CONFIDENTIAL

UCRL 585 Cy 76/A

C.2

DECLASSIFIED

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

BERKELEY, CALIFORNIA

UCRL-585 C.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA
Radiation Laboratory

Cover Sheet
Do not remove

INDEX NO. UCRL 585
This document contains 16 pages
This is copy 76 of 76 Series A

DECLASSIFIED

Issued to INFO. DIVISION

~~CONFIDENTIAL~~
Classification

Each person who receives this document must sign the cover sheet in the space below

Route to	Noted by	Date	Route to	Noted by	Date
	[illegible]	8-20-51			

CONFIDENTIAL

UCRL-585
Chemistry-Separation Processes
for Plutonium and Uranium

UNIVERSITY OF CALIFORNIA

DECLASSIFIED

Radiation Laboratory

Contract No. W-7405-eng-48

CLASSIFICATION CANCELLED
BY AUTHORITY OF THE DECLASSIFICATION
BRANCH USAEC per TID.1110
BY B. Forbell 2-15-56
SIGNATURE OF THE PERSON MAKING THE CHANGE DATE

ALKYL PHOSPHORIC ACIDS AS EXTRACTION AGENTS FOR URANIUM

D. C. Stewart

January 27, 1950

CAUTION

This document contains information affecting the National Defense of the United States. Its transmission or the disclosure of its contents in any manner to an unauthorized person is prohibited and may result in severe criminal penalties under applicable Federal laws.

Berkeley, California

Standard Distribution: Series A	Copy Numbers
Argonne National Laboratory	1-6
Armed Forces Special Weapons Project	7
Atomic Energy Commission, Washington	8-9
Brookhaven National Laboratory	10-13
Carbide and Carbon Chemicals Corporation (K-25)	14-19
Chicago Operations Office	20
General Electric Company, Richland	21-27
Hanford Operations Office	28
Idaho Operations Office	29-30
Iowa State College	31
Knolls Atomic Power Laboratory	32-35
Los Alamos	36-38
Mound Laboratory	39-41
New York Operations Office	42-45
Oak Ridge National Laboratory	46-57
Patent Branch, Washington	58
Technical Information Branch, ORE	59-73
University of California Radiation Laboratory	74-76
Total	76

INFORMATION DIVISION
Radiation Laboratory
Univ. of California
Berkeley, California

ALKYL PHOSPHORIC ACIDS AS EXTRACTION AGENTS FOR URANIUM

D. C. Stewart

DECLASSIFIED

INTRODUCTION

While studying the separation of zirconium and hafnium by means of tributyl phosphate extraction, D. B. Stewart and E. H. Huffman[1] observed that the amount of zirconium extracted increased somewhat with the length of time that the solvent was pretreated with acid. This suggested that the tributyl phosphate might be hydrolyzing, and that the products formed were more efficient extracting agents for zirconium than was the pure material itself. Eastmans' "n-butyl phosphoric acid" seemed to be the only such possible hydrolysis product commercially available, so some of it was obtained. It turned out to be a viscous oily liquid which was miscible with acid solutions in the proportions tested for the attempted zirconium extractions. These workers accordingly did nothing more along this line of investigation.

The recent interest in tributyl phosphate[2,3,4,5] as an extracting solvent for uranium indicated that consideration of n-butyl phosphoric acid for this application might be of interest if some way could be devised to overcome the manipulation and miscibility difficulties. It was found that if the material was placed in any one of a number of carrier solvents, it had a remarkably strong extractive effect on uranyl ion out

---

[1] D. B. Stewart and E. H. Huffman, personal communication.

[2] C. V. Ellison, D. E. Ferguson, and T. C. Runion, ORNL-258, (June 20, 1949).

[3] D. E. Ferguson and T. C. Runion, ORNL-260, (October 7, 1949).

[4] S. Vogler and R. Hildebrandt, ANL-4329.

[5] S. Vogler, H. Tyler, M. G. Berkman, and L. E. Ross, ANL-4372.

of acid solutions without a salting agent present. The effectiveness of the material suggested a study of other alkyl phosphoric acids, so the ethyl and n-propyl products were obtained. Both of these also proved to be good uranyl ion extractants. This preliminary report deals with some of the more qualitative aspects of the use of this group of substances for this purpose.

