO_4 . At each of these acid concentrations, the fluoride concentration ranged between about 1×10^{-9} M to 2×10^{-3} M. The different fluoride ion concentrations were obtained by adding the proper amount of sodium fluoride to all but the last solution. Stock

TABLE I
 AQUEOUS PHASE COMPOSITIONS: 2M HClO₄,
 3M NaClO₄ & NaF or HF

Fluoride Reagent	Total Fluoride C _A (M)	E _{cells} (Volts)	H ⁺ (M)	Fluoride Ion (M)
NaF	2.142 x 10 ⁻⁵		2.0	5.7 x 10 ⁻⁹
NaF	2.142 x 10 ⁻⁴		2.0	5.7 x 10 ⁻⁸
NaF	2.142 x 10 ⁻³		2.0	5.7 x 10 ⁻⁷
NaF	4.284 x 10 ⁻³		2.0	1.1 x 10 ⁻⁶
NaF	1.071 x 10 ⁻²		2.0	2.9 x 10 ⁻⁶
NaF	2.142 x 10 ⁻²		2.0	5.7 x 10 ⁻⁶
NaF	4.284 x 10 ⁻²		2.0	1.1 x 10 ⁻⁵
NaF	1.071 x 10 ⁻¹		2.0	2.9 x 10 ⁻⁵
NaF	1.051 x 10 ⁻¹	0.48578	1.9	2.9 x 10 ⁻⁵
NaF	2.101 x 10 ⁻¹	0.48496	1.9	6.1 x 10 ⁻⁵
NaF	5.103 x 10 ⁻¹	0.48243	1.6	1.7 x 10 ⁻⁴
NaF	9.827 x 10 ⁻¹	0.47694	1.2	4.2 x 10 ⁻⁴
NaF	1.659	0.45742	0.5	1.7 x 10 ⁻³
HF	3.514	0.49889	3.7	5.1 x 10 ⁻⁴

TABLE II
 AQUEOUS PHASE COMPOSITIONS: 3M HClO₄,
 2M NaClO₄ & NaF or HF

Fluoride Reagent	Total Fluoride C _A (M)	E _{cell} (Volts)	H ⁺ (M)	Fluoride Ion (M)
NaF	2.142 x 10 ⁻⁵		3.0	3.8 x 10 ⁻⁹
NaF	2.142 x 10 ⁻⁴		3.0	3.8 x 10 ⁻⁸
NaF	2.142 x 10 ⁻³		3.0	3.8 x 10 ⁻⁷
NaF	4.284 x 10 ⁻³		3.0	7.7 x 10 ⁻⁷
NaF	1.071 x 10 ⁻²		3.0	1.9 x 10 ⁻⁶
NaF	2.142 x 10 ⁻²		3.0	3.8 x 10 ⁻⁶
NaF	4.284 x 10 ⁻²		3.0	7.7 x 10 ⁻⁶
NaF	1.071 x 10 ⁻¹		3.0	1.9 x 10 ⁻⁵
NaF	1.051 x 10 ⁻¹	0.49612	3.0	1.9 x 10 ⁻⁵
NaF	2.101 x 10 ⁻¹	0.49583	3.0	3.7 x 10 ⁻⁵
NaF	5.103 x 10 ⁻¹	0.49406	2.8	9.9 x 10 ⁻⁵
NaF	9.827 x 10 ⁻¹	0.49176	2.5	2.1 x 10 ⁻⁴
NaF	1.659	0.48624	2.0	4.5 x 10 ⁻⁴
HF	3.514	0.50473	5.0	3.7 x 10 ⁻⁴

TABLE III
 AQUEOUS PHASE COMPOSITIONS: 4M HClO₄,
 1M NaClO₄ & NaF or HF

Fluoride Reagent	Total Fluoride C _A (M)	E _{cell} (Volts)	H ⁺ (M)	Fluoride Ion (M)
NaF	2.142 x 10 ⁻⁵		4.1	2.8 x 10 ⁻⁹
NaF	2.142 x 10 ⁻⁴		4.1	2.8 x 10 ⁻⁸
NaF	2.142 x 10 ⁻³		4.1	2.8 x 10 ⁻⁷
NaF	4.284 x 10 ⁻³		4.1	5.7 x 10 ⁻⁷
NaF	1.071 x 10 ⁻²		4.1	1.4 x 10 ⁻⁶
NaF	2.142 x 10 ⁻²		4.1	2.8 x 10 ⁻⁶
NaF	4.284 x 10 ⁻²		4.1	5.6 x 10 ⁻⁶
NaF	1.071 x 10 ⁻¹		4.1	1.4 x 10 ⁻⁵
NaF	1.051 x 10 ⁻¹	0.49960	3.8	1.5 x 10 ⁻⁵
NaF	2.101 x 10 ⁻¹	0.49933	3.7	3.0 x 10 ⁻⁵
NaF	5.103 x 10 ⁻¹	0.49857	3.6	7.5 x 10 ⁻⁵
NaF	9.827 x 10 ⁻¹	0.49709	3.3	1.6 x 10 ⁻⁴
NaF	1.659	0.49472	3.0	3.0 x 10 ⁻⁴
HF	3.514	0.51037	6.7	2.8 x 10 ⁻⁴

TABLE IV
AQUEOUS PHASE COMPOSITIONS:

5M HClO₄ & NaF or HF

Fluoride Reagent	Total Fluoride C _A (M)	E _{cell} (Volts)	H ⁺ (M)	Fluoride Ion (M)
NaF	2.142 x 10 ⁻⁵		5.0	2.3 x 10 ⁻⁹
NaF	2.142 x 10 ⁻⁴		5.0	2.3 x 10 ⁻⁸
NaF	2.142 x 10 ⁻³		5.0	2.3 x 10 ⁻⁷
NaF	4.284 x 10 ⁻³		5.0	4.6 x 10 ⁻⁷
NaF	1.071 x 10 ⁻²		5.0	1.1 x 10 ⁻⁶
NaF	2.142 x 10 ⁻²		5.0	2.3 x 10 ⁻⁶
NaF	4.284 x 10 ⁻²		5.0	4.6 x 10 ⁻⁶
NaF	1.071 x 10 ⁻¹		5.0	1.1 x 10 ⁻⁵
NaF	1.051 x 10 ⁻¹	0.50380	4.8	1.2 x 10 ⁻⁵
NaF	2.101 x 10 ⁻¹	0.50247	4.4	2.5 x 10 ⁻⁵
NaF	5.103 x 10 ⁻¹	0.50403	4.8	5.7 x 10 ⁻⁵
NaF	9.827 x 10 ⁻¹	0.50219	4.4	1.2 x 10 ⁻⁴
NaF	1.659	0.50132	4.2	2.1 x 10 ⁻⁴
HF	3.514	0.51231	7.5	2.5 x 10 ⁻⁴

hydrofluoric acid was added to this solution. The perchlorate ion concentration for all solutions was held constant at 5.0M by maintaining the sum of the perchloric acid and sodium perchlorate concentrations at 5.0M. The solutions were prepared in volumetric polyethylene bottles and stored in polyethylene bottles.

The amount of sodium fluoride to be added for the low-fluoride solution make-up (1×10^{-5} M or less) was calculated from the following:



$$C_H = (\text{H}^+) + (\text{HF}) + (\text{HF}_2^-) \quad \underline{22}$$

$$C_H - (\text{H}^+) = (\text{HF}) + (\text{HF}_2^-) = (\text{HF}) \text{ at low } (\text{F}^-) \quad \underline{23}$$

$$C_A = (\text{HF}) + 2(\text{HF}_2^-) + (\text{F}^-) \quad \underline{24}$$

Substituting equation 20-23 into equation 24

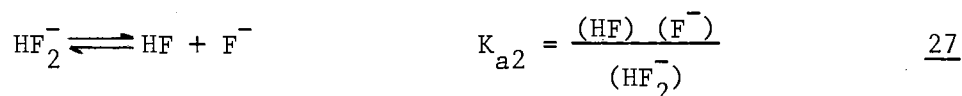
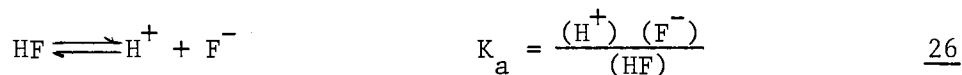
$$(\text{F}^-) = \frac{C_A}{\frac{(\text{H}^+)}{K_a} + 1 + \frac{2}{K_{a2}} [C_H - (\text{H}^+)]} \quad \underline{25}$$

For these low-fluoride solutions, the (H^+) was assumed to be equal to the total perchloric acid present in solution and equation 25 used directly to calculate the low-fluoride concentrations. This proved to be a good assumption as shown later when the (H^+) was measured in the high-fluoride solutions.

The values of K_a and K_{a2} in 3M NaClO_4 are given by Caglioti and

co-workers (13) as $K_a = 5.37 \times 10^{-4}$ and $K_{a2} = 8.1 \times 10^{-2}$. For the wide range of fluoride concentrations used and the accuracy needed, these were accurate enough.

The amount of sodium fluoride or hydrofluoric acid to be added for the high-fluoride solution make-up (greater than $1 \times 10^{-5}M$) was calculated as follows:



$$C_A = (HF) + 2(HF_2^-) + (F^-) \quad 28$$

Substituting equation 26 and 27 into equation 28

$$\frac{2(H^+)}{K_a K_{a2}} (F^-)^2 + \left[\frac{(H^+)}{K_a} + 1 \right] (F^-) - C_A = 0 \quad 29$$

For these higher fluoride solutions, the (H^+) changed due to the higher fluoride in solution and had to be measured experimentally. This was done potentiometrically using the quinhydrone electrode.

Determination of (H^+) . A Universal K-3 potentiometer, an Eppley standard cell, a Rubicon mirror galvanometer and a lead storage battery, as a working cell, were used. All equipment was shielded and the standard and working cells protected from sudden temperature changes. All equipment in contact with the test solutions was made of fluoride-resistant material. The test cell (a polyethylene beaker) was kept in a constant temperature water bath at $25^\circ C$ and the test solution stirred constantly with a polyethylene stirrer driven by an electric motor. The indicator electrode was a platinum wire and the reference electrode

was a commercial saturated KCl calomel. The tip of the reference electrode was placed in a polyethylene tube with an asbestos wick sealed in the tip. This tube or sleeve was filled with saturated NaCl solution. This sleeve provided a flowing salt bridge, prevented KClO_4 from precipitating and thus plugging up the wick of the calomel electrode, and protected the calomel electrode from the fluoride-containing solutions. Merck's reagent quinhydrone was recrystallized from 70°C water before use.

