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ALKYL PHOSPHORIC ACID EXTRACTIONS

D. C. Stewart and T. E. Hicks

August 9, 1950

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## ALKYL PHOSPHORIC ACID EXTRACTIONS

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August 9, 1950

## ABSTRACT

Organic solvent extraction techniques were used to separate the mono- and di-alkyl substituted commercial phosphoric acid mixtures. Extraction coefficients and titration curves for several systems are presented.

Tracer quantities of  $U^{233}$  were extracted by the separated acids. The equilibrium extraction reaction for the moderate-to high-initial-acid systems is proposed.

Tracer  $U^{233}$  extractions by TBP seemed to verify previous studies of the same system by other laboratories.

Tracer  $Pu^{239}$  extraction by dibutyl phosphoric acid from  $HNO_3$  solutions are presented.

Some preliminary experiments on the separability of  $U^{233}$  and  $Pu^{239}$ , by alkyl phosphoric acid extraction, were undertaken and the data presented.

## ALKYL PHOSPHORIC ACID EXTRACTIONS

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## INTRODUCTION

The use of alkyl phosphoric acids in organic solvent carriers as extracting agents for uranium was described in a previous report.<sup>1</sup> In this preliminary paper it was pointed out that the extraction mechanism probably involved the formation of an organic solvent-soluble, uranyl-alkyl-phosphate complex. Since the commercial alkyl phosphoric acids, as obtained, are mixtures of the mono- and di-alkyl substituted forms ( $H_2RPO_4$  and  $HR_2PO_4$ ), it was not possible at the time to state quantitatively the details of the extraction mechanism, since these mixtures were all that had been studied.

The preliminary report also presented evidence indicating the possibility of separating the two acid forms of the commercial product by taking advantage of the differences in their distribution between two non-miscible liquid phases. Such separations have since been made for a number of the alkyl phosphoric acids. The availability of these separated acids has made it possible to determine that with all the carrier solvents studied (save the higher alcohols) the uranium is primarily extracted as a complex with the  $HR_2PO_4$  acid form. Accordingly, this mechanism has been intensively studied, and it is now possible to write definite equations for the process occurring in systems containing moderate or high amounts of nitric acid. There is still some question as to the situation existing when the  $HR_2PO_4$  is used to complex uranium in low-acid solutions.

Uranium can be extracted by some of the mono-substituted ( $H_2RPO_4$ ) alkyl phosphoric acids if amyl alcohol is used as the organic solvent carrier. Some studies on this mechanism will be described. Some other miscellaneous experiments



have been made, including the effects of various anions on the extraction of uranium by alkyl phosphoric acids. The extractability of the  $\text{Pu}^{+4}$  ion was studied briefly. Some evidence will be given to corroborate the mechanism recently suggested by various investigators<sup>2-4</sup> for the extraction of uranium by the completely alkyl-substituted phosphoric acid, tributyl phosphate.

## II. FRACTIONATION OF ALKYL ACIDS

### A. Materials Received

The acid mixtures which have been studied are listed in Table I.

Table I  
Composition of Alkyl Phosphoric Acids as Received

|                                 | Concentrations           |                          | $\text{H}_2\text{RPO}_4/\text{HR}_2\text{PO}_4$<br>Ratio |
|---------------------------------|--------------------------|--------------------------|--|
|                                 | $\text{H}_2\text{RPO}_4$ | $\text{HR}_2\text{PO}_4$ |  |
| Ethyl Phosphoric Acid (Eastman) | 4.66 <sup>*</sup>        | 4.36 <sup>*</sup>        | 1.07 <sup>*</sup>  |
| n-propyl " " "                  | 4.36 <sup>*</sup>        | 3.15 <sup>*</sup>        | 1.385 <sup>*</sup>                                       |
| n-butyl " " "                   | 3.82 <sup>*</sup>        | 2.48 <sup>*</sup>        | 1.54 <sup>*</sup>  |
| Isobutyl " " (Monsanto)         | 3.57                     | 2.56                     | 1.39   |
| n-amyl " " "                    | 3.48                     | 1.81                     | 1.92   |
| n-octyl " " "                   | 2.01                     | 1.75                     | 1.15   |

\* Presented in former paper.<sup>1</sup>

The titration curves for the first three of these (ethyl, n-propyl, and n-butyl)\*\*

\*\* Note: Special long leads to the electrodes were used in the potentiometric apparatus employed for these first titrations. It was later discovered that their use resulted in a high pH reading at the high acid end of the curves and in a low pH reading at the alkaline end. The breaks in the curves, however, were unchanged. The titration curves of UCRL-585 are thus incorrect to the degree indicated. The titrations for Fig. 1 of this report were also made using the long leads.

were presented in the previous report. The last three (isobutyl, n-amyl, and n-octyl) were titrated with standardized NaOH in a similar manner, and the data obtained were used to calculate the quantities of the  $H_2RPO_4$  and  $HR_2PO_4$  forms present in the commercial products. As before, the assumption was made that no free phosphoric acid was present, meaning that the titre between the two breaks of the curve could be taken to represent the amount of  $H_2RPO_4$ , and this value subtracted from the titre to the first break, to represent the  $HR_2PO_4$ . The acid molarities calculated on this basis are summarized in Table I, including some values from UCRL-585 for comparison purposes.

Octyl phosphoric acid emulsifies very readily in water solutions, and it was found necessary to make a ten-fold volume dilution with 75% ethyl alcohol before making this titration.

#### Acid Separations

Fig. 1 comprises a series of titration curves which indicate the basis of the fractionation method used to separate any given pair of mono- and di-substituted alkyl phosphoric acids. In this experiment, a mixture of 40 volumes-percent butyl phosphoric acids in commercial dibutyl ether was equilibrated with an equal volume of water. The two phases were then separated, the aqueous phase washed with an equal volume of fresh dibutyl ether, and the organic phase washed with an equal volume of distilled water. Aliquots were then removed from each of the washed phases and from the wash liquids, and these were titrated. These curves are shown in Fig. 1 as unbroken lines. It will be seen that the relative positions of the breaks in the curves are changed by the washing treatment, indicating changes in the proportions of  $H_2BuPO_4$  and  $HBu_2PO_4$ , with the former favoring the aqueous phase and the latter the organic phase. The original dibutyl ether phase was then washed seven more times with equi-volume portions of water, and the original aqueous phase was washed twice more with

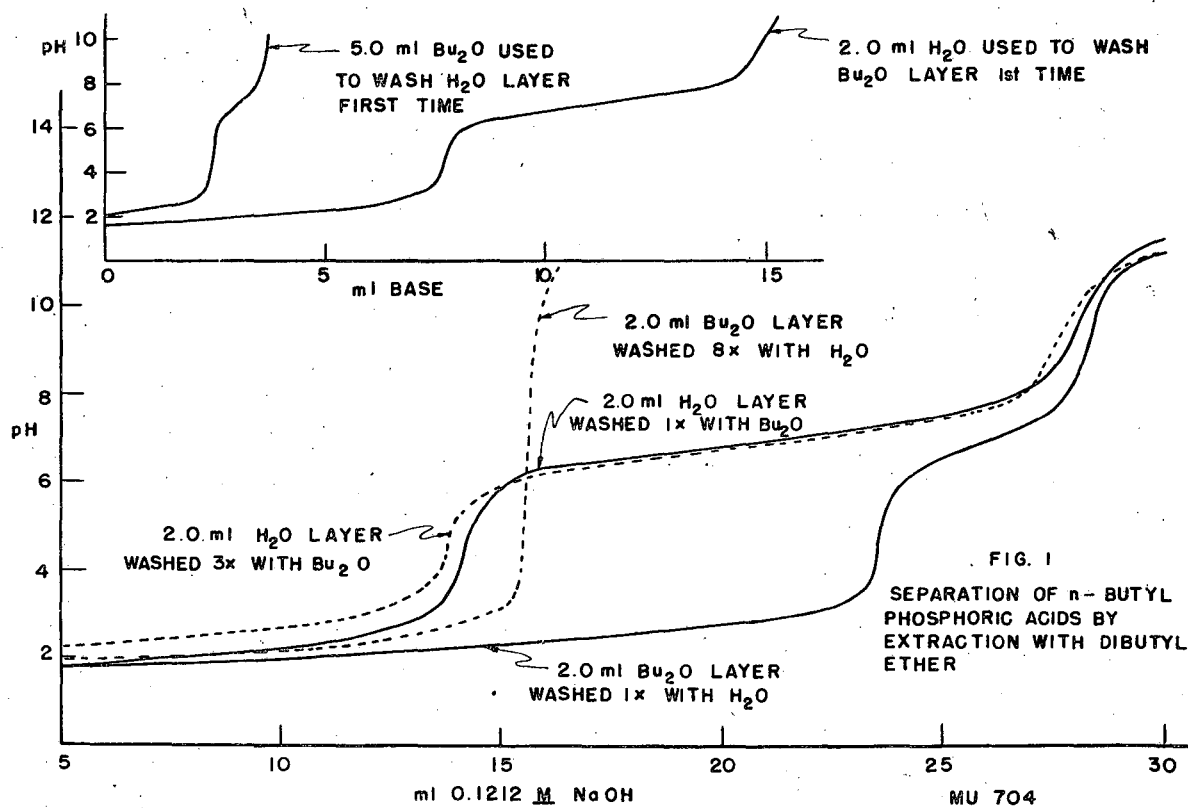


FIG. 1  
SEPARATION OF n-BUTYL  
PHOSPHORIC ACIDS BY  
EXTRACTION WITH DIBUTYL  
ETHER

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dibutyl ether. Aliquots of each of these washed phases were again removed and titrated, the curves being shown as dotted lines in Fig. 1. It will be seen that the "8X washed  $Bu_2O$ " curve now shows but one break, indicating that only  $H_{Bu_2}PO_4$  is present, whereas in the "3X washed  $H_2O$  layer," the titre between the two breaks is equal to the titre to the first break, indicating that the washed aqueous phase now contains only  $H_2BuPO_4$ .