URANIUM EXTRACTION

Table I gives two sets of distribution coefficients for the extraction of U^{233} labeled uranium out of nitric acid solutions. The solvent layers consist respectively of 2 vols. percent and 20 vols. percent n-butyl phosphoric acid in technical grade dibutyl ether. These coefficients were calculated from data obtained by plating and counting aliquots from each phase after 30 minute equilibration of equal volumes of aqueous phase and solvent in Teflon tubes. The equilibration was done in a water bath at 25°C on a mixing wheel of the type described by Cunningham.[6]

The values given for extraction into the 20 percent n-butyl phosphoric acid solvent are only approximations. With this concentration present in the original solvent layer, the uranium removal is so complete as to make an accurate estimate of the amount of activity left in the aqueous layer very difficult. The appearance of this series of equilibrated samples is quite striking, with all of the uranium color going into the organic phase, leaving the aqueous phase water-white.

---

[6] B. B. Cunningham, Nucleonics, (November, 1949), p. 62.

TABLE I

Extraction of U^{233} Labeled Uranyl Ion by n-butyl Phosphoric Acid (n-BPA) in Dibutyl-ether

Original Composition Aqueous Phase		Distribution Coefficient (org/aq)	
Uranium	HNO_3	2% n-BPA	20% n-BPA*
0.01M	0.34M	4.4	73?
0.023	0.34M	3.0	60
0.05	0.34M	1.5	56
0.10	0.34M	0.73	54
0.26	0.34M	--	41
0.10	1.0	0.49	--
0.10	2.0	0.44	--
0.10	4.0	0.59	--

*Approximations only - see text.

THE ALKYL PHOSPHORIC ACIDS

Data will be presented in this section to show that the alkyl phosphoric acids as obtained commercially are actually mixtures. Since all of the tests described in the present report were made with the unfractionated materials, the results must be interpreted with this in mind, and consideration of the probable composition of the commercial products is worthwhile before presenting further data.

All three of the alkyl phosphoric acids on hand are heavy oily liquids, with the color ranging from nearly white for the ethyl, to a brown for the n-propyl and to a darker brown for the n-butyl form. Aliquots of each have been potentiometrically titrated with standard base, using a glass electrode with the Type G Beckman pH meter. An aliquot of reagent

grade phosphoric acid has been similarly titrated for comparison. These titration curves are shown in Figure 1.

Cherbuliez and Weniger[7] have studied the reaction of phosphoric anhydride with aliphatic alcohols. When the simpler alcohols are used, they comment that very little H_3PO_4, almost no R_3PO_4, and H_2RPO_4 and HR_2PO_4 in a close ratio of 1:1 are formed. If it is assumed that this is the method used in preparing the commercial products titrated for Figure 1, the H_2RPO_4 and HR_2PO_4 concentrations can be calculated if it is also assumed that no H_3PO_4 is present. This has been done, and the values are given in Table II. It will be seen that the 1:1 ratio holds fairly well for ethyl phosphoric acid, but starts to increase as the size of the alkyl substituent increases.

TABLE II

Calculations from Titration Curves of Figure 1

Acid Used	ml 0.1212M Base First Break	Second Break	Corresponding Concentrations H_2RPO_4	HR_2PO_4	H_2RPO_4/HR_2PO_4
Ethyl phosphoric	14.9	22.6	4.66M	4.36M	1.06
n-propyl phosphoric	12.4	19.6	4.36	3.15	1.38
n-butyl phosphoric	10.4	16.7	3.82	2.48	1.54

Dr. H. W. Crandall has pointed out that the extraction of uranium is probably effected by the formation of a solvent-soluble uranyl-alkyl phosphate complex. All of the studies made to date support this view, but it is still not certain as to whether the reaction mechanisms involve the H_2BuPO_4, the HBu_2PO_4 form or both. Definite information on this point

[7] E. Cherbuliez and H. Weniger, Helv. Chim. Acta., 28, 1584 (1945).