The system just described was the result of several different systems that were tried. Considerable trouble was encountered with drift in the cell potential readings. Several modifications of the previously described system were tried to prevent this drift. A gold indicator electrode showed no advantage over the platinum electrode. A cotton wick sealed in the end of the polyethylene sleeve for the reference electrode did not decrease the drift. It was found that an asbestos wick of sufficient size to allow two or three drops of bridge solution to flow through under slight pressure from a rubber squeeze bulb in about one half minute gave the best results. After several runs it was found necessary to change the bridge solution and force some of the new bridge solution through the wick. The platinum electrode was also cleaned occasionally in $\text{H}_2\text{SO}_4\text{-KMnO}_4$ solution.

The cell potential readings usually rose to a maximum and then decreased. This maximum was not reproducible but an average of the cell potential readings over a thirty-minute period was found to be fairly reproducible.

To make a run, the quinhydrone was added to the test solution and after ten minutes the average of the cell potential readings taken

during the next thirty-minute period was taken as the cell potential. In ordinary pH measurements using quinhydrone, the cell potential can be converted directly to (H^+) by the equation:

$$E_{\text{cell}} = E^{\circ} - \frac{.059}{n} \log (H^+)^2 \quad \underline{30}$$

where E_{cell} is the measured cell potential of the unknown solution, E° is the standard potential of the cell, n is the number of electrons changed in the cell reaction and (H^+) is the hydrogen ion concentration. Because of the high salt content and the unknown junction potential, equation 30 could not be used directly without the addition of a correction term, γ , which is the sum of the activity corrections, liquid junction effects, and other factors.

$$E_{\text{cell}} = E^{\circ} - \frac{.059}{n} \log (H^+)^2 + \gamma \quad \underline{31}$$

Potential measurements were made on a series of standard solutions of perchloric acid of known (H^+) all 5.0M in perchlorate ion. Then, knowing E° , the correction term was essentially evaluated. In practice, however, a calibration curve was constructed plotting the measured cell potential against the hydrogen ion concentration (Figure 2). The hydrogen ion concentrations of the unknown fluoride solutions were then read directly from the curve. Several of these curves were constructed since recalibration was necessary when system changes were made (change of indicator electrode, sleeve, etc.). A typical composite curve is shown in Figure 2.

When the perchlorate ion concentration was not held constant but varied as the perchloric acid concentration varied, the curve showing the cell potential as a function of the hydrogen ion concentration had

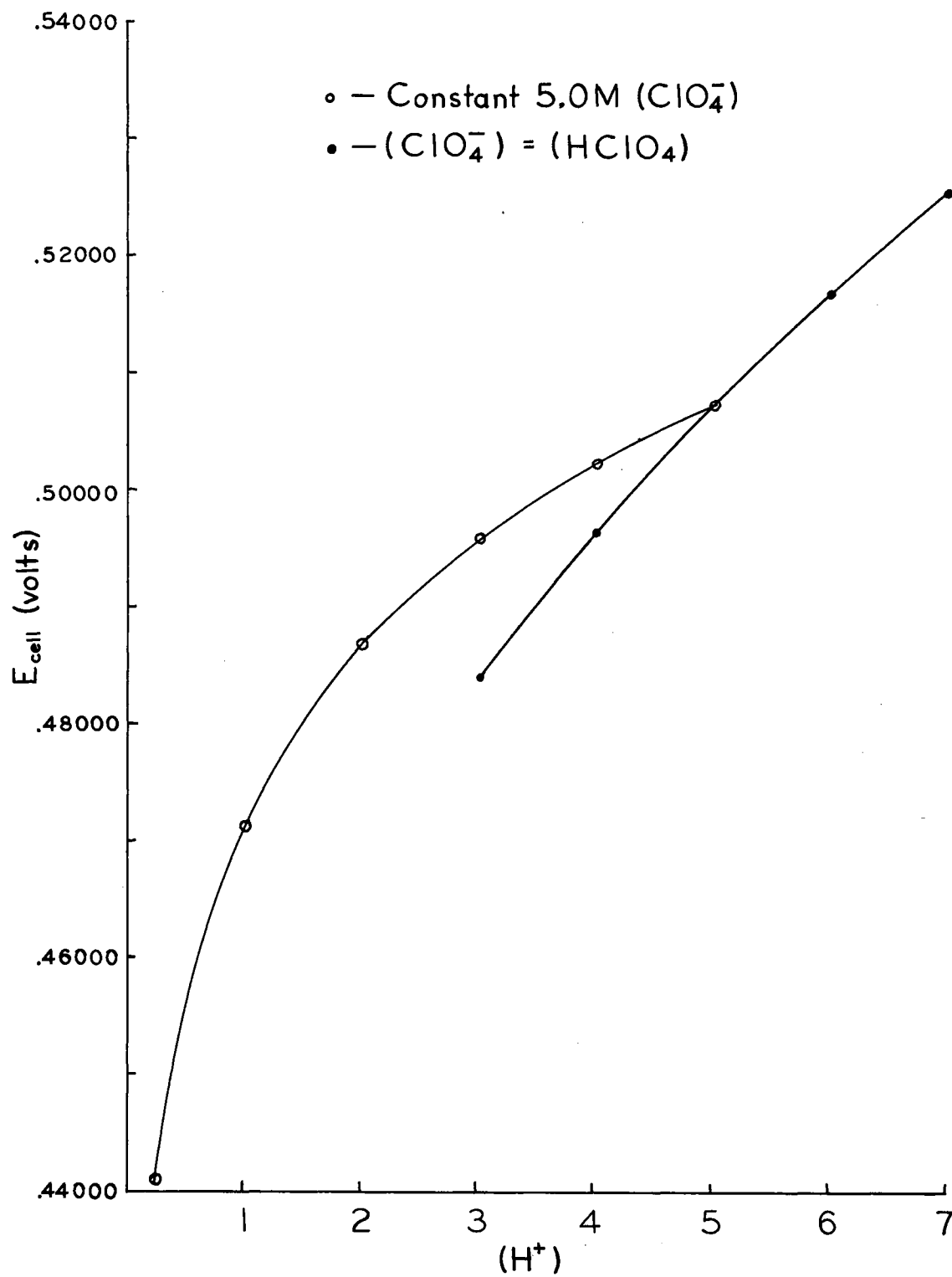


Figure 2. Standard Calibration Curve for Hydrogen Ion Concentration

a steeper slope, as shown in Figure 2.

Preparation of the Radioisotopes Ta-182 and Nb-95

The distribution of tantalum and niobium between the phases was followed using the radioisotopes Ta-182 and Nb-95, obtained from the Oak Ridge National Laboratories.

Tantalum-182. The Ta-182 was received as the tantalate in KOH with carrier present. About one to two millicuries of Ta-182 were put in a platinum crucible and evaporated just to dryness several times with concentrated hydrofluoric acid and then several more times to near dryness with more concentrated hydrofluoric acid. This was diluted with several milliliters of 3M HClO_4 and the solution evaporated as far as possible without the formation of a precipitate. This solution was transferred to a small polyethylene bottle and stored. This gave the tantalum as the fluoride. The concentration of this solution was of the order of 10^{-5} M.

Niobium-95. The carrier-free Nb-95 was obtained as the daughter product of Zr-95 in an oxalate solution. It was separated using a method similar to that used by Moore (47). About two millicuries of the Zr-Nb-95 mixture were put into five milliliters of 6M hydrochloric acid in a small glass separatory funnel equipped with a glass stirrer driven by an electric motor. Five milliliters of 0.5M 2-thenoyltri-fluoroacetone-xylene solution was added and the solution stirred for ten minutes. The two phases were allowed to settle and the aqueous phase, containing the Nb-95, drained into a platinum crucible. The process was repeated. The solution in the crucible was then evaporated to dryness several times with concentrated nitric acid and then with dilute nitric acid. Concentrated hydrofluoric acid was added and the

solution evaporated just to dryness several times and then to near dryness several more times. This was diluted with several milliliters of 3M HClO_4 and the solution transferred to a small polyethylene bottle and stored. This gave the niobium as the fluoride. The concentration of this solution was of the order of 10^{-12} M or less.

A cleaner separation would be obtained by destroying the oxalate in the Zr-Nb-95 mixture before the extraction of the Nb-95.

The purity of the Nb-95 was checked by running a decay curve. Thorium was used as a primary standard whose activity was assumed not to change significantly over the time interval of the decay curve because of its long half life. Each day the activity of the thorium standard and the Nb-95 sample was counted. By taking a ratio of the counts obtained each day to those obtained the first day, a corrected count could be obtained for the Nb-95 for each day that accounted for drift or changes in the counting equipment.

When $-\ln(A/A^0)$ is plotted against the time, a straight line should be obtained with a slope of λ . A is the activity of the Nb-95 on any particular day, A^0 is the original activity of the Nb-95 on the first day, and λ is the decay constant. If the isotope is impure, the line will begin to curve away from the theoretical line. Figure 3 is a least-square fit of the decay data along with the theoretical lines for pure Zr-95 and Nb-95. The least-square fit was done on the 7040 computer.

From these data, λ was found to be $(1.62 \pm .02) \times 10^{-2} \text{ d}^{-1}$ compared with the theoretical values of $1.05 \times 10^{-2} \text{ d}^{-1}$ for pure zirconium and $1.87 \times 10^{-2} \text{ d}^{-1}$ for pure niobium.