A similar series of batch extractions with dibutyl ether were carried out in order to separate the ethyl phosphoric and the propyl phosphoric acid combinations. With these, however, it was found that eight washings of the organic layer removed substantially all of the desired  $HR_2PO_4$  form of the acid, indicating a much decreased organic solvent extractability, particularly for the diethyl forms. Accordingly, a series of single batch equilibrations were carried out with the various alkyl phosphoric acids and an assortment of solvents in hopes of finding systems which would give more effective separations. These batch tests were made by equilibrating two volumes of the commercial phosphoric acid with four volumes each of water and the solvent. Aliquots of each phase were then taken and titrated as usual, the data being used to calculate the distribution coefficients of the mono- and di-alkyl acids. These constants are summarized in Table II. It will be seen that in every case a solvent was found which gave sufficiently different distribution ratios for the two acid forms to permit their separation by solvent extraction techniques. The most unsatisfactory separation is still that of the ethyl phosphoric acid where, even with amyl alcohol as a solvent, the difference between the two distribution constants is not great and the distribution of  $HET_2PO_4$  into the solvent is comparatively low. This means that a number of extractions are required for good separation; but, even if these are carried out, the final yield of  $HET_2PO_4$  is very poor.

Table II  
Distribution of Mono- and Di-alkyl Phosphoric Acids  
Between Immiscible Phases

| Acid                           | Distribution Ratio (E) | Into Solvents from H <sub>2</sub> O |                |
|--------------------------------|------------------------|-------------------------------------|----------------|
|                                |                        | Solvent                             | $E_{H_2RPO_4}$ |
| Ethyl phosphoric (Eastman)     | n-primary amyl alcohol | 0.69                                | 1.7            |
|                                | Dibutyl carbitol       | 0.14                                | 0.51           |
| n-propyl phosphoric (Eastman)  | n-primary amyl alcohol | 0.86                                | 5.4            |
|                                | Dibutyl carbitol       | 1.4                                 | 1.2            |
| n-butyl phosphoric (Eastman)   | n-primary amyl alcohol | 2.9                                 | ∞ ?            |
|                                | Dibutyl carbitol       | 2.1                                 | 39             |
|                                | Dibutyl ether          | 0.66                                | 15             |
| Isobutyl phosphoric (Monsanto) | Dibutyl ether          | 0.54                                | 11             |
| n-amyl phosphoric (Monsanto)   | Dibutyl ether          | 0.72                                | 6.2            |
| n-octyl phosphoric* (Monsanto) | Diethyl ether          | 42                                  | ~760           |
|                                | Hexone                 | 28                                  | ~106           |
|                                | Dibutyl ether**        | 0.44**                              | 7.0**          |

\*Emulsifies very strongly in water systems with diethyl, isopropyl and dibutyl ethers, and with hexone or carbon tetrachloride. Volume changes, however, indicate very high distribution of both acid forms into the organic phase in each case.

\*\*Out of diethylene glycol rather than H<sub>2</sub>O.

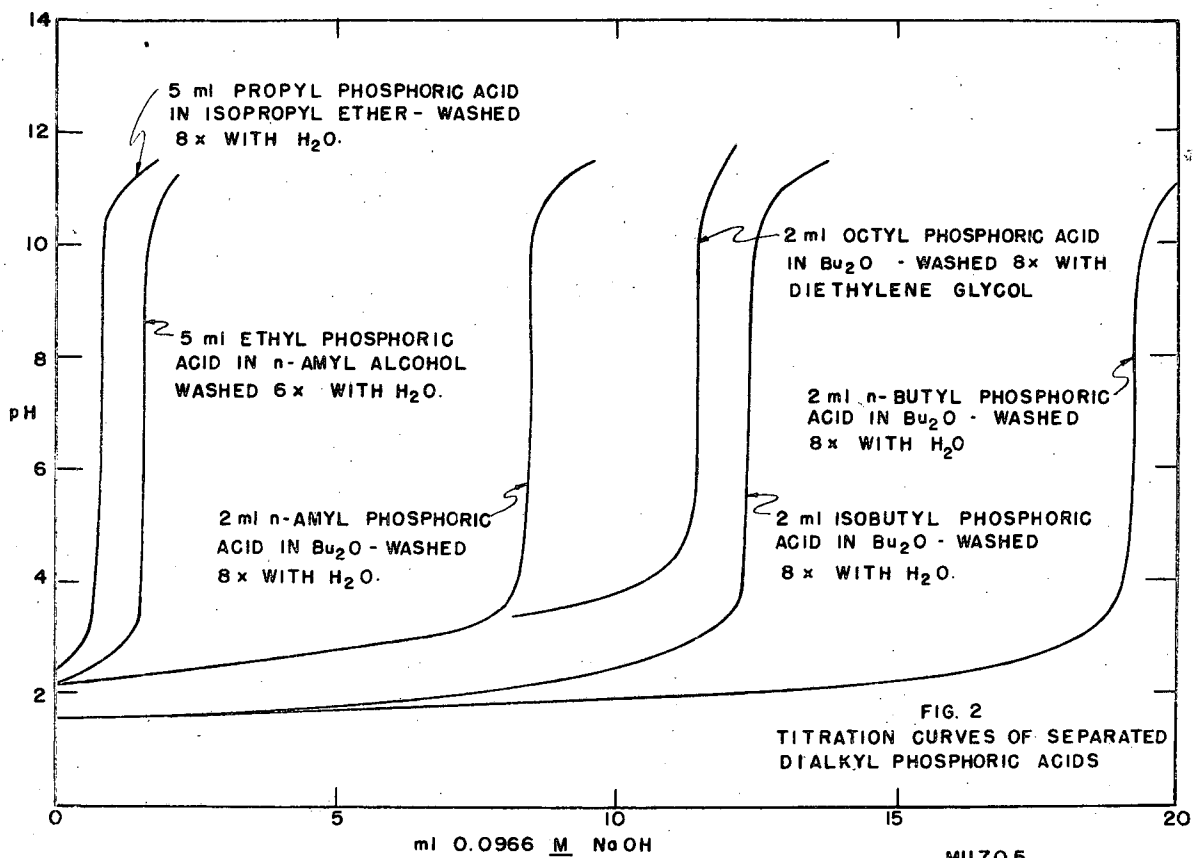
The octyl phosphoric acid was again a special case, since it emulsified so strongly whenever water was used as one of the partitioning phases. Approximate distribution ratios were obtained in some cases by centrifuging the equilibrated mixtures for long periods to break the emulsion. The data obtained indicated that the solvent extraction of both octyl acid forms out of water was very high, which would make a separation very difficult or even impossible. However, it was found that if diethylene glycol was used to replace the water

phase, the emulsion difficulties not only were eliminated, but the octyl phosphoric acid distribution ratios into dibutyl ether were of the proper magnitude to ensure good separation. The distribution coefficients for this system are also indicated in Table II.

Fig. 2 gives the titration curves for a number of the separated di-alkyl phosphoric acids. The n-butyl, isobutyl and n-amyl forms were prepared by equilibrating two volumes of the commercial acid with four volumes each of water and dibutyl ether. The water phase was then discarded, and the organic phase washed seven more times with equal volumes of water. The n-propyl acid was similarly suspended and washed eight times in iso-propyl ether, and the ethyl acid was suspended in n-amyl alcohol. In this last case, a total of only six water equilibrations was used. The n-octyl acid was suspended in dibutyl ether, this mixture being equilibrated eight times with diethylene glycol. As before, the titration of the separated octyl acid had to be carried out in a ten-fold dilution with ethyl alcohol. The other titrations were all made on aliquots which had been diluted with 20 ml of water.

Most of the various proposed plant processes using tributyl phosphate as an extracting agent for uranium involve the use of a hydrocarbon carrier solvent (kerosene, hexane, etc.). If small amounts of the mono- or di-butyl acids were formed by hydrolysis, the extraction results would change markedly. It therefore was of interest to determine the maximum solubility of these forms in n-hexane, and it was found that a saturated solution at room temperature contained  $0.152M$   $H_2BuPO_4$  and  $0.186M$   $HBu_2PO_4$ .

In regard to the same problem, a 20 volume-percent solution of tributyl phosphate in dibutyl ether was left in contact with  $6M$   $HCl$  for a period of six weeks. At the end of this time, an aliquot of the organic phase was titrated and showed only one break in the curve, indicating that if any hydrolysis of



the tributyl phosphate had occurred, it had not progressed as far as the  $H_2BuPO_4$  stage.