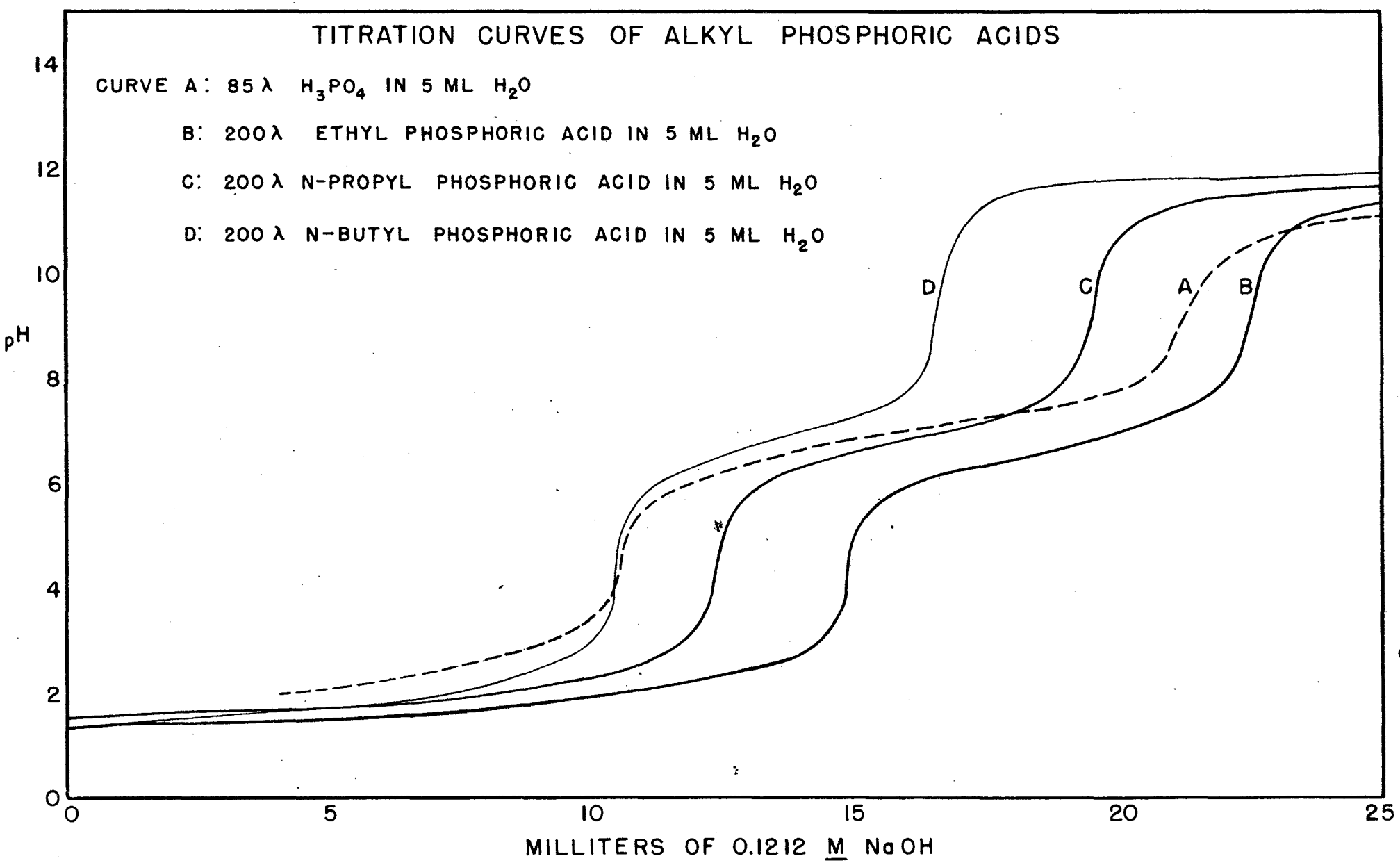
TITRATION CURVES OF ALKYL PHOSPHORIC ACIDS
CURVE A: 85 λ H_3PO_4 IN 5 ML H_2O
B: 200 λ ETHYL PHOSPHORIC ACID IN 5 ML H_2O
C: 200 λ N-PROPYL PHOSPHORIC ACID IN 5 ML H_2O
D: 200 λ N-BUTYL PHOSPHORIC ACID IN 5 ML H_2O
pH
0
2
4
6
8
10
12
14
0
5
10
15
20
25
MILLITERS OF 0.1212 M NaOH
A
B
C
D

FIG. 1

must wait until the two acids have been satisfactorily fractionated. Considerable progress has been made in this direction, and the preliminary indications are that the HBu_2PO_4 is almost entirely responsible for the extraction. Work is under way on the detailed determination of the net reaction or reactions, and will be presented in collaboration with Dr. Crandall in a subsequent report.