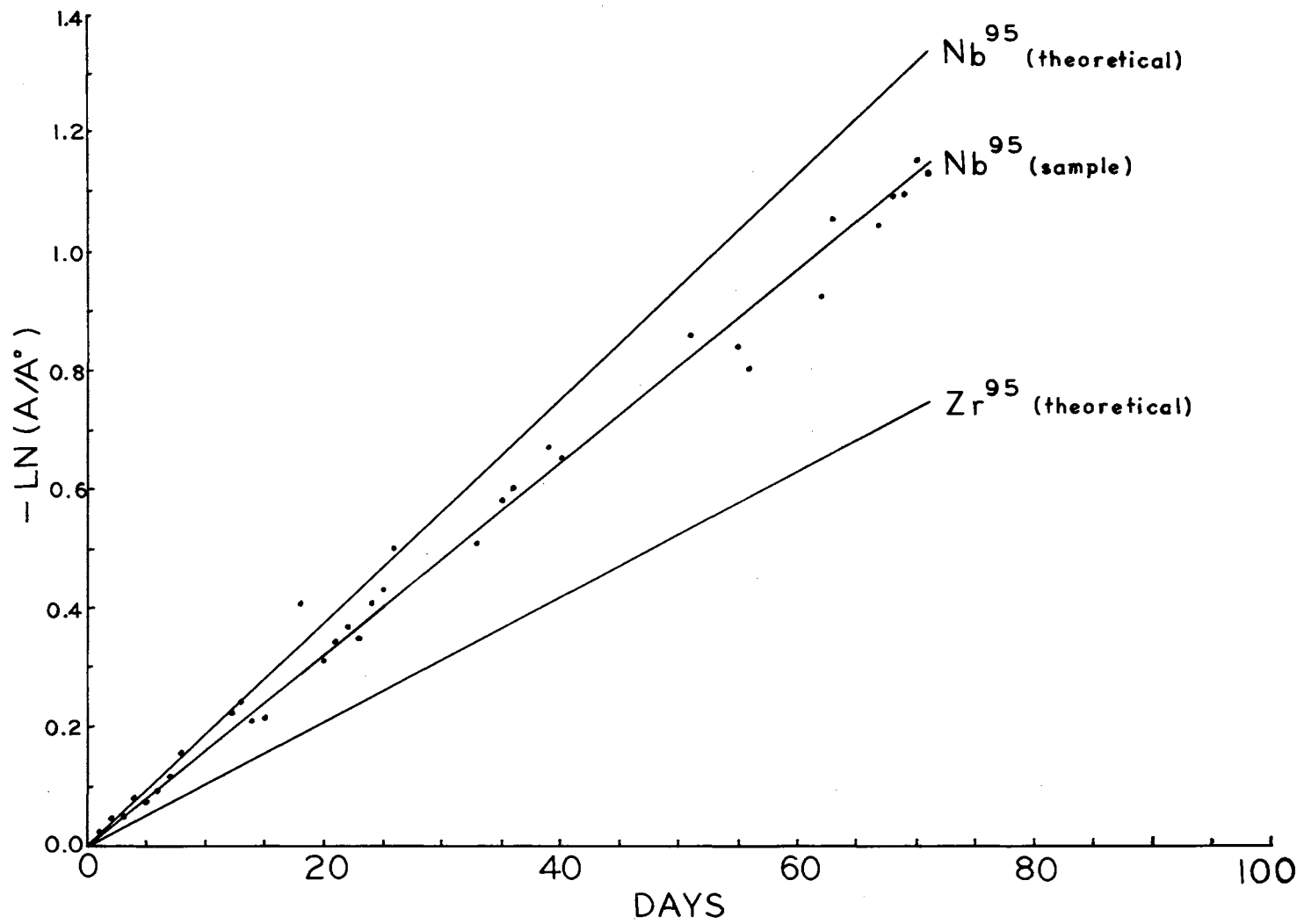


Figure 3. Decay Curve for Niobium-95 Stock Solution With Theoretical Niobium-95 and Zirconium-95 Lines

Experimental Technique for Individual Extraction Curves

Sample Preparation and Equilibration. The experimental technique for the tracer concentrations of metals consisted of the following. For the individual distribution curves, five-milliliter portions of the organic phase (1×10^{-3} M BPHA in chloroform), containing about 20 microliters of the Ta-182 or Nb-95 stock solutions, were equilibrated with five-milliliter portions of the prepared aqueous phase in a fifty-milliliter polyethylene tube for 16 to 18 hours on a water bath shaker at 25°C. This time was chosen mainly for convenience.

Sampling. After equilibration, the samples were centrifuged, to separate the phases, and the two phases carefully sampled with volumetric pipets. The volume of the aliquot was adjusted until a total count of about 10,000 was obtained within a reasonable length of time. Since the standard deviation of a single count is equal to the square root of the total count, an accuracy of one percent in counting statistics was obtained.

When sampling the lower organic phase, contamination of the sample by the aqueous phase was avoided by slowly forcing air through the pipet while passing it down through the aqueous phase into the organic phase. A little of the organic phase was drawn up and then forced out several times before an aliquot was taken. After removing the pipet from the equilibrium mixture, the pipet was wiped clean and the aliquot transferred to a shell vial. All pipets used in sample preparation and in sampling the fluoride solutions were polyethylene except the micropipets, which were borosilicate glass. These were recalibrated periodically with mercury.

Analysis of Phases. The samples were counted in stoppered, shell

vials using a Detectolab well-type scintillation counter with a gamma-sensitive NaI crystal. Detectolab models DS-4 scaler and DZ-9 scaler control were used with Baird Atomic models 432-A ratemeter-high voltage supply and 250 amplifier-analyzer along with the scintillation tube. The scintillation tube was operated at about 850 to 950 volts.

Gamma-Spectrums. Figure 4 shows the gamma spectrum for a mixture of Ta-182 and Nb-95. This was obtained using a Nuclear Data Incorporated 512 channel analyzer. The main Ta-182 and Nb-95 peaks are marked. The counter was set on the energy peak of the metal to be analyzed and the activity of this metal counted in each phase.

Calculations. The distribution ratio, ϕ , was defined in Chapter III. Since the concentration of the metal isotope is directly proportional to the activity, the $(\text{counts/min./ml.})_{\text{org}} / (\text{counts/min./ml.})_{\text{aq}}$ was taken as the distribution coefficient ϕ . Background corrections were made on all counts.

The percent extraction for one extraction using equal phase volumes can be calculated from:

$$\% \text{ Extn.} = \frac{\phi}{1 + \phi} \times 100 \quad \underline{32}$$

Experimental Technique for Mixtures of Ta and Nb

Mixture Preparation and Equilibration. The experimental technique for the separation of tracer quantities of tantalum and niobium from a synthetic mixture of these two consisted of the following. Five-milliliter portions of the organic phase (1×10^{-3} M BPHA in chloroform), containing 20 microliters of the stock tantalum-182 and 20 microliters of the stock niobium-95, were equilibrated with five milliliters of the desired aqueous phase in a fifty-milliliter polyethylene tube for 16 to

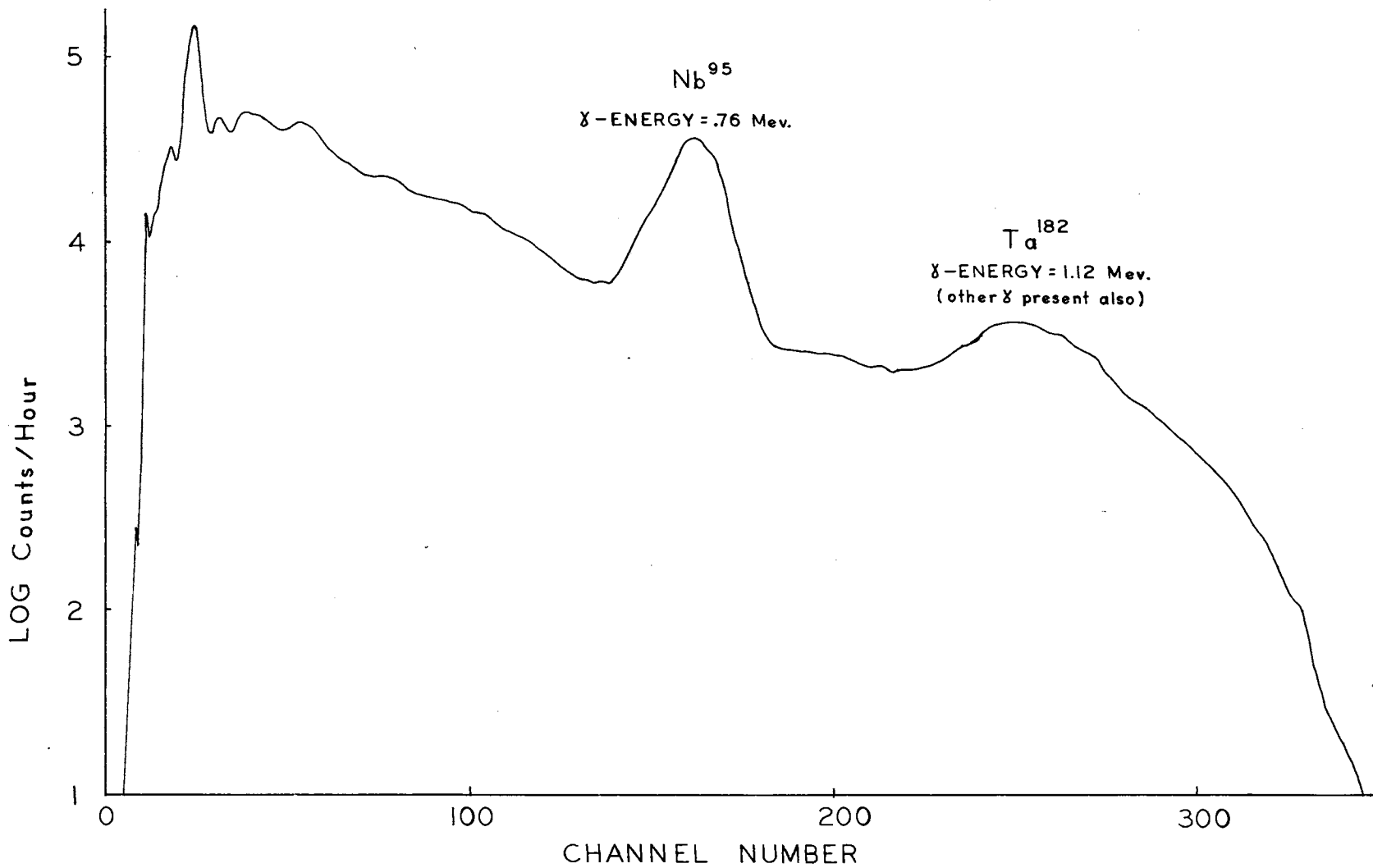


Figure 4. Gamma Spectrum of a Mixture of Tantalum-182 and Niobium-95

18 hours on a water bath shaker at 25°C.

Sampling. The phases were sampled in the same way as was done for the individual extractions for each metal.

Counting of the Phases. The same equipment was used here to measure the activity of the phases as described above. The method of counting the phases had to be modified slightly, however. To measure the activity of the Nb-95 and Ta-182, the phases were first counted with the counter set at the energy of the Nb-95 peak. See Figure 4. These same phases were then recounted with the counter set at the energy of the Ta-182 peak. As an inspection of the gamma spectrums of Ta-182 and Nb-95 will reveal, the activity under the Nb-95 peak was not due to that of Nb-95 alone but also to Ta-182. To obtain a net corrected count for Nb-95, a standard Ta-182 sample was run along with the phases at both energies. The net Nb-95 activity, Nb' , in any one phase was:

$$Nb' = Nb_g^{Nb} - \frac{Ta_o^{Nb}}{Ta_o^{Ta}} \times Ta_g^{Ta} \quad 33$$

where Nb_g^{Nb} is the gross counts of the phase with the counter set at the Nb-95 energy peak, Ta_o^{Nb} is the activity of the Ta-182 standard at the Nb-95 energy peak, Ta_o^{Ta} is the activity of the Ta-182 standard at the Ta-182 energy peak and Ta_g^{Ta} is the gross counts of the phase with the counter set at the Ta-182 energy peak.