### III. EXTRACTION BY DI-SUBSTITUTED ACIDS

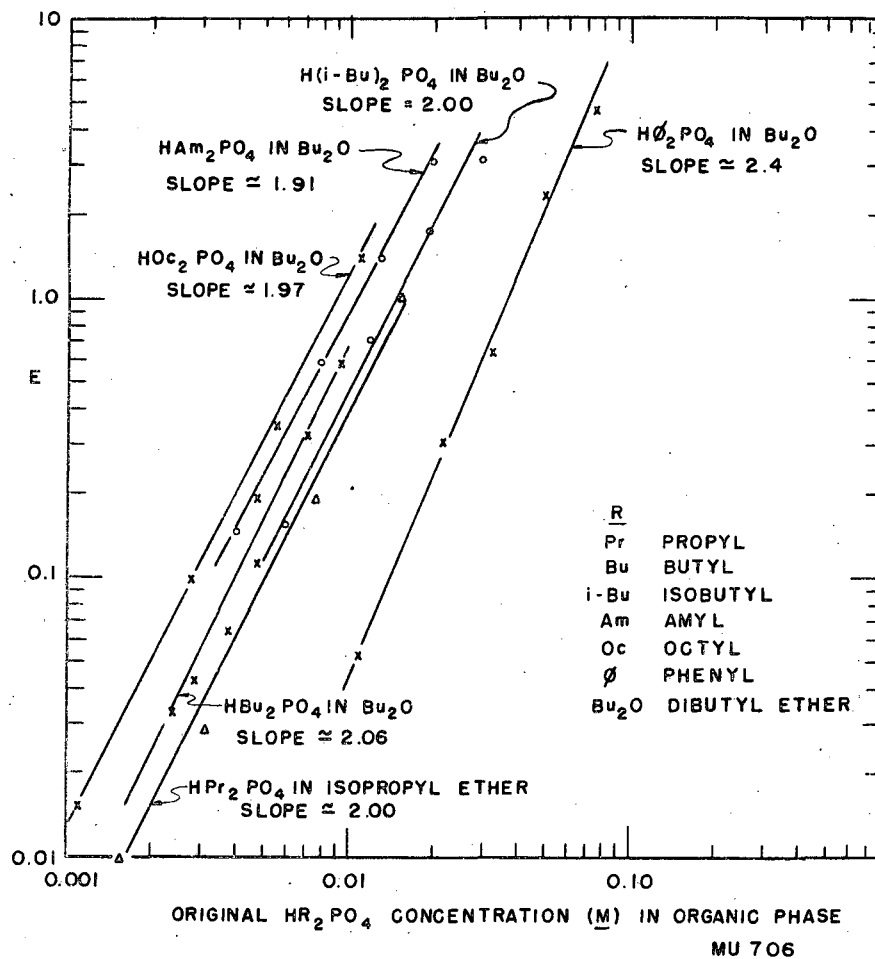
#### A. Effect of Substituents

Each of the separated di-alkyl forms whose titration curves are shown in Fig. 2 was used to prepare a series of more dilute solutions of the acid in the same solvent. Portions of each of these diluted solutions were then equilibrated with equal volumes of  $U^{233}$  tracer in  $1.98M$   $HNO_3$ . After equilibration, aliquots of each phase were removed, plated, and the number of alpha-counts present determined by the usual methods. The data thus obtained were used to calculate E, the distribution ratio of the  $U^{233}$  between the organic and aqueous phases. The results of these experiments are shown in Fig. 3, where E is plotted on a log-log scale against the  $HR_2PO_4$  concentration in the original organic solvent phase. The amount of diethyl phosphoric acid available after the separation process described in the first section was too small to permit preparation of a series of diluted solutions. A single experiment indicated an E value for  $U^{233}$  of about 0.06 when  $0.031M$   $HEt_2PO_4$  in n-amyl alcohol was equilibrated with the  $1.98M$   $HNO_3$  tracer solution.

In addition to the di-alkyl acids which were obtained by the batch extraction methods described, a sample of diphenyl phosphoric acid was tested for its extractive effect on  $U^{233}$ , and the resulting curve is also included in Fig. 3. This diphenyl phosphoric acid is a product of Dow Chemical Company, and is a pinkish solid which is soluble to about  $0.12-0.15M$  in dibutyl ether at room temperature. A saturated solution thus prepared was diluted slightly with more dibutyl ether, and an aliquot was titrated with standardized sodium hydroxide. The titration curve obtained showed but one break, the titre corresponding to an  $H_2PO_4$  concentration of  $0.107M$ . This stock was further diluted to give the



FIG. 3  
EFFECT OF VARYING ALKYL PHOSPHORIC ACID CONCENTRATIONS  
ON THE EXTRACTION OF  $U^{235}$  FROM 1.98 M  $HNO_3$



series of solutions equilibrated with the 1.98M acid U<sup>233</sup> tracer solution.

Comparison of Fig. 3 with the distribution coefficients of the acids themselves (Table II) reveals the following likenesses and differences:

(a) The di-octyl phosphoric acid is the most efficient extractive for uranium as might be predicted from the very high distribution of the acid into organic solvents from water solutions, the only surprising feature being that the observed difference between its effect and that of the others is not greater than it is.

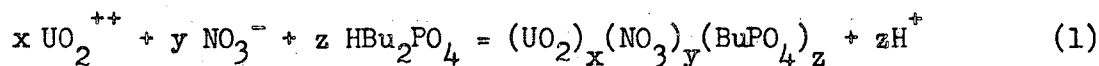
(b) On the other hand, dipropyl phosphoric acid, which apparently has a low distribution into dibutyl or di-isopropyl ethers, is almost as effective an extractive agent for uranium as dibutyl or di-octyl phosphoric acids.

(c) The effectiveness of the amyl versus the isobutyl forms as uranium extractives is in the reverse order from the distribution of the free acids themselves.

Some of these effects might possibly be explained on the basis of the size of the complex molecule formed.

### B. Equilibrium Extraction Conditions

It would seem reasonable, as a first assumption, to suppose that the experiments whose results are plotted in Fig. 3 involve only uranyl ion, dibutyl phosphoric acid, hydrogen ion and perhaps nitrate ion. On this basis, a general expression might be written:



$$K = \frac{[(\text{UO}_2)_x (\text{NO}_3)_y (\text{BuPO}_4)_z] (\text{H}^+)^z}{(\text{UO}_2^{++})^x (\text{NO}_3^-)^y (\text{HBu}_2\text{PO}_4)^z} \quad (2)$$

If it is now assumed:

- (a) That all of the complex ion goes into the solvent layer,
- (b) That concentrations can be substituted for activities,

Then:

$$K = E \frac{(H^+)^z}{(NO_3^-)^y (HBu_2PO_4)^z} \quad (3)$$

or:

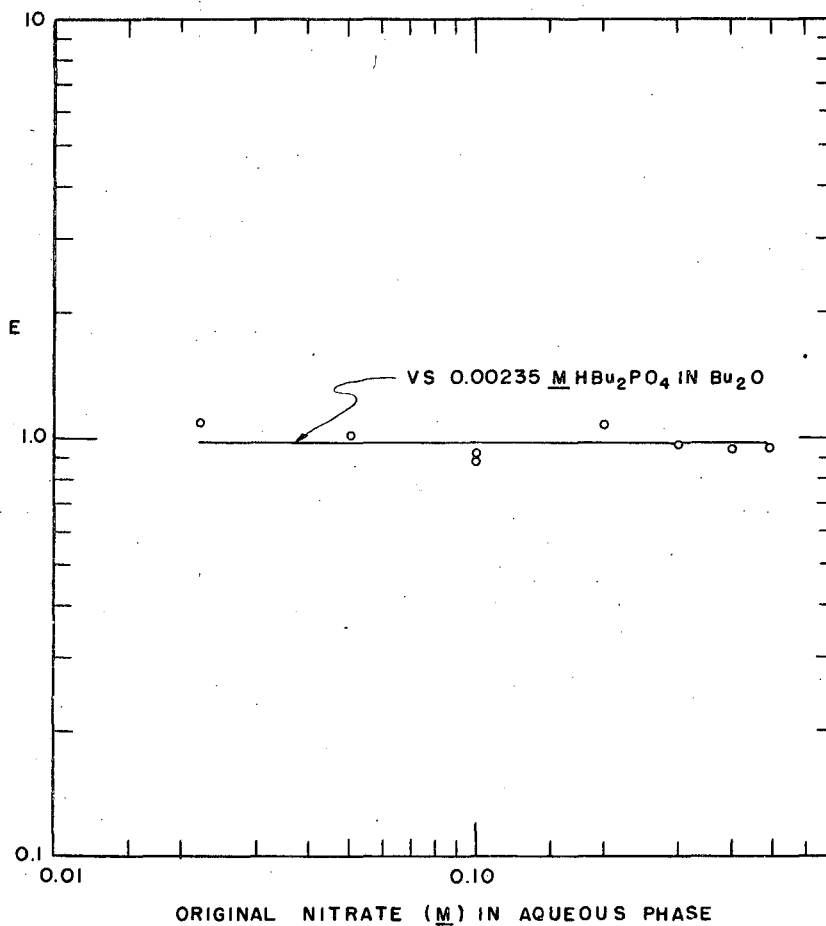
$$\log E = \log K - z \log (H^+) + y \log (NO_3^-) + z \log (HBu_2PO_4) \quad (4)$$

In the experiments of Fig. 3, no appreciable amount of free  $(H^+)$  was produced as a result of the reaction, since the uranium was present only in tracer amounts (0.00013-0.00032M). Therefore, the hydrogen ion and nitrate concentrations could be considered as being constant, and the slope of the lines of Fig. 3 should equal "z" in the equations above. It will be seen that this value was essentially two for all the di-substituted acids tested in dibutyl ether carriers.

Using dibutyl phosphoric acid as a prototype for the series, an experiment was then run to determine whether or not nitrate ion was involved in the reaction mechanism. A series of  $U^{233}$  tracer solutions was prepared in which the acidity was held constant at 0.05M  $HClO_4$ , and the  $Na^+$  concentration at 0.5M. In these solutions the  $NO_3^-$  concentration was varied from 0.0 to 0.5M, the anion strength being balanced by corresponding changes in  $ClO_4^-$  concentration from 0.5M to 0.0. Portions of these solutions were then equilibrated with equal volumes of 0.00235M  $HBu_2PO_4$  in dibutyl ether, and the distribution ratios were again obtained by plating and counting aliquots of each phase. These E values are graphed against the nitrate ion concentration in Fig. 4. In this experiment, the nitrate ion is the only varying quantity, therefore, it would appear that "y" of Equation 4 is equal to zero and that nitrate ion does not enter into the reaction. On this

FIG. 4

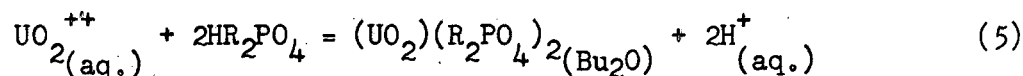
EFFECT OF VARYING NITRATE CONCENTRATION ON THE EXTRACTION OF  $U^{233}$  BY  $H\text{Bu}_2\text{PO}_4$  IN DIBUTYL ETHER FROM 0.05 M  $\text{HClO}_4$ , CONSTANT IONIC STRENGTH, SOLUTIONS.