A second series of titrations has been made and is of some interest in this regard. Aliquots were taken from the aqueous phases after equilibrating various water solutions with 20 percent n-butyl phosphoric acid in dibutyl ether. These aliquots were titrated with standard base as before, and the curves are shown in Figure 2. Since it is known that the n-butyl phosphoric acid is a mixture, it is not possible to draw any very positive conclusions from these curves. However, if it is again assumed that H_2BuPO_4 and HBu_2PO_4 are the only titratable species present, and if it is also assumed that the volume changes of the two phases are negligible, the data shown in Table III can be calculated. These are of interest with respect to two main points. The first is that it appears to be quite possible to fractionate the H_2BuPO_4 and HBu_2PO_4 by solvent extracting the latter away from the former, and secondly, that, within the limitations of the data, it would appear that one hydrogen ion appears in the aqueous phase for each uranium going into the organic layer. This is a very tentative conclusion and may be modified by further studies with the fractionated acids.

The solvent extraction method for separating the two acids has been investigated further, and a material giving only one break in the titration curve (HBu_2PO_4) has been prepared. Its behavior will be described in the later report.

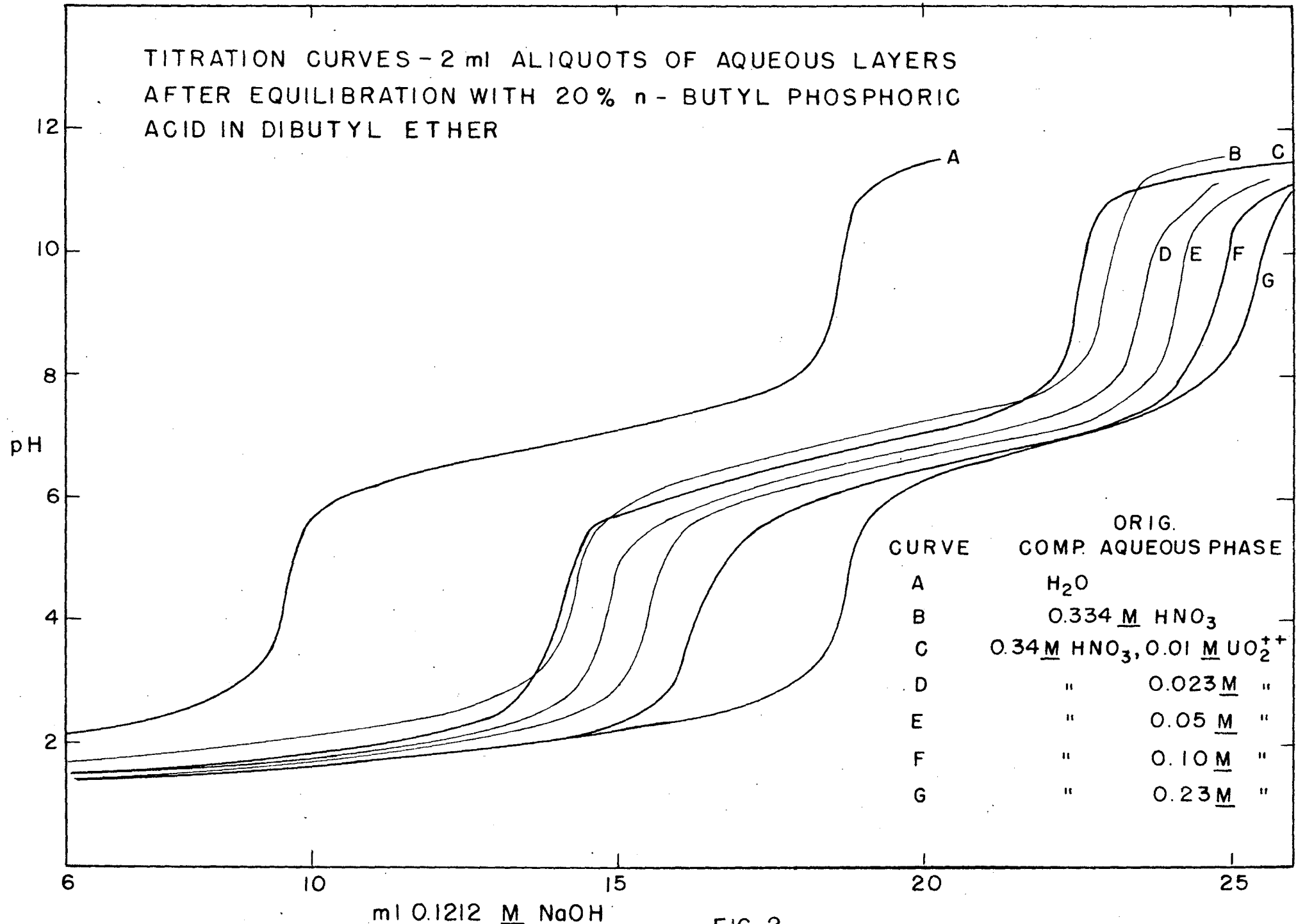
TITRATION CURVES - 2 ml ALIQUOTS OF AQUEOUS LAYERS AFTER EQUILIBRATION WITH 20% n - BUTYL PHOSPHORIC ACID IN DIBUTYL ETHER
pH
12
10
8
6
4
2
6
10
15
20
25
ml 0.1212 M NaOH
A
B
C
D
E
F
G
CURVE
ORIG. COMP. AQUEOUS PHASE
A H_2O
B 0.334 M HNO_3
C 0.34 M HNO_3, 0.01 M UO_2^{++}
D " 0.023 M "
E " 0.05 M "
F " 0.10 M "
G " 0.23 M "