It was found that the activity under the Ta-182 peak was due only to Ta-182 and no corrections for Nb-95 activity had to be made. A Nb-95 standard was always run to check this however. Background corrections were made on all counts.

Millimolar Concentration of Metals

Following a study of the extraction of tracer quantities of tantalum from tracer quantities of niobium, investigations into the extraction of millimolar quantities of tantalum and niobium were undertaken. Evidence indicated that the high acidity and high salt concentrations were decreasing the efficiency of the separation of tantalum and niobium so a study was undertaken to separate millimolar quantities of tantalum from millimolar quantities of niobium using an organic phase of BPHA in chloroform and an aqueous phase containing only hydrofluoric acid.

Aqueous Phase Preparation

Millimolar Tantalum. Millimolar tantalum was obtained by weighing out the proper amount of K_2TaF_7 into a platinum crucible. Enough of the Ta-182, that had been used in the tracer studies, was added so as to give approximately the same activity per sample as was used in the tracer studies. This solution was evaporated to near dryness several times with concentrated hydrofluoric acid in order to get a homogeneous mixture of the K_2TaF_7 and Ta-182. This was then evaporated to near dryness twice with $3.0 \times 10^{-5} M$ HF to lower the hydrofluoric acid concentration. $3.0 \times 10^{-5} M$ HF was added and the solution was transferred to a volumetric polyethylene bottle.

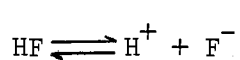
Millimolar Niobium. Millimolar niobium was obtained by weighing out the proper amount of K_2NbF_7 into a platinum crucible. This was probably slightly hydrolyzed. However, by using an average molecular weight between K_2NbF_7 and K_2NbOF_5 , the solution should be accurate to about $\pm 5\%$. Since the metal concentration will vary in subsequent runs,

an accuracy of $\pm 5\%$ is sufficient.

The salt in the crucible was evaporated to near dryness several times with concentrated hydrofluoric acid to convert any hydrated species to the fluoride. Enough of the Nb-95, that had been used in the tracer studies, was then added so as to give approximately the same activity per sample as was used in the tracer studies. This solution was again evaporated to near dryness several times with concentrated hydrofluoric acid to obtain a homogeneous solution. This was evaporated to near dryness with $3.0 \times 10^{-5} \text{M}$ HF to lower the hydrofluoric acid concentration. More $3.0 \times 10^{-5} \text{M}$ hydrofluoric acid was added, but the small amount of precipitate that had been formed did not seem to go into solution. A drop of concentrated hydrofluoric acid was added to dissolve this precipitate and the solution was evaporated down as far as possible without the formation of a precipitate. The resulting solution was transferred to the volumetric polyethylene bottle containing the millimolar tantalum. This solution of millimolar tantalum and niobium was diluted to the desired volume with $3.0 \times 10^{-5} \text{M}$ HF.

To obtain the higher fluoride solutions, more hydrofluoric acid was added to the millimolar solution of tantalum and niobium. This hydrofluoric acid was concentrated enough so as not to significantly change the metal concentration of the solution.

Calculation of Fluoride Concentration. The fluoride concentration of these aqueous phases was calculated from the dissociation equation of hydrofluoric acid.



$$K_a = \frac{(\text{H}^+) (\text{F}^-)}{(\text{HF})}$$

or

$$K_a = \frac{(F^-)^2}{C_{HF} - (F^-)} \quad \underline{35}$$

where C_{HF} is the analytical concentration of hydrofluoric acid. The equilibrium constant for this reaction is given by Pick (54) as

$$K_a = 7.2 \times 10^{-4}$$

Organic Phase Composition

The computer results (see Chapter V) indicated two molecules of BPHA were needed for each molecule of tantalum or niobium. Therefore, for the millimolar extractions, the BPHA concentration in chloroform was increased to $2.5 \times 10^{-2} M$ which was in excess of the amount needed to complex the tantalum and niobium.

Mixtures of Ta and Nb

Equilibration, Sampling, Counting and Calculations. These processes were performed in the same manner as was done in the tracer mixtures of tantalum and niobium already described.

CHAPTER V

DISCUSSION OF RESULTS

Computer Results

Lower Limit of Fluoride Ion Concentration

In the tracer studies, aqueous stock solutions with fluoride concentrations as low as 1×10^{-9} M were prepared. However, the lowest fluoride concentrations reached in a sample were probably on the order of 10^{-7} M fluoride due to the fact that the tracer Ta-182 and Nb-95 stock solutions themselves contained hydrofluoric acid. When the proper amount of these tracer solutions was added to the samples and the samples equilibrated, failure of the distribution ratio to maximize (see Tables V, VI, VII, and VIII) indicated that the low fluoride concentrations were not reached (70). Since the distribution data appeared to level out at about 10^{-7} M fluoride, only the data at that concentration and above were considered in the computer work.

Tantalum:

For the tantalum system, the data from Tables VII and VIII for the 4M and 5M HClO_4 systems were used for the computer work. At 4M and 5M HClO_4 concentrations the distribution of the metal appeared to be governed by the same hydrogen ion dependency, indicating that hydrolysis was not significant. The best model for the extracting system was found for $j = 3$, $m = 2$, $n = 3$, and $r = 0$ in equation 17 so that the

TABLE V
 EXTRACTION DATA: 2M HClO₄, 3M NaClO₄ & F⁻
 1 x 10⁻³ M BPHA

Fluoride Ion (M)	H ⁺ (M)	Nb		Ta	
		∅	% Extn.	∅	% Extn.
5.7 x 10 ⁻⁹	2.0	2.36 x 10 ⁺¹	96.	3.00 x 10 ⁺²	100.
5.7 x 10 ⁻⁸	2.0	2.33 x 10 ⁺¹	96.	2.92 x 10 ⁺²	100.
5.7 x 10 ⁻⁷	2.0	2.54 x 10 ⁺¹	96.	2.42 x 10 ⁺²	100.
1.1 x 10 ⁻⁶	2.0	2.50 x 10 ⁺¹	96.	1.75 x 10 ⁺²	99.
2.9 x 10 ⁻⁶	2.0	2.48 x 10 ⁺¹	96.	1.48 x 10 ⁺²	99.
5.7 x 10 ⁻⁶	2.0	2.34 x 10 ⁺¹	96.	7.72 x 10 ⁺¹	99.
1.1 x 10 ⁻⁵	2.0	1.42 x 10 ⁺¹	93.	2.07 x 10 ⁺¹	95.
2.9 x 10 ⁻⁵	2.0				
2.9 x 10 ⁻⁵	1.9	9.27 x 10 ⁻¹	48.	7.33	88.
6.1 x 10 ⁻⁵	1.9	3.52 x 10 ⁻²	3.4	1.55	61.
1.7 x 10 ⁻⁴	1.6	1.13 x 10 ⁻²	1.1	1.09 x 10 ⁻¹	9.8
4.2 x 10 ⁻⁴	1.2	3.19 x 10 ⁻³	0.32	8.82 x 10 ⁻³	0.87
1.7 x 10 ⁻³	0.5	4.72 x 10 ⁻⁴	0.047	4.54 x 10 ⁻⁴	0.045
5.1 x 10 ⁻⁴	3.7			6.70 x 10 ⁻⁴	0.067

TABLE VI
 EXTRACTION DATA: 3M HClO₄, 2M NaClO₄ & F⁻
 1 x 10⁻³M BPHA

Fluoride Ion (M)	H ⁺ (M)	Nb		Ta	
		∅	% Extn.	∅	% Extn.
3.8 x 10 ⁻⁹	3.0	2.55 x 10 ⁺¹	96.	7.15 x 10 ⁺²	100.
3.8 x 10 ⁻⁸	3.0	2.57 x 10 ⁺¹	96.	6.33 x 10 ⁺²	100.
3.8 x 10 ⁻⁷	3.0	2.57 x 10 ⁺¹	96.	5.30 x 10 ⁺²	100.
7.7 x 10 ⁻⁷	3.0	2.56 x 10 ⁺¹	96.	3.72 x 10 ⁺²	100.
1.9 x 10 ⁻⁶	3.0	2.15 x 10 ⁺¹	95.	4.21 x 10 ⁺²	100.
3.8 x 10 ⁻⁶	3.0	1.67 x 10 ⁺¹	94.	9.91 x 10 ⁺¹	99.
7.7 x 10 ⁻⁶	3.0	1.44 x 10 ⁺¹	93.	7.34 x 10 ⁺¹	99.
1.9 x 10 ⁻⁵	3.0				
1.9 x 10 ⁻⁵	3.0	2.03	67.	1.32 x 10 ⁺¹	93.
3.7 x 10 ⁻⁵	3.0	1.34 x 10 ⁻¹	12.	1.83	65.
9.9 x 10 ⁻⁵	2.8	2.69 x 10 ⁻²	2.6	1.66 x 10 ⁻¹	14.
2.1 x 10 ⁻⁴	2.5	7.61 x 10 ⁻³	0.75	1.95 x 10 ⁻²	1.9
4.5 x 10 ⁻⁴	2.0	2.77 x 10 ⁻³	0.28	2.52 x 10 ⁻³	0.25
3.7 x 10 ⁻⁴	5.0			4.22 x 10 ⁻³	0.42

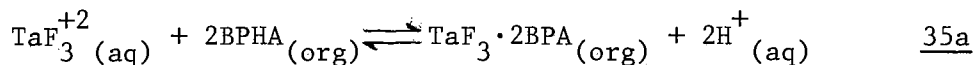
TABLE VII
 EXTRACTION DATA: 4M HClO₄, 1M NaClO₄ & F⁻
 1 x 10⁻³ M BPHA