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basis, Equation 1 would then reduce to:



The next step was to test the hydrogen ion dependence of the reaction. The results of the experiments on this point are given in Fig. 5. Disregarding the lower curves for the moment, the uppermost line represents an experiment in which  $\text{U}^{233}$  solutions were prepared with the total nitrate concentration held at  $3\text{M}$  and the  $\text{H}^+$  concentration varied between  $1\text{M}$  and  $3\text{M}$ , the difference in the amount of cation present being made up by lithium ion. Portions of these solutions were equilibrated with  $0.0188\text{M}$   $\text{HBu}_2\text{PO}_4$  in dibutyl ether, and the distribution coefficients for the  $\text{U}^{233}$  were determined as usual. In this experiment, the hydrogen ion is the only variable, and the slope of approximately minus two found for the upper curve of Fig. 5 then corroborates Equation 5 as being the equilibrium reaction for the extraction of uranyl ion by dibutyl phosphoric acid in dibutyl ether carrier solvent out of aqueous solutions containing one molar or higher initial nitric acid.

The qualifications made in the last statement should be noted, since it is evident from the other curves of Fig. 5 that the simple mechanism shown in Equation 5 does not hold at lower acidities. Before discussing this point, it might be of interest to calculate the equilibrium constant  $K$  for the conditions where Equation 5 does apply. This has been done for the dibutyl phosphoric acid system in two ways: (1) by using the data used to draw its curve in the constant acid, varying  $\text{HBu}_2\text{PO}_4$  situation of Fig. 3, and (2) from the varying high acid, constant  $\text{HBu}_2\text{PO}_4$  curve of Fig. 5. The results of these calculations are given in Table III.

FIG. 5  
EFFECT OF VARYING ACIDITY ON THE EXTRACTION OF  $U^{233}$   
BY  $HBu_2PO_4$  IN  $Bu_2O$  (CONSTANT NITRATE CONCENTRATION)

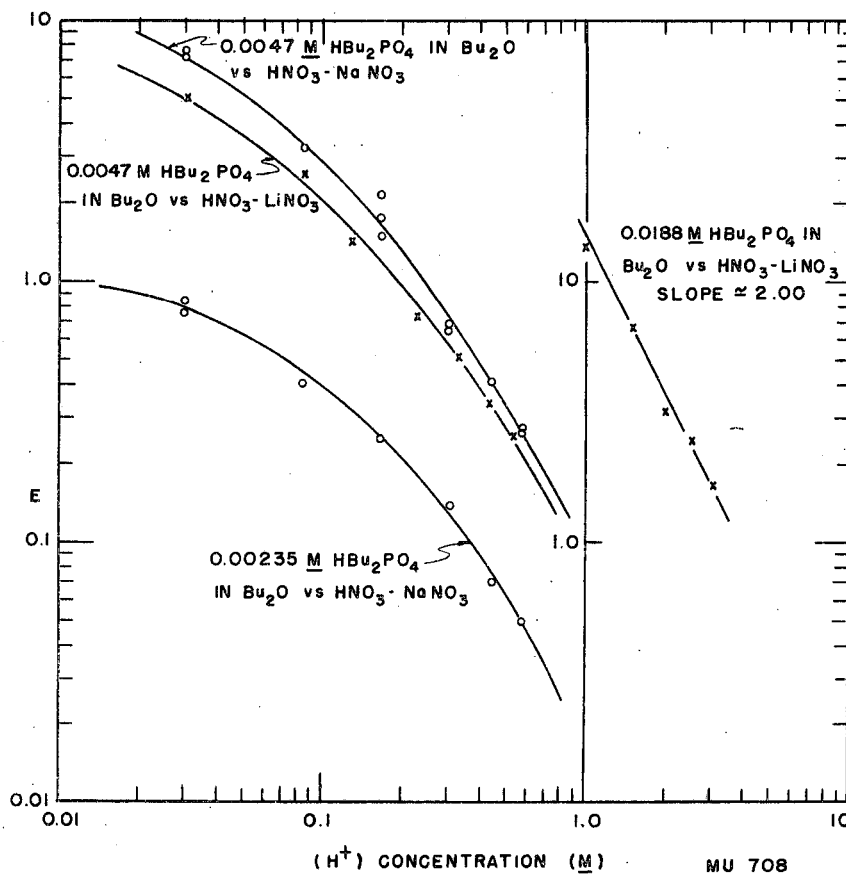


Table III

Calculation of K for Equation 5, Using Dibutyl Phosphoric Acid Data

| Experiment                             | $-2 \log (\text{HBu}_2\text{PO}_4)$ | $2 \log (\text{H}^+)$ | $\log E$  | $\log K$  | K   |
|--|-------------------------------------|-----------------------|---|---|---|
| Constant ( $\text{H}^+$ )              | 5.257                               | 0.594                 | -1.481  | 4.370   | 23400   |
| Varying ( $\text{HBu}_2\text{PO}_4$ )  | 5.098                               | "                     | -1.464  | 4.228   | 16900   |
|  | 4.848                               | "                     | -1.194  | 4.249   | 17700   |
|  | 4.656                               | "                     | $\left\{ \begin{array}{l} -0.720 \\ -0.946 \end{array} \right.$ | $\left\{ \begin{array}{l} 4.530 \\ 4.304 \end{array} \right.$ | $\left\{ \begin{array}{l} 33850 \\ 20100 \end{array} \right.$ |
|  | "                                   | "                     |   |   |   |
|  | 4.303                               | "                     | -0.494  | 4.403   | 25250   |
|  | 4.052                               | "                     | -0.236  | 4.410   | 25650   |
| Average K = 23300 $\pm$ 4300           |                                     |                       |   |   |   |
| Constant ( $\text{HBu}_2\text{PO}_4$ ) | 3.452                               | 0.000                 | 1.128   | 4.580   | 38000   |
| Varying ( $\text{H}^+$ )               | "                                   | 0.352                 | 0.825   | 4.629   | 42500   |
|  | "                                   | 0.603                 | 0.500   | 4.555   | 35850   |
|  | "                                   | 0.797                 | 0.390   | 4.639   | 43500   |
|  | "                                   | 0.955                 | 0.212   | 4.619   | 41550   |
| Average K = 40300 $\pm$ 2700           |                                     |                       |   |   |   |

The variance between the equilibrium constants calculated for the mean constant- $(\text{H}^+)$ -data and mean constant- $(\text{HBu}_2\text{PO}_4)$ -data probably indicates the incompleteness of the assumed simple equation for representing the equilibrium system. The equilibrium reaction may involve another constant which will explain the deviation from second order  $(\text{H}^+)$  and  $(\text{HBu}_2\text{PO}_4)$  dependence as the acidity is decreased below one molar. The appreciable deviation in the higher acid data represents the available accuracy in reproducibility of equilibrium conditions.

The data of Fig. 3 may be similarly used to calculate the K values when the other di-substituted acids are used to complex uranium in high acid solution. This has also been done, and the data are summarized in Table IV. In these cases, a single value (at E = 1) was taken from each curve to use in calculating the K values shown.

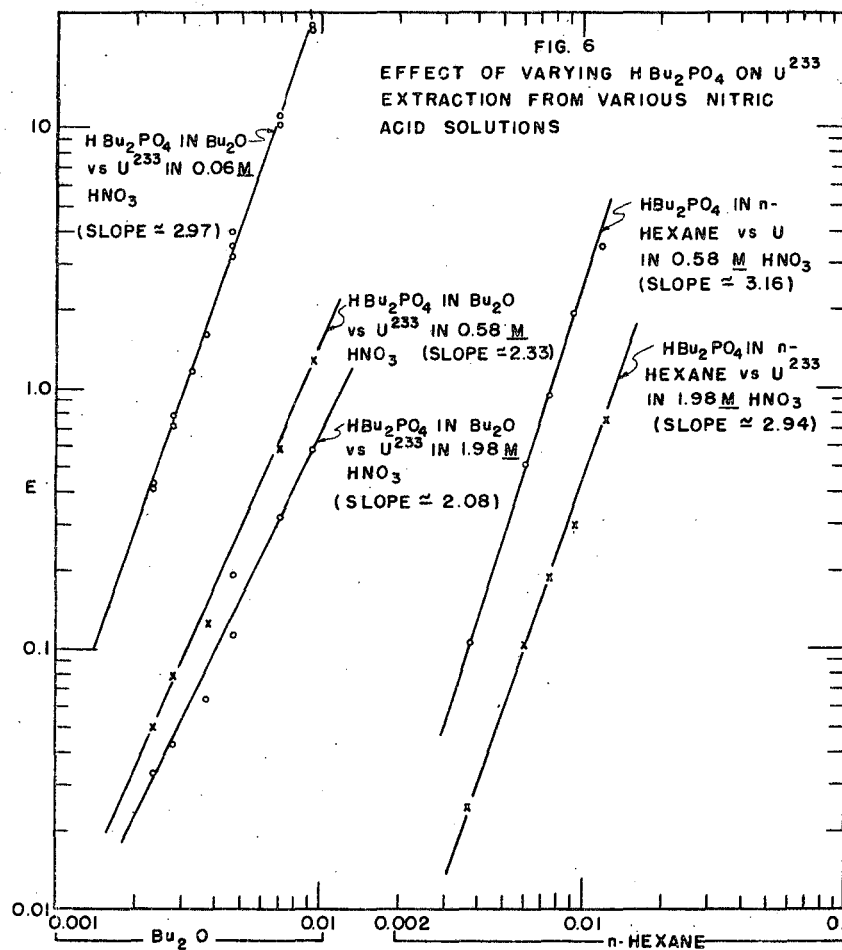
Table IV  
Approximate K Values for Equation 5  
(Calculated from data of Figure 3)

| Acid                                 | log E | 2 log (H <sup>+</sup> ) | -2 log (HR <sub>2</sub> PO <sub>4</sub> ) | log K | K     |
|--------------------------------------|-------|-------------------------|---|-------|-------|
| HPr <sub>2</sub> PO <sub>4</sub>     | 0.0   | 0.594                   | 3.580                                     | 4.174 | 14900 |
| HBu <sub>2</sub> PO <sub>4</sub>     | "     | "                       | 3.820                                     | 4.414 | 25900 |
| H(i-Bu) <sub>2</sub> PO <sub>4</sub> | "     | "                       | 3.658                                     | 4.252 | 17850 |
| HAm <sub>2</sub> PO <sub>4</sub>     | "     | "                       | 3.940                                     | 4.534 | 34200 |
| H <sub>2</sub> PO <sub>4</sub>       | "     | "                       | 4.086                                     | 4.680 | 46750 |
| H <sub>2</sub> PO <sub>4</sub>       | "     | "                       | 2.852                                     | 3.446 | 2790  |

C. Extraction at Lower Acidities

Fig. 6 shows the change in E when varying concentrations of HBu<sub>2</sub>PO<sub>4</sub> were used in dibutyl ether and n-hexane as extracting agents for U<sup>233</sup> tracer solutions in various strengths of nitric acid. It will be seen that as the initial acidity of the systems with dibutyl ether is decreased, a change occurs in the slope of the line from approximately 2 at 1.98M HNO<sub>3</sub> to 3 at 0.06M nitric acid. In the n-hexane systems, the slope is almost 3, even when the nitric acid concentration is 1.98M. In other words, at lower acidities in dibutyl ether systems, and even in moderately high acid concentrations in n-hexane systems, the second order dependence of the reaction mechanism on hydrogen ion concentration has





$\text{H Bu}_2\text{PO}_4$  CONCENTRATION (M) IN ORIGINAL ORGANIC PHASE

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disappeared, and Equation 5 apparently no longer holds as the sole reaction taking place.