FIG. 2

14570-1

TABLE III

Calculated Values from Titration Curves of Figure 2

Orig. Comp. of Aq. Phase	Equilibrium Concentrations H_2BuPO_4 Aq.	H_2BuPO_4 Org.	HBu_2PO_4 Aq.	HBu_2PO_4 Org.	(H^+) Increase in Aq. Phase
Water	0.601M	0.163M	0.024M	0.472M	--
0.334M HNO_3	0.571	0.193	0.000	0.496	--
0.34M HNO_3, 0.01M UO_2^{++}	0.50	--	--	--	--
0.34M HNO_3, 0.023	0.528	--	--	--	0.018M
0.34M HNO_3, 0.05	0.520	--	--	--	0.06
0.34M HNO_3, 0.10	0.510	--	--	--	0.115
0.34M HNO_3, 0.23	0.405	--	--	--	0.25

EFFECT OF SOLVENT AND OF TYPE OF ACID

If the uranium extraction depends on the formation of a solvent-soluble complex, it would be expected that the type of organic liquid used as a carrier for the n-butyl phosphoric acid would be of importance when macro amounts of the complex are present to be dissolved. If n-hexane is used as the carrier, it is found that only a small amount of the acid itself will dissolve, and that even this low concentration causes precipitation of uranium. With 20 percent n-butyl phosphoric acid in dibutyl ether, a precipitate forms if the original uranium concentration is above about 0.1M. Below 0.25M uranium, however, this precipitate redissolves to give the characteristic intensely yellow organic layer. On the other hand, when primary n-amyl alcohol is the carrier solvent with the same concentration of n-butyl phosphoric acid, the mixture may be used with saturated

uranium solutions without the formation of precipitates.

The behavior of tracer amounts of U^{233} is less solvent-dependent, although, even here, there is an effect as can be seen in Table IV. The various solvents shown were employed with 0.4 vols. percent concentration of n-butyl phosphoric acid and were equilibrated with equal volumes of U^{233} tracer in 0.127M HNO_3.

TABLE IV

Effect of Various Carrier Solvents on the Extraction of Uranium by 0.4 Vols.% n-butyl Phosphoric Acid

Solvent	Observed Equil. Coefficients	Average E Value
Benzene (Reagent)	2.83 2.12 2.43	2.5
n-Hexane (Tech.)	2.33 2.42 2.66 3.15 2.75	2.7
Dibutyl Ether (Tech.)	2.19 2.72 2.50	2.5
Methyl Isobutyl Ketone (Tech.)	0.750 0.723 0.771 0.861	0.78
Primary n-amyl alcohol (Reagent)	2.45 2.37 2.01	2.3

Table V shows the extraction of U^{233} from the same acid solution by 0.4 vols. percent of the three different alkyl phosphoric acids on hand. Primary n-amyl alcohol was used as the carrier in each case for this series. It is quite apparent that the affinity of the solvent for the final complex

increases with the size of the alkyl substituent, or, stated in another way, the smaller molecules tend to be relatively more water soluble.