Fluoride Ion (M)	H ⁺ (M)	Nb		Ta	
		∅	% Extn.	∅	% Extn.
2.8 x 10 ⁻⁹	4.1	2.70 x 10 ⁺¹	96.	9.09 x 10 ⁺²	100.
2.8 x 10 ⁻⁸	4.1	2.61 x 10 ⁺¹	96.	8.63 x 10 ⁺²	100.
2.8 x 10 ⁻⁷	4.1	2.61 x 10 ⁺¹	96.	5.33 x 10 ⁺²	100.
5.7 x 10 ⁻⁷	4.1	2.81 x 10 ⁺¹	97.	8.31 x 10 ⁺²	100.
1.4 x 10 ⁻⁶	4.1	2.11 x 10 ⁺¹	95.	4.72 x 10 ⁺²	100.
2.8 x 10 ⁻⁶	4.1	2.36 x 10 ⁺¹	96.	1.66 x 10 ⁺²	99.
5.6 x 10 ⁻⁶	4.1	1.48 x 10 ⁺¹	94.	6.39 x 10 ⁺¹	98.
1.4 x 10 ⁻⁵	4.1				
1.5 x 10 ⁻⁵	3.8	3.30	77.	1.62 x 10 ⁺¹	94.
3.0 x 10 ⁻⁵	3.7	3.20 x 10 ⁻¹	24.	1.70	63.
7.5 x 10 ⁻⁵	3.6	3.37 x 10 ⁻²	3.3	1.79 x 10 ⁻¹	15.
1.6 x 10 ⁻⁴	3.3	2.48 x 10 ⁻²	2.4	2.61 x 10 ⁻²	2.5
3.0 x 10 ⁻⁴	3.0	7.90 x 10 ⁻³	0.78	2.78 x 10 ⁻³	0.28
2.8 x 10 ⁻⁴	6.7				

TABLE VIII
 EXTRACTION DATA: 5M HClO₄ & F⁻
 1 x 10⁻³M BPHA

Fluoride Ion (M)	H ⁺ (M)	Nb.		Ta.	
		∅	% Extn.	∅	% Extn.
2.3 x 10 ⁻⁹	5.0	2.82 x 10 ⁺¹	97.	8.35 x 10 ⁺²	100.
2.3 x 10 ⁻⁸	5.0	2.53 x 10 ⁺¹	96.	4.33 x 10 ⁺²	100.
2.3 x 10 ⁻⁷	5.0	2.81 x 10 ⁺¹	97.	4.28 x 10 ⁺²	100.
4.6 x 10 ⁻⁷	5.0	3.02 x 10 ⁺¹	97.	4.04 x 10 ⁺²	100.
1.1 x 10 ⁻⁶	5.0	2.66 x 10 ⁺¹	96.	3.46 x 10 ⁺²	100.
2.3 x 10 ⁻⁶	5.0	2.60 x 10 ⁺¹	96.	1.92 x 10 ⁺²	99.
4.6 x 10 ⁻⁶	5.0	2.01 x 10 ⁺¹	95.	5.57 x 10 ⁺¹	98.
1.1 x 10 ⁻⁵	5.0				
1.2 x 10 ⁻⁵	4.8	8.26	89.	1.12 x 10 ⁺¹	92.
2.5 x 10 ⁻⁵	4.4	8.45 x 10 ⁻¹	46.	2.26	69.
5.7 x 10 ⁻⁵	4.8	1.94 x 10 ⁻¹	16.	2.22 x 10 ⁻¹	18.
1.2 x 10 ⁻⁴	4.4	5.22 x 10 ⁻²	5.0	3.43 x 10 ⁻²	3.3
2.1 x 10 ⁻⁴	4.2	5.31 x 10 ⁻²	5.0	1.02 x 10 ⁻²	1.0
2.5 x 10 ⁻⁴	7.5			1.15 x 10 ⁻³	0.11

extraction data were best represented by the extraction of TaF_3^{+2} according to the equation:



The equilibrium constant for this reaction was found to be:

$$K = \frac{(\text{TaF}_3 \cdot 2\text{BPA})_{\text{org}} (\text{H}^+)_{\text{aq}}^2}{(\text{TaF}_3^{+2})_{\text{aq}} (\text{BPHA})_{\text{org}}^2} = 2.0 \times 10^{10} \quad \underline{36}$$

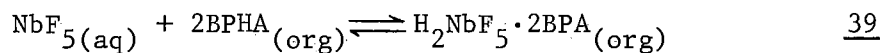
which is in line with Wakley's high K value using a similar system (70). The data indicated that two other species, TaF_4^{+1} and TaF_6^{-1} , were present also in the aqueous phase. The formation constants for these species were found to be:

$$\beta_4 = \frac{(\text{TaF}_4^{+1})}{(\text{TaF}_3^{+2}) (\text{F}^-)} = 1.6 \times 10^6. \quad \underline{37}$$

$$\beta_6 = \frac{(\text{TaF}_6^{-1})}{(\text{TaF}_3^{+2}) (\text{F}^-)^3} = 1.8 \times 10^{16}. \quad \underline{38}$$

Niobium

The niobium system was treated in a similar manner using the 4M HClO_4 data from Table VII. The computer results indicated that the best model for the extraction was:



The equilibrium constant for this reaction was found to be:

$$K = \frac{(\text{H}_2\text{NbF}_5 \cdot 2\text{BPA})_{\text{org}}}{(\text{NbF}_5)_{\text{aq}} (\text{BPHA})_{\text{org}}^2} = 3.0 \times 10^7 \quad \underline{40}$$

One other aqueous-phase species, NbF_7^{-2} , was indicated by the computer results. The formation constant for this was calculated to be:

$$\beta_7 = \frac{(\text{NbF}_7^{-2})}{(\text{NbF}_5) (\text{F}^-)^2} = 4.6 \times 10^{10} \quad \underline{41}$$

The results on these two extraction systems are not final and more work should be done, especially chemical analyses of the systems. This work does, however, give a good indication of the proper models for the two systems, thereby giving a theoretical basis for the work as a whole.

Extraction of Tracer Metal Concentrations

Determination of Optimum Metal Concentrations

As mentioned in the section on theory, the extraction of tantalum and niobium was found to be a function of the metal concentration, owing probably to the formation of hydrolytic polymers at higher metal concentrations. Since the concentration of metal in an equilibrated sample was proportional to the volume of stock metal solution taken, metal volumes were used instead of concentrations in the work to be described.

To determine the optimum metal concentration, a plot of the distribution ratio, \emptyset , as a function of the volume of stock tracer solution was prepared. This is shown in Figure 5. The indicated aliquots of stock tracer solutions of tantalum and niobium were added to five milliliters of the aqueous phase and equilibrated with five milliliters of the organic phase. The phases were counted, as already described, and \emptyset calculated.

From Figure 5, it can be seen that the distribution ratio for

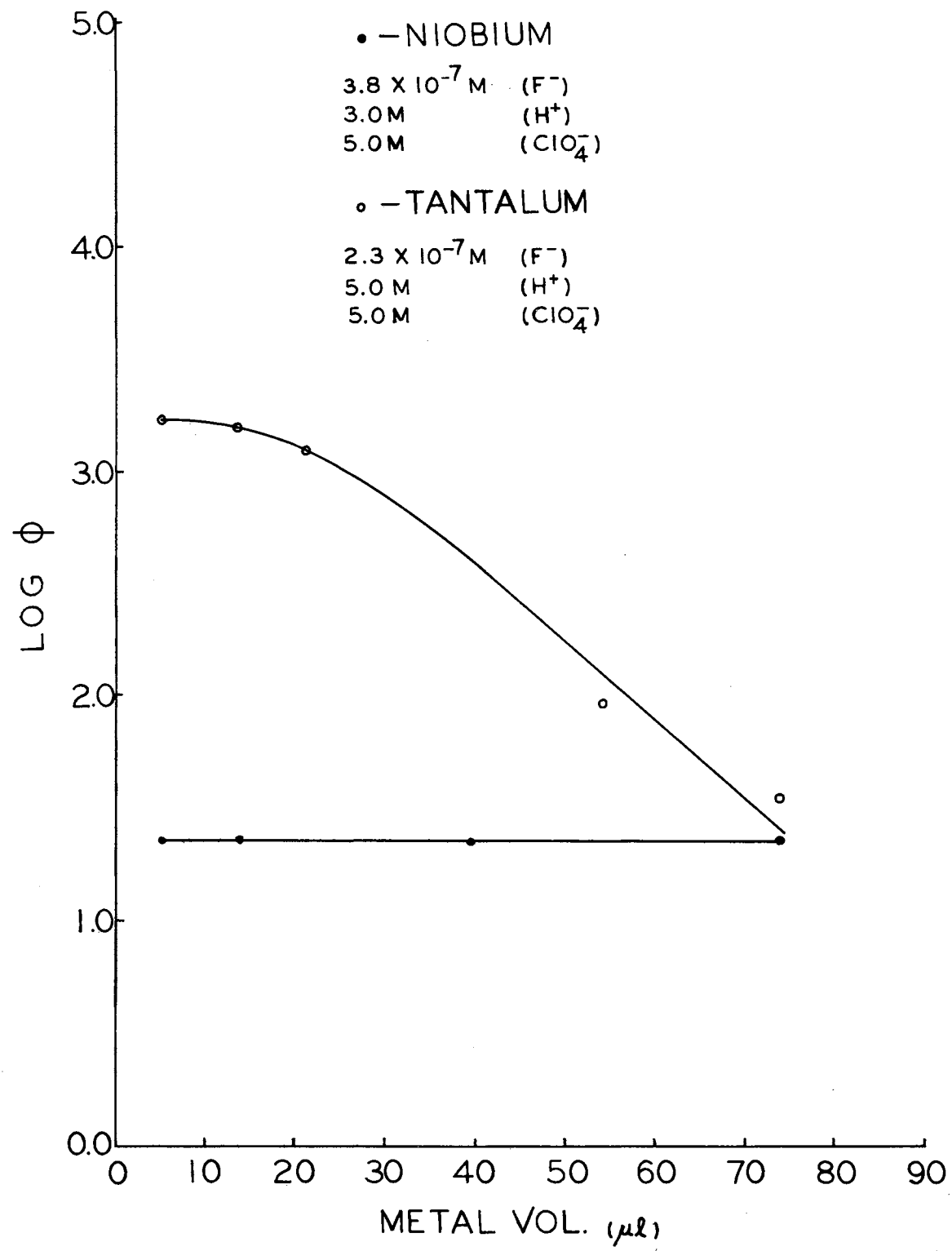


Figure 5. Dependence of the Distribution Ratio Upon the Metal Concentration

niobium varied only slightly over a wide range of stock tracer solution volumes, e.g., metal concentrations. This may be explained by noting that the niobium stock solution was carrier-free ($< 10^{-12}$ M), thus favoring the formation of monomeric species with distribution behavior independent of the metal concentration.

From Figure 5, it is seen that the distribution ratio for tantalum varied considerably over the range of metal concentrations. This behavior was explained by the fact that the tantalum stock solution was not carrier-free ($\sim 10^{-5}$ M), being many orders of magnitude more concentrated than the niobium. However, for aliquots less than about 20 microliters, the distribution curve reached a plateau.