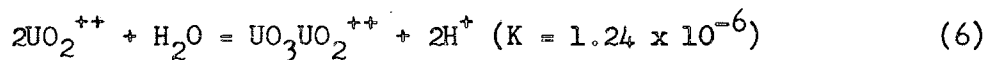
Since the nitrate dependence experiment (whose results are graphed in Fig. 4) was done at a low acid concentration, it still seems safe to eliminate nitrate ion as a possible reactant at low acidities. The hydrogen ion dependence was checked several times in the  $0.03 \longrightarrow 0.6M (H^+)$  range. The first series of  $U^{233}$  test solutions to be made was prepared using  $NaNO_3$  and  $HNO_3$ , varying the proportions of each so as to maintain a constant ionic strength. This series of aqueous solutions was tested with two different concentrations of  $HBu_2PO_4$  in dibutyl ether, and the resulting changes in E with acidity are shown in Fig. 5. Since these curves did not have a constant slope as anticipated, it was thought that the fault might lie in the fact that the activity coefficients of  $NaNO_3$  and  $HNO_3$  are not identical through this range. A fresh series of test  $U^{233}$  tracer solutions using  $HNO_3-LiNO_3$  combinations gave the same type of curve however, as will also be seen in Fig. 5. Commercial n-butyl phosphoric acid (the mixture of  $H_2BuPO_4 + HBu_2PO_4$ ) also gave the same type of curves when tested against these constant nitrate solutions (results not shown here).

It is difficult to write a single reaction which will account for these observed facts, i.e., the third power dependence on  $HBu_2PO_4$  concentration, no involvement of free nitrate ion, and a hydrogen ion dependence which apparently is approaching zero at low acidities. A number of possibilities were tested, none of which gave a satisfactory explanation.

(1) Presence of carbonate: If substantial amounts of carbonate were present in the  $NaNO_3-HNO_3$  and  $LiNO_3-HNO_3$  series of solutions used for the varying  $H^+$  experiments of Fig. 5, this might account for the low E values observed since this would complex uranium in the aqueous phase. Tests on the nitrate salts used did reveal the presence of small amounts of carbonate, particularly in the

NaNO<sub>3</sub> series. However, calculation indicates that even assuming 0.1M H<sub>2</sub>CO<sub>3</sub>, at 0.03M H<sup>+</sup> the concentration of HCO<sub>3</sub><sup>-</sup> will be 10<sup>-6</sup>M and of CO<sub>3</sub><sup>-</sup> will be less than 10<sup>-9</sup>M. Since the effect on the slopes of the curves of Fig. 5 apparently starts even at much higher acidities, the concentration of the carbonate ions present must be far too low to be of consequence. Too, the assumption that the competitive action of carbonate was causing the low E values of Fig. 5 would not account for the third power dependence on HBU<sub>2</sub>PO<sub>4</sub> seen in Fig. 6.

(2) Hydration of uranyl ion: This might cut down the effective concentration of uranyl ion if the hydrated form did not complex with butyl phosphoric acid. Sutton<sup>5</sup> studied uranyl ions in perchloric acid solutions and determined that the probable hydration reaction at pH 2 was:

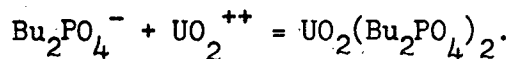


Assuming this reaction to hold at 0.03M acid (pH = 1.52), the (UO<sub>3</sub>UO<sub>2</sub><sup>++</sup>)/(UO<sub>2</sub><sup>++</sup>)<sup>2</sup> ratio is 0.0015. In other words, if the tracer uranyl concentration is 10<sup>-4</sup>M, the concentration of hydrated form is 1.5 x 10<sup>-11</sup>, which represents far too small a loss of uranyl ion to be of any significance.

(3) Complexing of uranyl ion by nitrate: The data of Fig. 4 would indicate that no uranyl is being tied up as a non-extractable uranyl-nitrate complex.

(4) Dissociation of dibutyl phosphoric acid: Since it would seem probable that the uranyl species present is not the cause of the anomalous behavior noted, consideration was next given to the properties of the alkyl acid. Kumler and Eiler<sup>6</sup> report a value of 1.72 for the pK<sub>a</sub> of HBU<sub>2</sub>PO<sub>4</sub>, and this figure has been roughly confirmed by titrations and pH measurements made during the present work. The fact that the alkyl phosphoric acid is only a moderately strong one would mean that: (a) both BU<sub>2</sub>PO<sub>4</sub><sup>-</sup> and unionized HBU<sub>2</sub>PO<sub>4</sub> would be present at lower acidities, and (b) free hydrogen ion would be produced by the dissociation

of the complexing acid so the actual acid concentrations in the experiments of Fig. 5 would be higher than the nominal values. This latter effect would move the more left-hand points of the lower curves of Fig. 5 to the right, and the first effect would perhaps account for the tendency of the equilibrium reaction to assume a zero dependence on  $(H^+)$ :



Both of these effects would help explain the shape of the curves of Fig. 5 in a qualitative way, although they would not do so for the third power dependence on the  $HBu_2PO_4$  concentration as shown in Fig. 6. Also, calculation indicates that the amount of free hydrogen ion contributed by the dissociating acid is a small amount and inadequate to do much in straightening out the upper part of the curves of Fig. 5.

(5) Effect of acidity on alkyl phosphoric acid extraction: If the ionized form of the butyl phosphoric acid is non-extractable, the apparent distribution of the complexing agent into the organic phase should change as a function of the acidity. This was checked by equilibrating 0.707M  $HBu_2PO_4$  in dibutyl ether with aqueous phases containing varying amounts of nitric acid. Aliquots of each phase were titrated at this point, and the balance of the aqueous phase was then extracted with fresh dibutyl ether. Aliquots of these organic phases were then titrated. Blanks were also run, using dibutyl ether and the nitric acid solutions alone. These data permitted calculating the E value for the  $HBu_2PO_4$  in two different ways, first by taking the difference in the titre of the equilibrated aqueous phase and its  $HNO_3$  content as representing the  $HBu_2PO_4$  present, and secondly, by assuming that the second dibutyl ether phase contained substantially all of the  $HBu_2PO_4$  which had been left in the aqueous phase of the first equilibration. Both methods involved taking the differences between large

numbers, as well as the application of substantial blank corrections for  $\text{HNO}_3$  at the higher acidities. For this reason, the values shown in Fig. 7, where the distribution ratio of  $\text{HBu}_2\text{PO}_4$  is shown as a function of the original acid concentration in the aqueous phase, are only approximate. They do indicate that the hydrogen ion concentration has a definite effect on the amount of dibutyl phosphoric acid present in the aqueous phase. However, attempts to use this as an explanation for the low-acid uranium extractability behavior have been unsuccessful. At the present time, it would appear that such an explanation cannot be given. A curve showing the calculated percent ionization of  $\text{HBu}_2\text{PO}_4$  as a function of acidity is also included in Fig. 7.

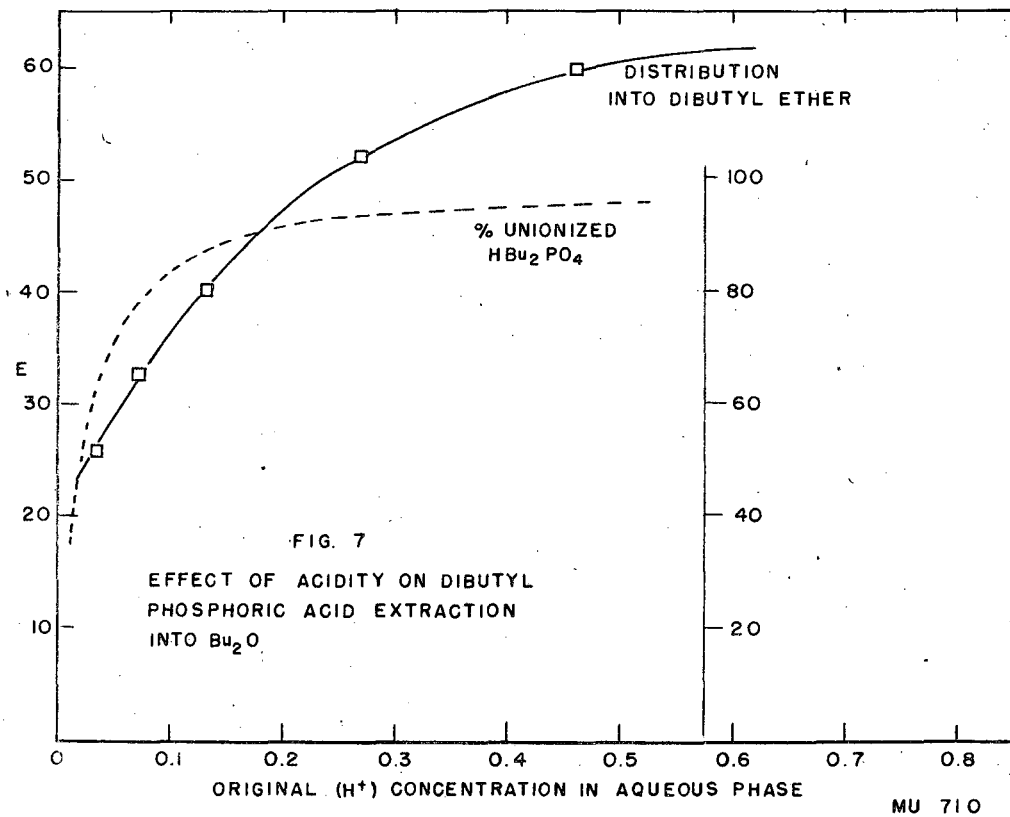
#### D. Stability of $\text{HBu}_2\text{PO}_4$