From these data, it was decided that 20 microliters was the best volume of metal stock solution to use. A smaller amount could not be used because the activity of the tantalum became so low that a good analysis of the phases could not be obtained. This made the concentration of the tantalum in the samples about 10^{-7} M and less than 10^{-14} M for the niobium in the samples.

Individual Extraction Curves for Ta and Nb

Tantalum. Figure 6 shows the percent extraction of tracer quantities of tantalum as a function of the $\log (F^-)$ for the four perchloric acid concentrations used. The concentration of this tantalum in each sample was on the order of 10^{-7} M. The percent extraction of tantalum can be seen to be a function of the aqueous phase fluoride ion concentration. At low fluoride, the BPHA formed a stronger complex with tantalum than did the fluoride. At higher fluoride concentrations, however, the situation was reversed and the fluoride formed a stronger complex with tantalum than did the BPHA, thus holding the tantalum in

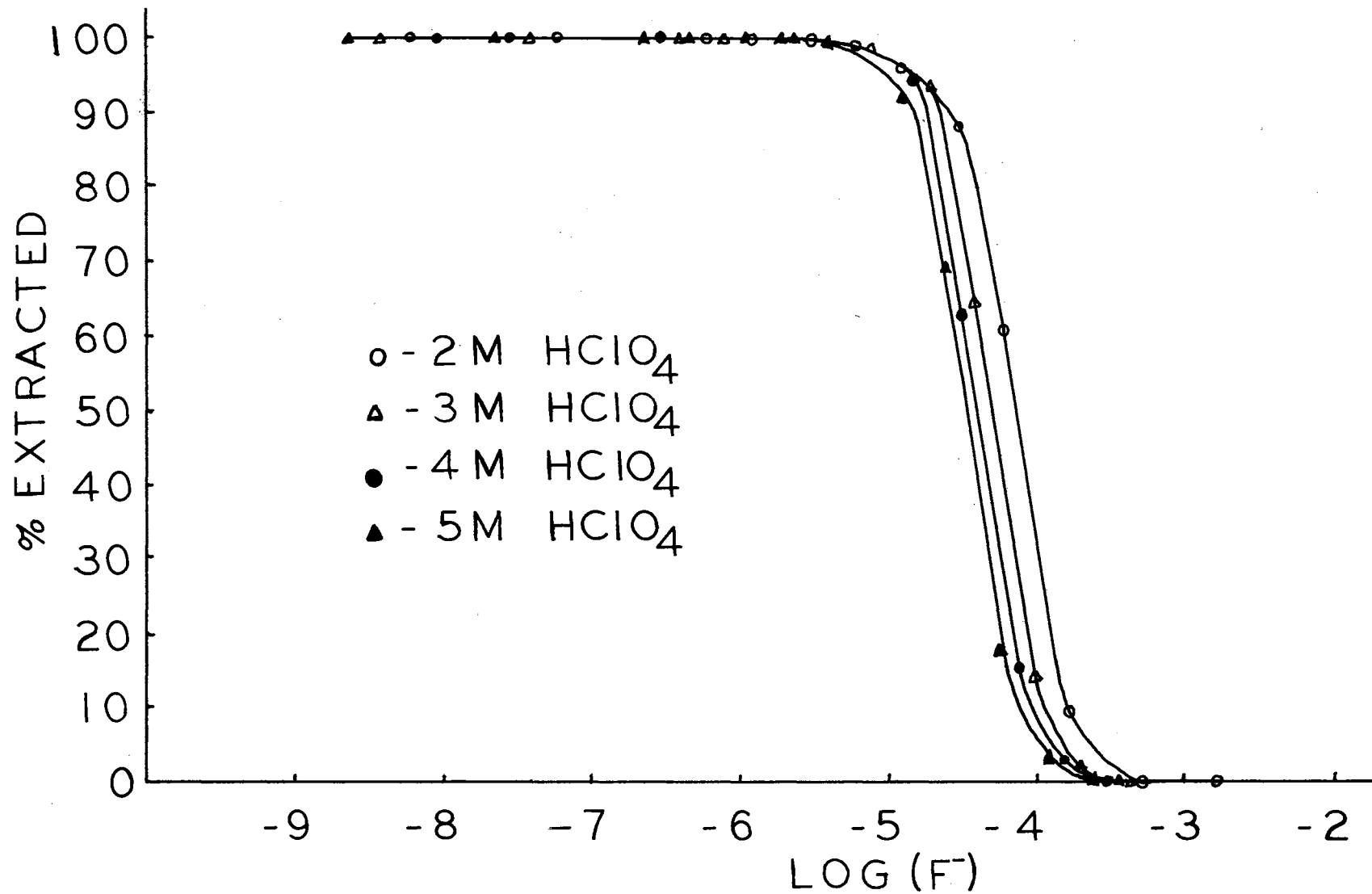


Figure 6. Individual Extraction Curves for Tantalum-182

the aqueous phase.

It can be seen also that, at the lower acidities, the extraction dropped off at the higher fluoride concentrations. The greatest separation, according to the extraction curves of Figure 6, was realized at aqueous phase acidities between 2M and 3M HClO_4 . The next largest separation occurred between the 3M and 4M HClO_4 , and the smallest separation was found between 4M and 5M HClO_4 . This indicated that the extraction was a function of some power of the (H^+) . This fact was borne out in the extraction model proposed for tantalum (see equation 35a).

Niobium. Figure 7 shows the percent extraction of tracer quantities of Nb-95 as a function of the $\log (\text{F}^-)$ for the four perchloric acid concentrations used. The concentration of the niobium in each sample was on the order of 10^{-14} M or less. Figure 7 shows a dependency of the percent extraction of niobium with fluoride similar to that observed with tantalum. However, niobium did not show a systematic dependency on the acidity and the separation between the curves was not very great. The separation was not too much more than the experimental error. From the results of the computer work, the extraction model did not indicate a direct dependency on the acidity (see equation 39).

Figures 8 and 9 show selected data from Figures 6 and 7. Figure 8 shows the percent extraction as a function of $\log (\text{F}^-)$ for tantalum and niobium, both at 2.0M HClO_4 . As can be seen, at constant 2.0M HClO_4 the percent extraction of niobium began to fall off at a lower fluoride concentration than did that of tantalum. At a fluoride ion concentration of 6.1×10^{-5} M, optimum separation of the tantalum from the niobium was affected with the tantalum extracting preferentially into the

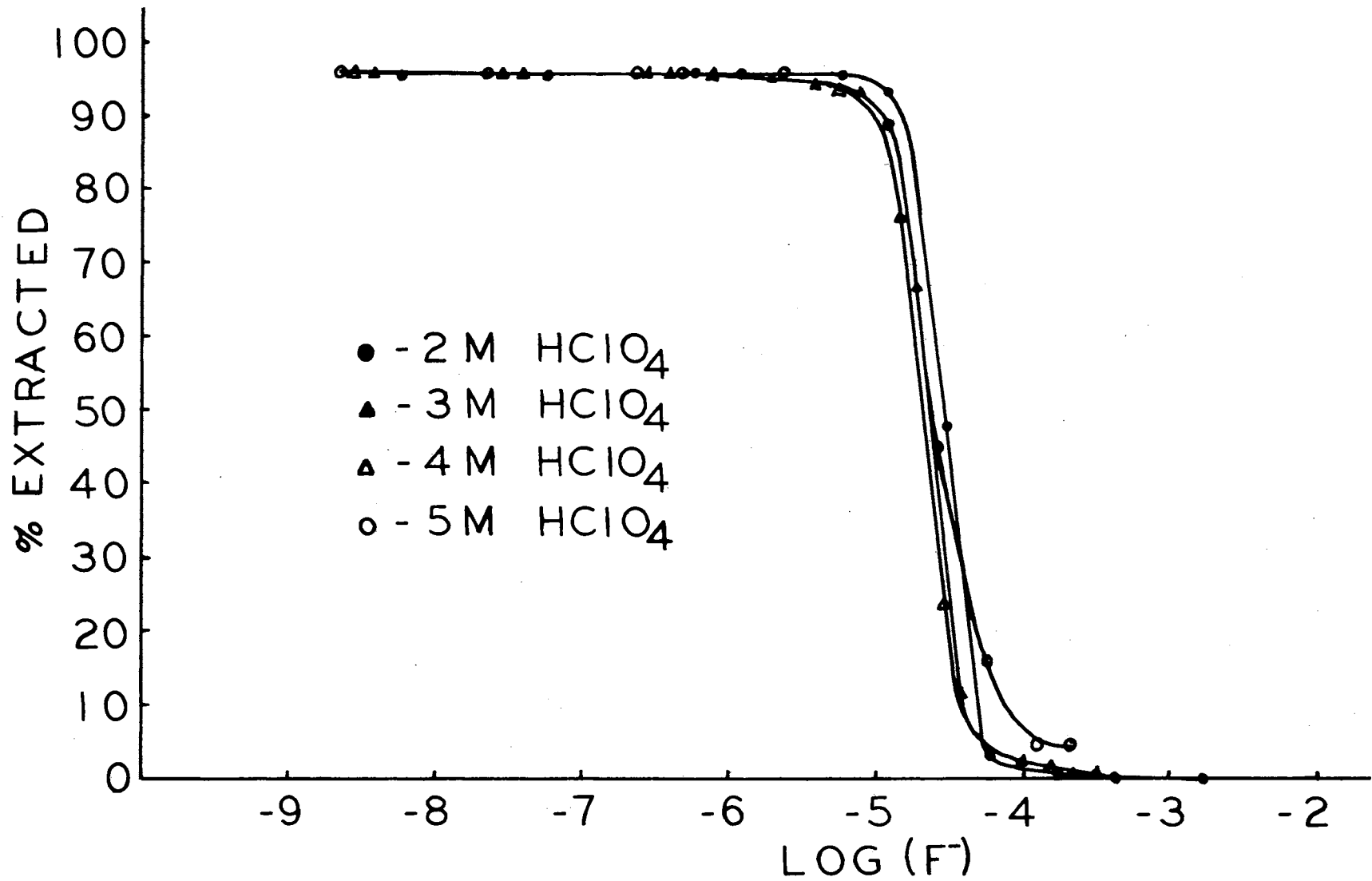


Figure 7. Individual Extraction Curves for Niobium-95

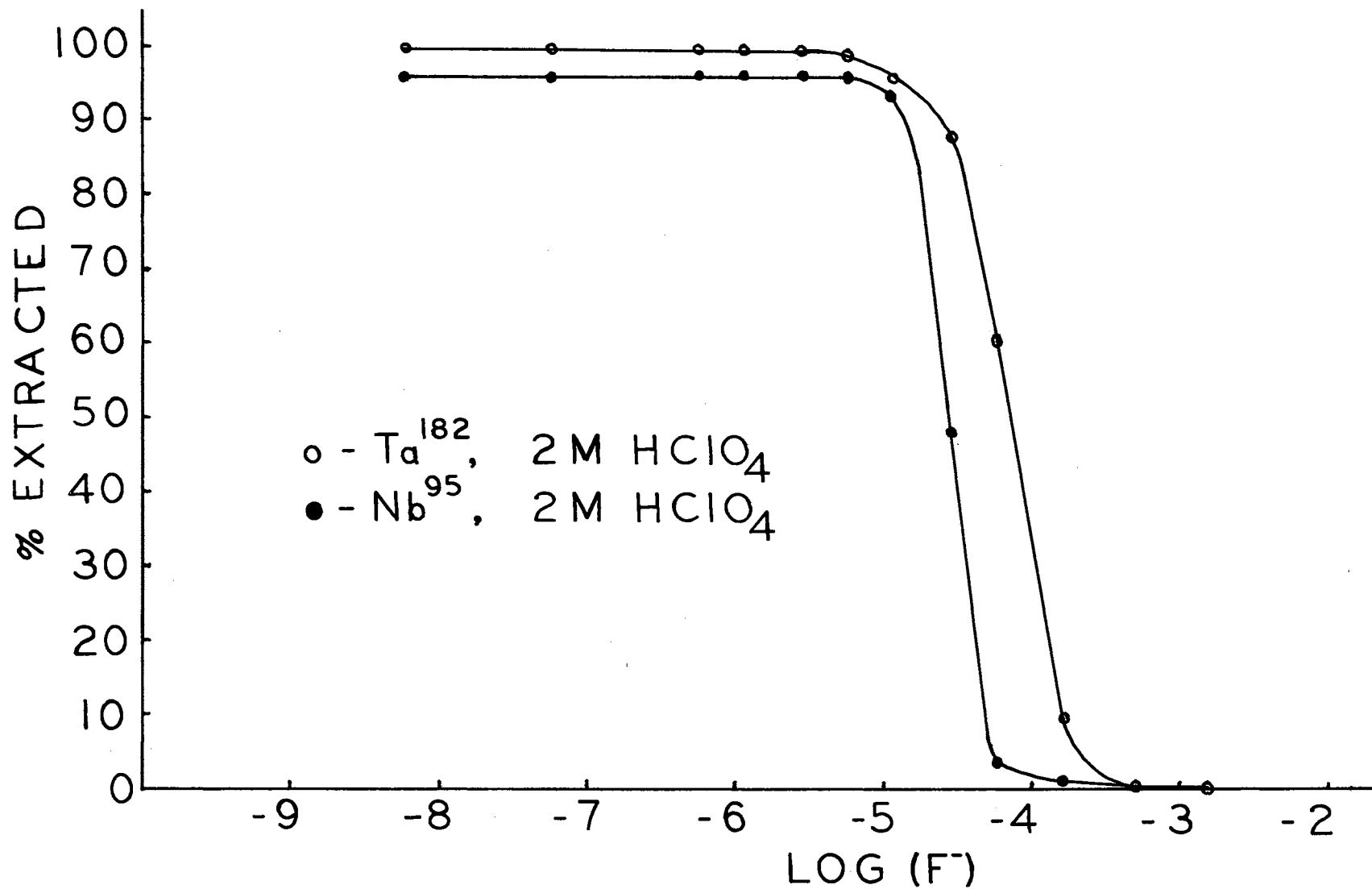


Figure 8. Individual Extraction Curves for Tantalum-182 and Niobium-95 in 2M Perchloric Acid

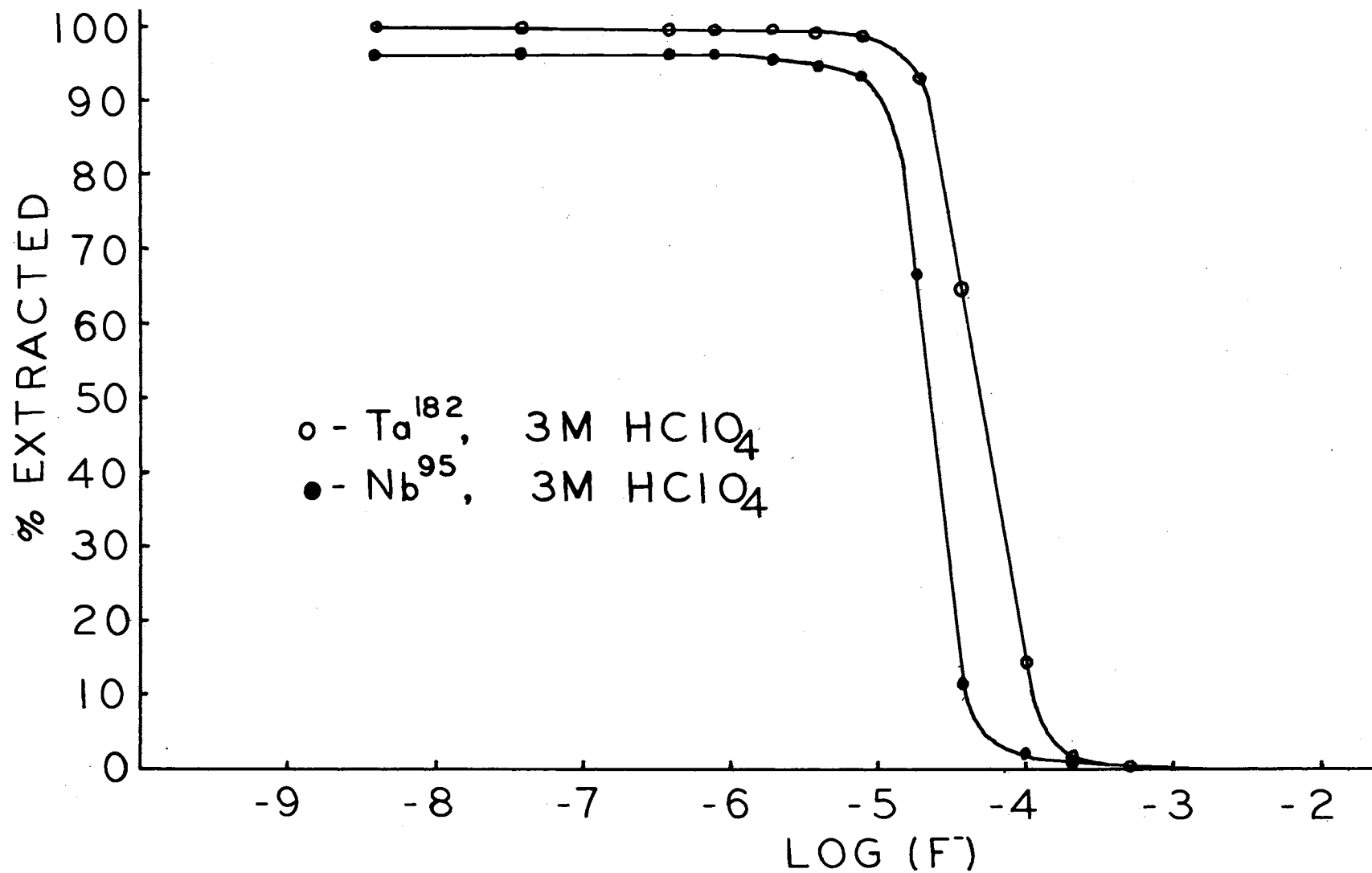


Figure 9. Individual Extraction Curves for Tantalum-182 and Niobium-95 in 3M Perchloric Acid

chloroform phase.

Figure 9 shows data similar to that of Figure 8 for a perchloric acid concentration of 3.0M. At this acidity it was seen that a separation of tantalum from niobium should be possible at a fluoride concentration of 3.7×10^{-5} M.

Separations at 4M and 5M HClO_4 concentrations were not tried because the extraction curves in Figures 6 and 7 did not indicate the possibility of better separations at these acidities than at the lower acidities.

Separation of Ta from Nb in a Mixture of the Two

Expressions of Separation. When dealing with mixtures of tantalum and niobium, there are many ways to express the separation. One is the percent extraction, which has already been discussed.

A second expression is the decontamination factor (D.F.). This is a measure of the amount of tantalum left in the aqueous phase after extraction compared to the amount of niobium left in the aqueous phase.

$$\text{D.F. } (C_{\text{aq}}^{\text{Nb}} / C_{\text{aq}}^{\text{Ta}}) = \frac{C_{\text{aq}}^{\text{Nb}} / C_{\text{aq}}^{\text{Ta}}}{C_{\text{o}}^{\text{Nb}} / C_{\text{o}}^{\text{Ta}}} \quad 42$$

C_{o}^{Nb} and C_{o}^{Ta} represent the initial concentration of niobium and tantalum respectively before extraction. $C_{\text{aq}}^{\text{Nb}}$ and $C_{\text{aq}}^{\text{Ta}}$ represent the concentration of niobium and tantalum in the aqueous phase after equilibration.

The equation for the distribution law for equal phase volumes and one extraction is:

$$C_{\text{aq}} = C_{\text{o}} \left(\frac{1}{\phi + 1} \right) \quad 43$$

where C_{aq} is the concentration of the metal in the aqueous phase after

equilibration, C_0 is the initial metal concentration before equilibration, and ϕ is the distribution ratio. Substituting equation 43 into 42 and simplifying:

$$D.F. = \frac{\phi_{Ta} + 1}{\phi_{Nb} + 1} \quad 44$$

The larger the D.F. value the more efficient the separation of the tantalum from the niobium.

A third expression is the amount of tantalum in the separated organic phase compared to the total metal concentration extracted into the organic phase. This will be referred to as the relative purity of the tantalum. The concentration of metal in the separated organic phase, $(M)_{org}$, is:

$$(M)_{org} = (M^0) - (M)_{aq} \quad 45$$

where (M^0) is the concentration of the metal before equilibration and $(M)_{aq}$ is the metal concentration in the aqueous phase after equilibration. The fraction of tantalum in the organic phase after equilibration is:

$$\frac{(Ta)_{org}}{(Ta)_{org} + (Nb)_{org}} \quad 46$$

The percent extraction of a metal is:

$$\% \text{ Extraction} = \frac{\phi}{\phi + 1} \quad 47$$

Substituting equations 45 and 47 into 46 and simplifying:

$$\frac{(Ta)_{org}}{(Ta)_{org} + (Nb)_{org}} = \frac{(Ta^0) \times \% \text{ Extn. Ta}}{(Ta^0) \times \% \text{ Extn. Ta} + (Nb^0) \times \% \text{ Extn. Nb}} \quad 48$$

If equation 48 is multiplied by 100, the relative purity of tantalum

in the organic phase is obtained.

$$\text{Rel. Purity of Ta in Org.} = \frac{(\text{Ta}^{\circ}) \times \% \text{ Extn. Ta} \times 100}{(\text{Ta}^{\circ}) \times \% \text{ Extn. Ta} + (\text{Nb}^{\circ}) \times \% \text{ Extn. Nb}} \quad 49$$

Separation of Ta from Nb. The experimental technique for the separation of tracer quantities of Nb-95 and Ta-182 from a mixture of these two has been explained in Chapter IV. The results of these experiments are shown in Table IX. This table indicated that tantalum was preferentially extracted from niobium.