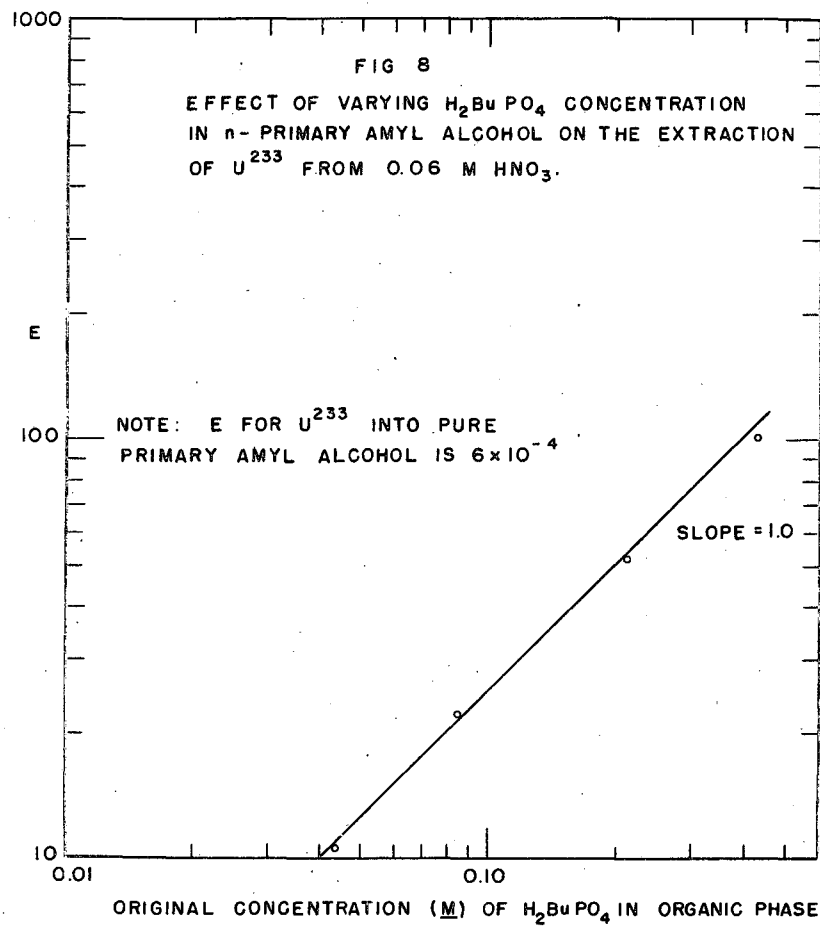
Samples of  $\text{HBu}_2\text{PO}_4$  in dibutyl ether were left in contact with 2.75M  $\text{HNO}_3$  solutions for varying periods. None showed any evidence of a second break in their titration curves upon being titrated, even after more than three months time.

#### E. Extraction by Monobutyl Phosphoric Acid

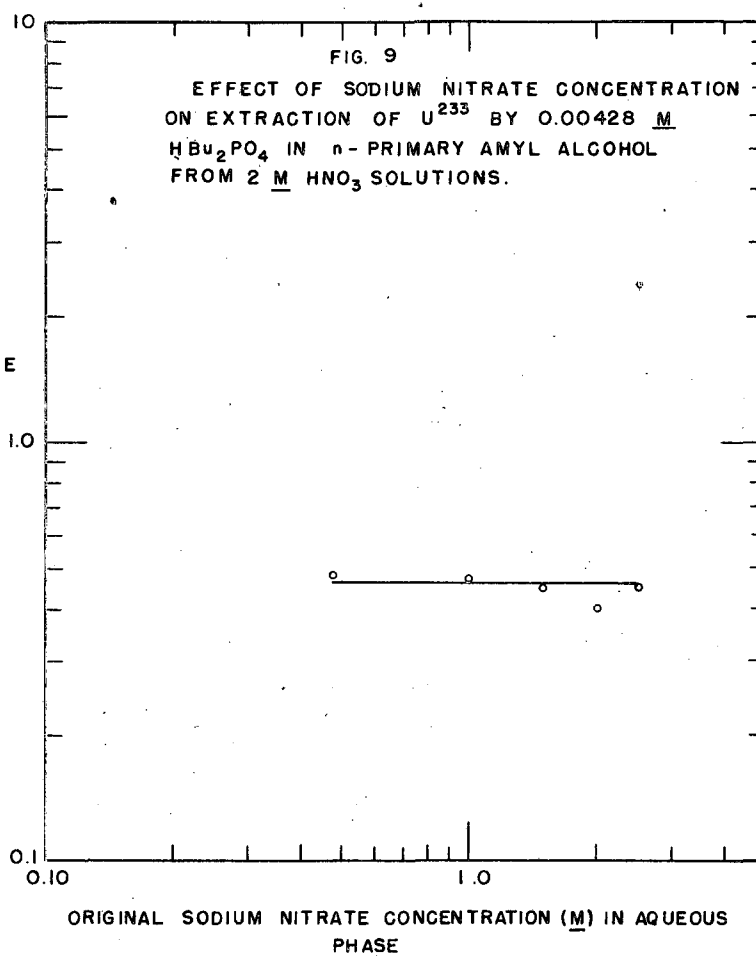
When monobutyl phosphoric acid ( $\text{H}_2\text{BuPO}_4$ ) was suspended in dibutyl ether or n-hexane, and the resulting solutions equilibrated with  $\text{U}^{233}$  tracer solutions, the extraction of uranyl ion was found to be essentially zero. However, when the "3 x  $\text{Bu}_2\text{O}$  washed" aqueous layer of Fig. 1 was treated with n-primary amyl alcohol, it was found that the resulting organic layer gave good extraction of  $\text{U}^{233}$ . Monobutyl phosphoric acid was the only one of the monoalkyl acids thus prepared, and only preliminary studies have been made on its reaction mechanisms with uranium.

Fig. 8 shows the effect of varying  $\text{H}_2\text{BuPO}_4$  in n-amyl alcohol on the extraction of  $\text{U}^{233}$  from 0.06M  $\text{HNO}_3$  solution. Fig. 9 indicates the nitrate ion





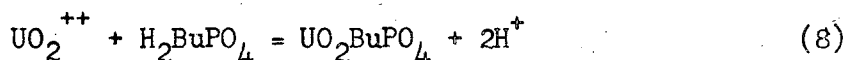
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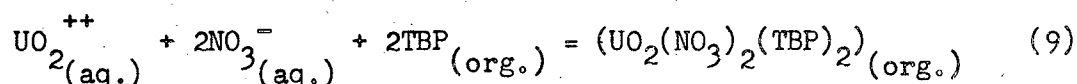
dependence of this system to be zero, as with the dibutyl form, and Fig. 10 gives the experimental results of tests for the hydrogen ion dependence. Again, the low acid behavior seems to be different from the picture when high acid solutions are used. In the latter case, it seems probable that the mechanism is simply:



The acid dependence data of Fig. 10, while admittedly incomplete, would seem to indicate that the full second power dependence on  $(\text{H}^+)$  is not arrived at until the initial  $\text{HNO}_3$  concentration is well past one molar.

#### F. Extraction by Tributyl Phosphate

Ellison, Ferguson, and Runion,<sup>2</sup> while studying the use of tributyl phosphate for recovering uranium from metal waste, concluded from their data that a solvent soluble complex formed and that it "--- apparently involves two moles of the solvent and apparently two moles of nitric acid per mole of uranium." Moore<sup>3</sup> studied the complex-forming reaction directly, using 20% tributyl phosphate ("TBP," " $\text{Bu}_3\text{PO}_4$ ") in  $\text{CCl}_4$ . He set the probable reaction as being:



$$K \approx 7.7 \text{ at } 25^\circ\text{C.}$$

Berkman<sup>4</sup> reported about the same time that two TBP molecules were involved per mole of uranium extracted, but had not completed his studies on the nitrate ion or nitric acid roles in the mechanism at the time of the report.

Figs. 11, 12, and 13 give the results of some tests which were made during the present study to determine the TBP, the hydrogen ion and nitrate ion dependence of the TBP-uranyl ion reaction mechanism. The methods used were those employed in the experiments already described, i.e., the distribution of tracer  $\text{U}^{233}$  was

FIG. 10  
ACID DEPENDENCE OF THE EXTRACTION OF  $U^{233}$  BY  $H_2BuPO_4$  IN  
n- PRIMARY AMYL ALCOHOL.