A problem was encountered in this system of expressing the relative purity of tantalum in the organic phase. As already mentioned the tantalum was not carrier-free and its concentration was about 10^{-7} M. The niobium, however, was carrier-free and its concentration was less than 10^{-14} M. This meant that the mixture, even before separation, was essentially 100% tantalum so that even if complete separation of the tantalum from the niobium were achieved, little difference would be seen in the relative purity of the tantalum in the organic phase. Also, since the concentration of tantalum and niobium were known only approximately, any value obtained from equation 49 would be an approximation.

A meaningful number was obtained from equation 49 by using the counting activities of each of these isotopes instead of molar concentrations. The activity of each isotope would be proportional to its concentration. The value obtained from equation 49 then indicated the change in the purity of tantalum in the organic phase with respect to the niobium. Nb° and Ta° were found by adding together the activities of each isotope in the aqueous and organic phase. The data are tabulated in Table IX as counts/minute/milliliter.

It should be borne in mind that the values calculated from

TABLE IX

SEPARATION OF MIXTURES OF TRACER Ta-182 AND Nb-95

(HClO ₄)	Fluoride Ion Conc:	Nb ^o C/M/ml	Ta ^o C/M/ml	Nb-95		Ta-182		D.F.	Change in Ta Purity In Org.
				∅	% Extn.	∅	% Extn.		
2.0M	6.1 x 10 ⁻⁵ M	17341	4940	.0781	7.2	1.92	66	2.7	72%
3.0M	3.7 x 10 ⁻⁵ M	18865	4904	.215	18.	3.26	76	3.5	52%

equation 49 were only approximate since the difference in gamma ray energies and counting efficiencies were not considered. The numbers do, however, give one an idea of the purity of the tantalum in the organic phase.

Extraction of Millimolar Metal Concentrations

From the previous results, it was decided that better separation of tantalum from niobium could be obtained from a mixture of the two if the perchloric acid and sodium perchlorate were left out, using only hydrofluoric acid in the aqueous phase. Experiments were carried out to test this. Also, it was of interest to see if concentrations of tantalum and niobium in the millimolar range could be separated effectively. The experimental techniques have been described in Chapter IV.

Separation of Ta from Nb

Table X shows the data for the separation of millimolar tantalum from millimolar niobium using 2.5×10^{-2} M BPHA in chloroform as the organic phase and only varying amounts of hydrofluoric acid in the aqueous phase to obtain the proper fluoride concentration. It can be seen that separation of tantalum from niobium was obtained. The decontamination factors were much better than those obtained with the tracer concentrations with perchloric acid and sodium perchlorate present. Almost all of the tantalum was extracted while only about 12% niobium was extracted.

The relative purity of the tantalum in the organic phase was good, being as high as 92%. This relative purity of tantalum in the organic phase decreased slightly as the fluoride ion concentration was increased. However, the decontamination factor (D.F.) increased considerably.

TABLE X

SEPARATION OF MIXTURES OF MILLIMOLAR CONCENTRATIONS OF Ta AND Nb

F ⁻ Conc. (M)	Initial Ta Conc. (M)	Initial Nb Conc. (M)	Ta		Nb		D.F.	Relative Ta Purity In Org.
			ϕ	% Extn.	ϕ	% Extn.		
2.9×10^{-5}	1.00×10^{-3}	0.93×10^{-3}	55.7	98.	0.100	9.1	51	92
1.0×10^{-4}	0.84×10^{-3}	0.78×10^{-3}	65.3	98.	0.140	12.3	58	90
2.1×10^{-4}	0.83×10^{-3}	0.77×10^{-3}	66.3	98.	0.138	12.1	59	90
1.0×10^{-3}	0.81×10^{-3}	0.75×10^{-3}	79.9	99.	0.152	13.2	70	89

The percent extraction of the tantalum was very good with 98% to 99% extracting while only 9% to 13% of the niobium extracted. The extraction of both the tantalum and niobium increased with an increase in the fluoride ion concentration.

An interesting observation was made during these extractions. Within a few minutes after the tantalum and niobium were added to the samples to be equilibrated, the organic phase became a dark "wine" red color. The color appeared completely developed after about 15 to 30 minutes. This would indicate that, under these conditions using millimolar concentrations of the metals, either the tantalum or niobium or both formed a red complex with BPHA. No effort was made to identify this material.

CHAPTER VI

CONCLUSION

The dependence of the extraction of tantalum and niobium upon the concentrations of these two metals has been studied. The extraction of niobium was essentially independent of the metal concentration when the metal concentration was approximately 10^{-14} M. The extraction of tantalum was dependent upon the metal concentration at the higher metal concentrations. However, at the lower metal concentrations ($\sim 10^{-7}$ M) the extraction of tantalum became less dependent upon the metal concentration.

The extraction curves for tantalum and niobium were obtained at 2M, 3M, 4M, and 5M HClO_4 concentrations as a function of the fluoride ion concentration. Both metals were quantitatively extracted into the organic phase at low fluoride concentrations. At about 10^{-5} M fluoride, the extractions dropped sharply and were essentially nonextracted at fluoride concentrations greater than about 3×10^{-4} M.

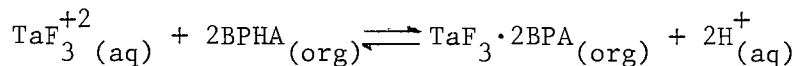
The acidity did not affect the extraction of the niobium as much as it did tantalum. At a constant fluoride ion concentration, the lower acidities increased the extraction of the tantalum and to a lesser extent, niobium.

At a constant perchloric acid concentration and a given fluoride ion concentration the tantalum was extracted to a greater extent than was the niobium, thereby providing a means of separation.

Partial separation of tantalum from niobium from a mixture of the two was achieved by extracting the tantalum into an organic phase of 1×10^{-3} M BPHA in chloroform from an aqueous phase of perchloric acid and the proper fluoride ion concentration (determined from the individual extraction curves). At 2M HClO_4 and 6.1×10^{-5} M fluoride, 66% of the tantalum was extracted while 7.2% of the niobium was extracted. At 3M HClO_4 and 3.7×10^{-5} M fluoride, 76% of the tantalum extracted and 18% of the niobium extracted.

Good separation of millimolar tantalum from millimolar niobium was achieved by extracting the tantalum into an organic phase of 2.5×10^{-2} M BPHA from an aqueous phase containing only small amounts of hydrofluoric acid. The extraction of both metals and the decontamination factors both increased with increasing fluoride ion concentration. At 1.0×10^{-3} M fluoride, 99% of the tantalum extracted while only 13% of the niobium extracted. The decontamination factor was 70.

Computer results indicated the best extraction model for tantalum was:



The equilibrium constant for this reaction was:

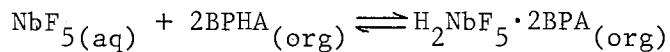
$$K = \frac{(\text{TaF}_3 \cdot 2\text{BPHA})_{\text{org}} (\text{H}^+)_{\text{aq}}^2}{(\text{TaF}_3^{+2})_{\text{aq}} (\text{BPHA})_{\text{org}}^2} = 2.0 \times 10^{10}$$

Two other species, TaF_4^{+1} and TaF_6^{-1} , were also present in the aqueous phase. The formation constants for these species are:

$$\beta_4 = \frac{(\text{TaF}_4^{+1})}{(\text{TaF}_3^{+2}) (\text{F}^-)} = 1.6 \times 10^6$$

$$\beta_6 = \frac{(\text{TaF}_6^{-1})}{(\text{TaF}_3^{+2}) (\text{F}^-)^3} = 1.8 \times 10^{16}$$

The best model for the extraction of niobium was:



The equilibrium constant for this reaction was:

$$K = \frac{(\text{H}_2\text{NbF}_5 \cdot 2\text{BPA})_{\text{org}}}{(\text{NbF}_5)_{\text{aq}} (\text{BPHA})_{\text{org}}^2} = 3.0 \times 10^7$$

One other species, NbF_7^{-2} , was found in the aqueous phase. Its formation constant was:

$$\beta_7 = \frac{(\text{NbF}_7^{-2})}{(\text{NbF}_5) (\text{F}^-)^2} = 4.6 \times 10^{10}$$

The organic phase, in the millimolar extractions of tantalum and niobium, was a dark "wine" red color. This would indicate a colored complex of either tantalum or niobium or both with BPHA. If this is true, a spectrophotometric method instead of a tracer method could possibly be worked out for the analysis of the phases.

This work indicated a separation scheme could be worked out, especially if two or three successive extractions were carried out. Studies would, of course, have to be made on the effect of other metals on the separation.

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"Analytical Chemistry of Niobium and Tantalum", The
MacMillan Co., N. Y., 1964.

VITA

James Spencer Erskine

Candidate for the Degree of

Master of Science

Thesis: SELECTIVE SOLVENT EXTRACTION OF TANTALUM AND NIOBIUM
FLUORIDES USING N-BENZOYL-N-PHENYLHYDROXYLAMINE

Major Field: Chemistry

Biographical:

Personal Data: Born in Alva, Oklahoma, July 21, 1941, the son of Jack and Mary Erskine.

Education: Attended grade school in Alva, Oklahoma; graduated from Alva High School in 1959; received the Bachelor of Science degree in chemistry from Northwestern State College, Alva, Oklahoma in May, 1963 and completed the requirements for the Master of Science degree in May, 1966.

Professional experience: Worked on a National Science Foundation Undergraduate Research Assistantship during the summer of 1962 and worked for Phillips Petroleum Company during the summers of 1963 and 1964. Was a teaching assistant at Oklahoma State University while doing graduate work. Was named to the Dean's Honor Roll for six semesters as an undergraduate, was named to Who's Who in American Colleges and Universities in 1963, was a recipient of two tuition scholarships in 1959 and 1960, and was recipient of a Dow Chemical Scholarship for graduate research during the summer of 1965. Is also a member of Phi Lambda Upsilon.