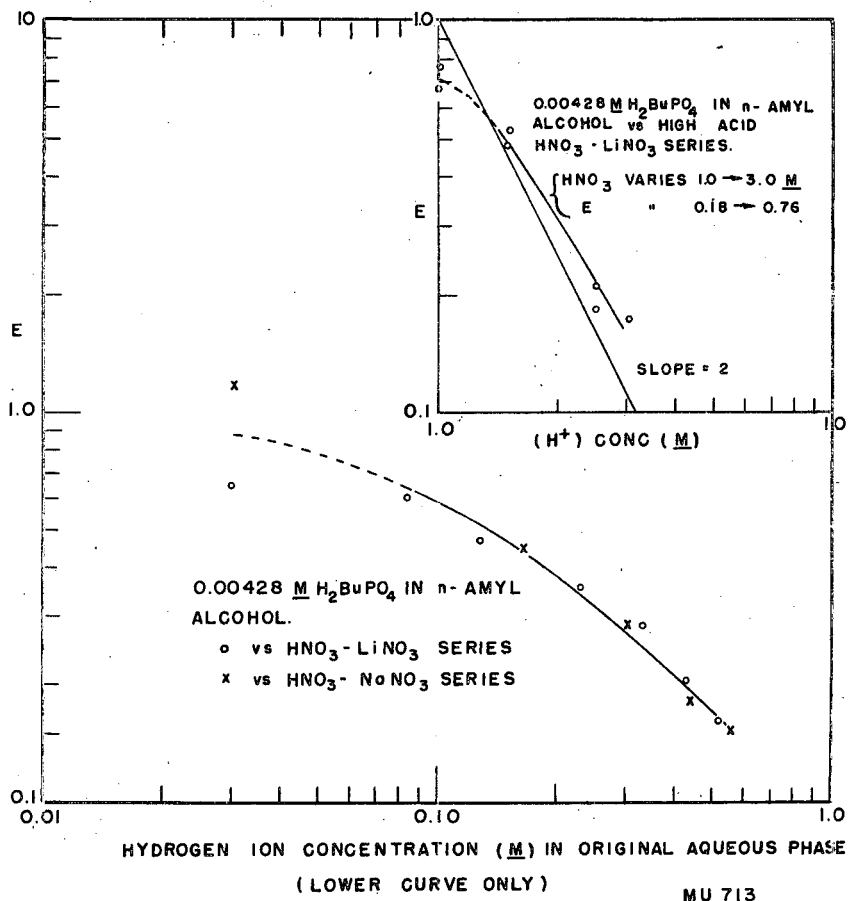
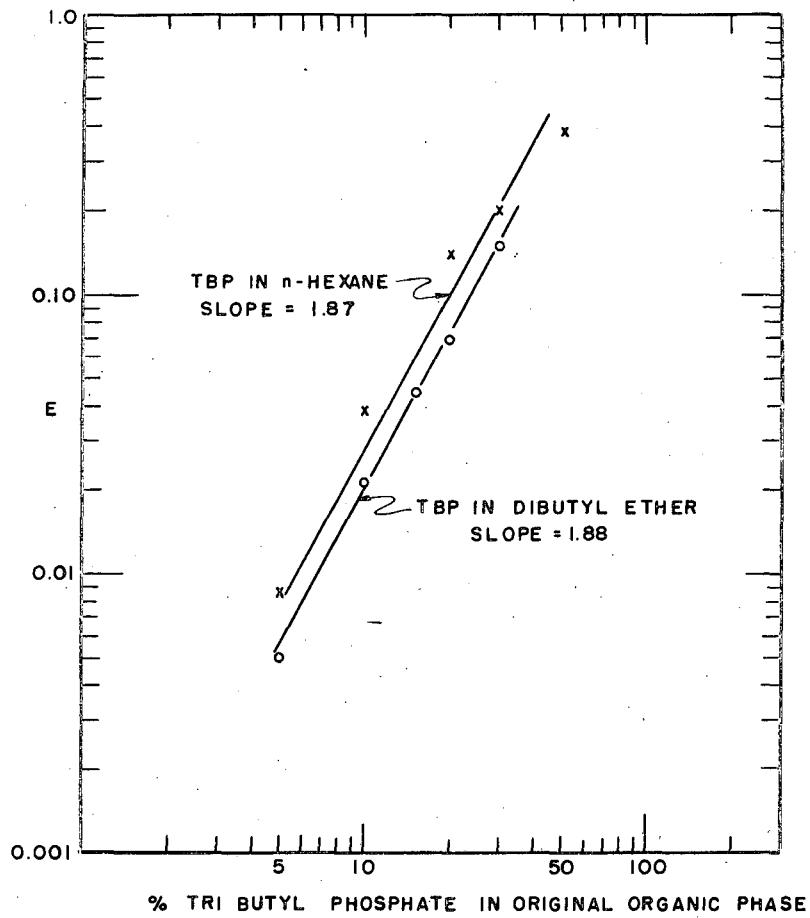


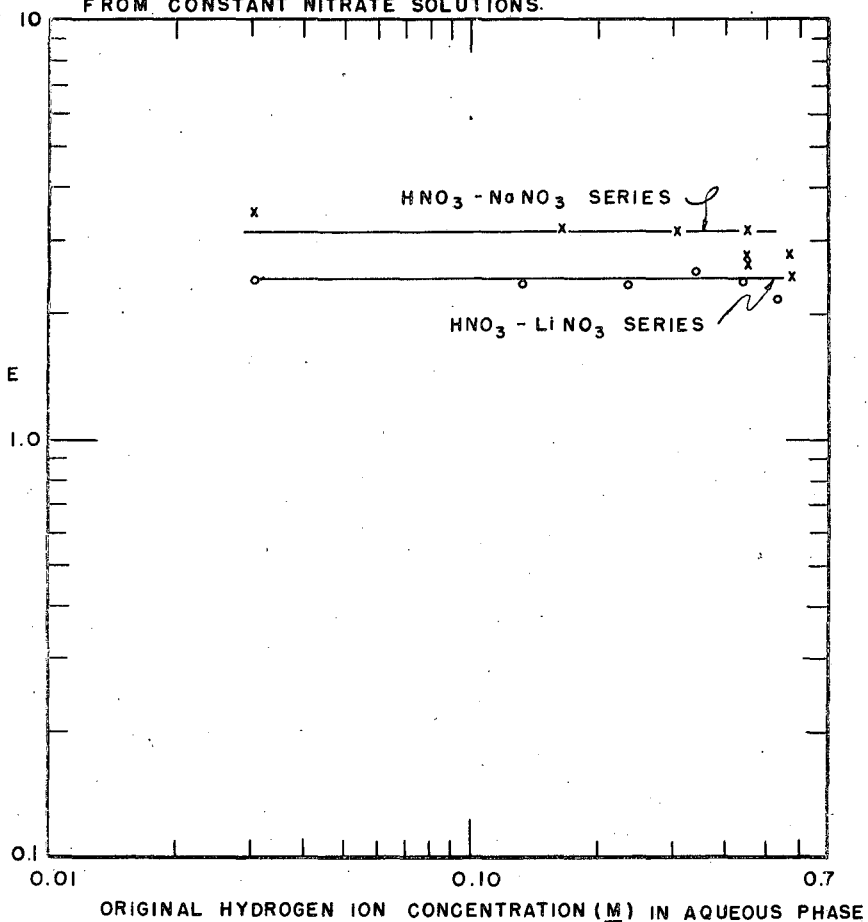
FIG. II  
EFFECT OF TRI BUTYL PHOSPHATE CONCENTRATION  
ON THE EXTRACTION OF  $U^{233}$  FROM 0.06 M  $HNO_3$



MU 714

FIG. 12

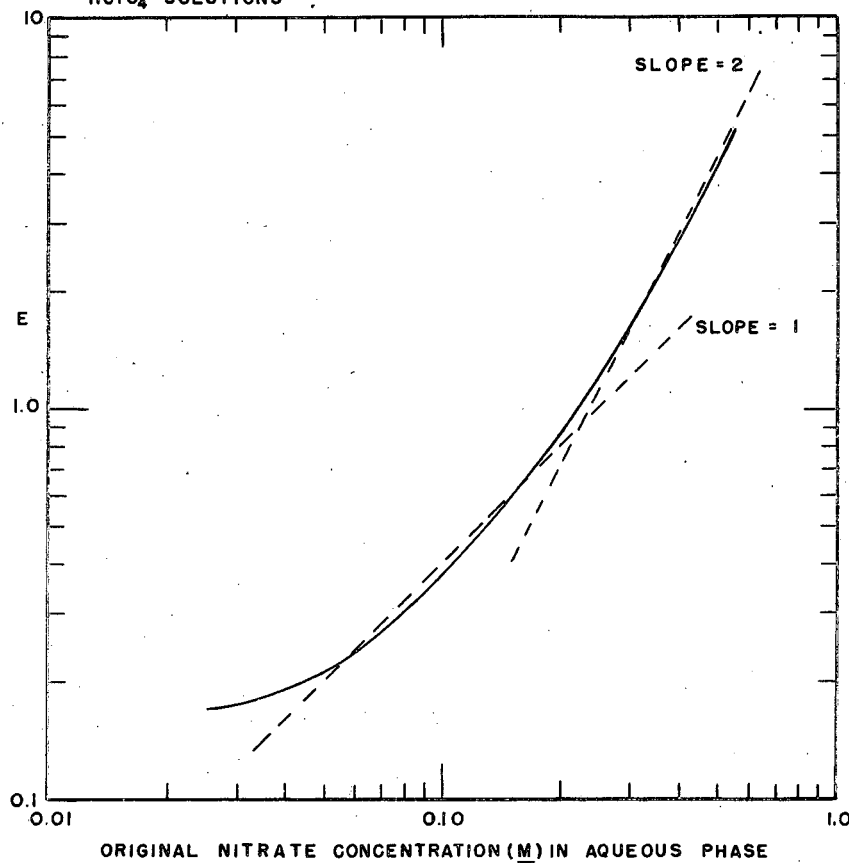
EFFECT OF HYDROGEN ION CONCENTRATION ON THE EXTRACTION OF  $U^{233}$  BY TRI-BUTYL PHOSPHATE IN n-HEXANE FROM CONSTANT NITRATE SOLUTIONS.



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FIG. 13  
EFFECT OF NITRATE CONCENTRATION ON EXTRACTION OF  $U^{233}$   
BY 20% TRI-BUTYL PHOSPHATE IN n-HEXANE FROM 0.05 M  
 $HClO_4$  SOLUTIONS



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determined in each case from a series of solutions in which one component only was being varied.

Some of the experimental points obtained show considerable scattering, but Figs. 11 and 12 would seem to corroborate the second order TBP and zero order hydrogen ion dependence indicated by Equation 10. The reaction with nitrate ion, however, may be partially a function of nitrate concentration, as is indicated in Fig. 13. In this experiment, a constant slope was not obtained when the distribution ratio for  $U^{233}$  was plotted against the molarity of nitrate present in a series of constant ionic strength,  $0.05M HClO_4$  solutions. Admittedly, the exact position drawn for the upper part of the curve is somewhat arbitrary but it would appear that the slope is approaching 2 at the higher nitrate concentrations as would be called for if Equation 10 is correct.

#### G. Effect of Anions on $U^{233}$ Extraction

Since uranium must often be recovered from solutions of an unknown nature, it was of interest to determine the effects of various anions on the extraction of uranyl ion by dibutyl phosphoric acid in dibutyl ether. A series of  $U^{233}$  tracer solutions containing known amounts of various anions was prepared, and the uranium distribution coefficients determined after the series was equilibrated with  $0.0094M HBu_2PO_4$  in dibutyl ether. The distribution coefficients found are given in Table V.

The low E values found for some of the systems would be of practical value if it was desired to recover uranium from an organic layer after it had been complexed by dibutyl phosphoric acid.

Table V

Effect of Anions on the Extraction of  $U^{233}$   
by  $H\text{Bu}_2\text{PO}_4$  in Dibutyl Ether

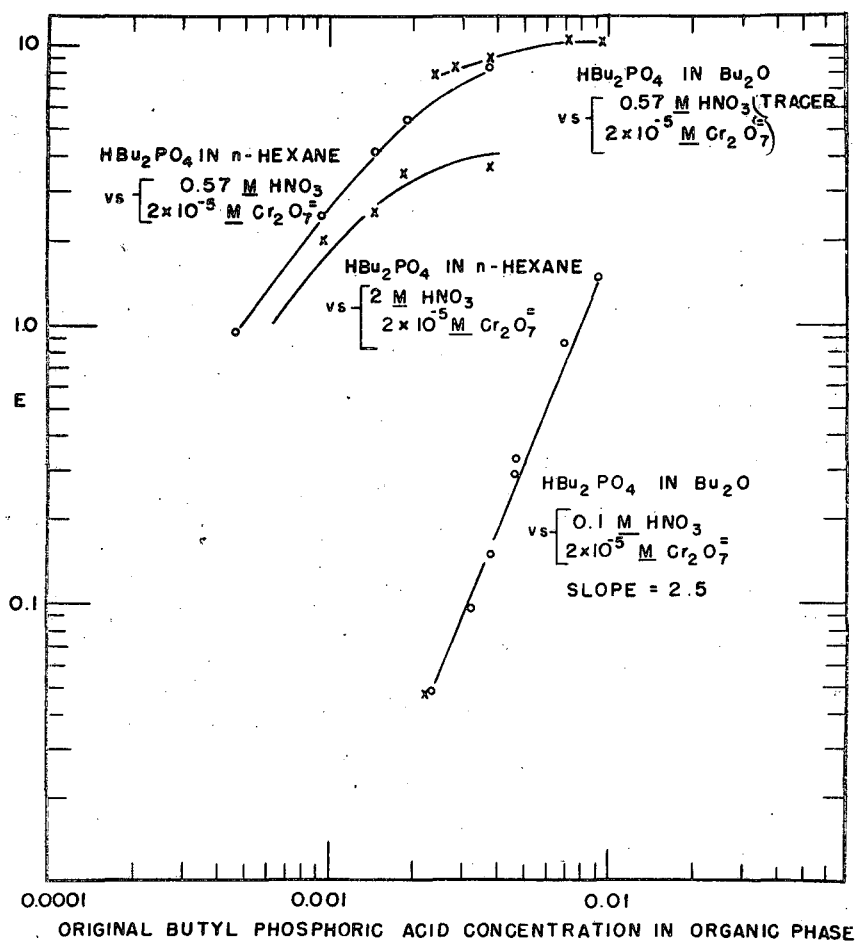
| Aqueous Layer  | Organic Layer   | (E)    |
|--|---|--------|
| 0.53M $\text{HNO}_3$                                 | 0.094M $H\text{Bu}_2\text{PO}_4$ in $\text{Bu}_2\text{O}$ | ~25.8  |
| 0.5M $\text{HAc}$<br>0.03M $\text{HNO}_3$            | "   | 23.6   |
| 0.5M $\text{HCl}$<br>0.03M $\text{HNO}_3$            | "   | 0.85   |
| 0.5N $\text{H}_2\text{SO}_4$<br>0.03M $\text{HNO}_3$ | "   | 0.42   |
| 0.5N $\text{H}_3\text{PO}_4$<br>0.03M $\text{HNO}_3$ | "   | 0.068  |
| 0.5M $\text{HF}$<br>0.03M $\text{HNO}_3$             | "   | 0.034  |
| 0.5N $\text{Na}_2\text{CO}_3$                        | "   | 0.0011 |

This table is rather a poor representation of anionic effect since the pH varies from 0.276 to greater than 7 in the various solutions. However, one may get a rough indication of the actual effect on E by calculating the pH from the acid dissociation constants and making a suitable correction to E.

#### H. Extraction of Plutonium

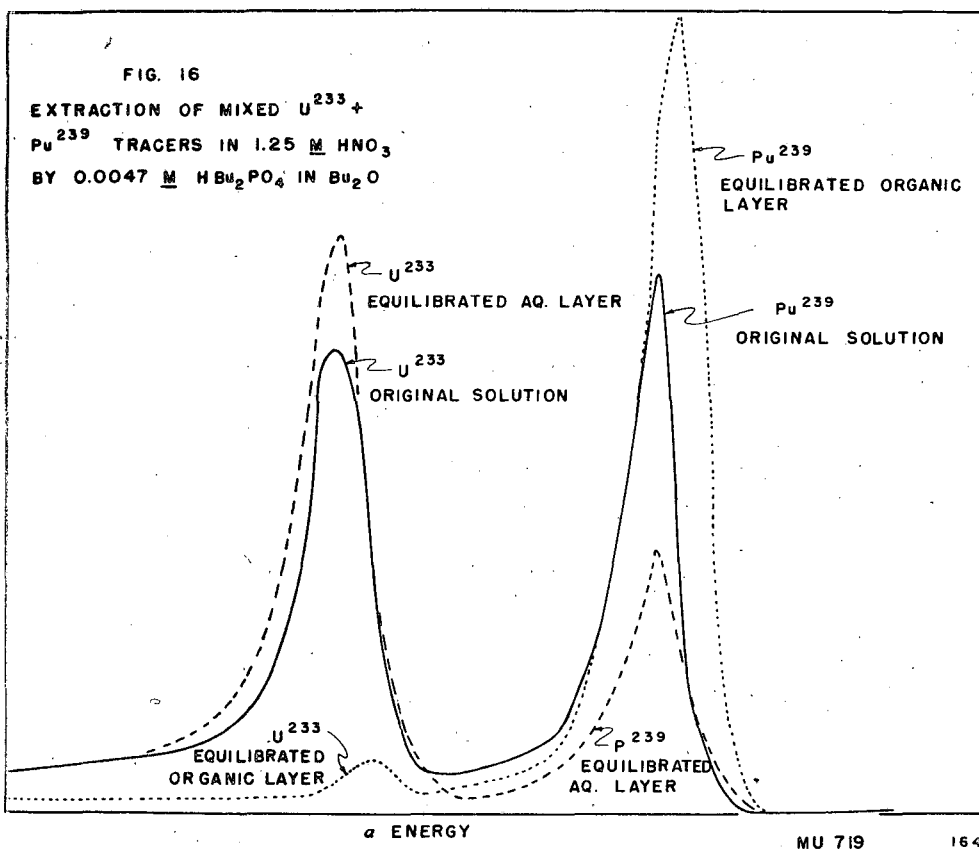
The results of some very preliminary experiments using Pu(IV) tracer are presented in Figs. 14 and 15. The former shows the effect of varying  $H\text{Bu}_2\text{PO}_4$  concentration on the extraction of plutonium, and the latter the effect of varying  $\text{H}_2\text{BuPO}_4$ . In the case of the dibutyl phosphoric acid, two different solvent carriers were used, each being tested with Pu(IV) tracer solutions of different  $\text{HNO}_3$  strength.

FIG. 14  
EXTRACTION OF Pu(IV) BY DIBUTYL PHOSPHORIC ACID



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#### IV. MISCELLANEOUS

A few qualitative tests were made to add to the general observations reported in UCRL-585. Dibutyl phosphoric acid in amyl alcohol will remove all of the color from the aqueous phase when it is equilibrated with an aqueous gold solution; and, does not produce a precipitate when used with a praseodymium solution. The mixed butyl phosphoric acids in 0.4% concentration in tertiary amyl alcohol gives an E value of about 2.3 for  $U^{233}$  out of 0.13M  $HNO_3$ . This is approximately the same value as was found, and previously reported, when benzene, n-hexane, dibutyl ether or n-amyl alcohol were used as the carriers.

#### REFERENCES

1. D. C. Stewart, University of California Radiation Laboratory report UCRL-585 (January 26, 1950).
2. C. V. Ellison, D. E. Ferguson, and T. C. Runion, Oak Ridge National Laboratory report ORNL-258 (September 20, 1949).
3. R. L. Moore, Hanford Works report HW-15230 (September 1, 1949).
4. M. G. Berkman, Argonne National Laboratory Report ANL-4372 (October, 1949).
5. J. Sutton, Canadian Research Council report CRC-325 (March 21, 1947).
6. W. D. Kumler and J. J. Eiler, J. Am. Chem. Soc. 65, 2355 (1943).