It is quite probable that the precipitation behavior of macro amounts of uranium will be quite different from that described above when pure H_2BuPO_4 or HBu_2PO_4 is used as the extracting agent.

TABLE V

Effect of the Type of Phosphoric Acid at 0.4 Vols.% Concentration in Primary n-amyl Alcohol on the Extraction of Uranium

Acid	Observed Equil. Coefficients	Average E Value
n-butyl phosphoric (Tech.)	2.45 2.37 2.01	2.3
n-propyl phosphoric (Tech.)	0.450 0.460	0.45
ethyl phosphoric (Tech.)	0.035 0.035	0.035

BEHAVIOR OF OTHER CATIONS

A brief survey was made of the behavior of 20 vols. percent n-butyl phosphoric acid in dibutyl ether towards solutions of cations other than uranium. These qualitative observations are summarized in Table VI. The first group of solutions was prepared by dissolving weighed amounts of the nitrate salts to a cation concentration of 0.1M. The mixed solvent was also tested against a number of solutions prepared by R. H. Goeckermann for bombardment work. It is believed that the most of these are also nitrate solutions.

TABLE VI

Qualitative Behavior of Cation Solutions Towards 20% n-butyl Phosphoric Acid in Dibutyl Ether

Salt	Approximate Concentration	Observed Behavior
$Ca(NO_3)_2$	0.1M	No change
$Co(NO_3)_2$	0.1M	No change
$Cu(NO_3)_2$	0.1M	No change
$Mn(NO_3)_2$	0.1M	No change
$Zn(NO_3)_2$	0.1M	No change
$Pb(NO_3)_2$	0.1M	Moderately heavy white ppt in solvent layer
$Al(NO_3)_3$	0.1M	Light white ppt in both layers
$Fe(NO_3)_3$	0.1M	Immediate heavy white precipitate
$Cr(NO_3)_3$	0.1M	No change
$La(NO_3)_3$	0.1M	No change. Light ppt when 2 drops Ce(III) added
$Ce(NO_3)_3$	0.1M	White ppt in solvent layer
$Pr(NO_3)_3$	10 g/l	Precipitate in organic layer
$Th(NO_3)_4$	0.1M	Immediate heavy white precipitate
"Mixed nitrates" + UO_2^{++} (Centrifuged)	--	Colorless aqueous, yellow organic layers. White ppt at interface
$CsNO_3$	10 g/l	No change
$Cd(NO_3)_2$	10 g/l	No change
$Pd(NO_3)_2$	10 g/l	No change
OsO_4 Soln.	10 g/l	No change
As (?)	10 g/l	No change

TABLE VI (Cont.)

Salt	Approximate Concentration	Observed Behavior
Au (?)	?	Both layers equally yellow. No ppt.
Mo (?)	10 g/l	Tan color in organic, colorless aqueous layer
Cb (?)	10 g/l	Heavy white ppt in aqueous layer
$Bi(NO_3)_3$	10 g/l	White ppt, both phases
Cr (as Cr_2O_7?)	10 g/l	Green organic layer
$CoCl_2$ in HCl	--	No change
$UO_2(ClO_4)_2$	0.075M	Yellow organic, colorless aqueous layer
$FeCl_3$ in HCl	--	Heavy white ppt.
UO_2^{++} in 1-4M HNO_3	0.5M	No ppt - very little color in organic layer
$PmCl_3$ tracer in 0.3M HCl	--	Essentially no counts extracted by 1% n-BPA in Bu_2O

The "mixed nitrate" stock referred to in the table was prepared by mixing equal volumes of the following 0.1M nitrate solutions: Cu(II), Pb(II), Zn(II), Co(II), Ca(II), Mn(II), La(III), Ce(III), Cr(III), Al(III), Fe(III), and Th(IV).

It will be seen from the table that the univalent and most of the divalent cations did not form precipitates, whereas, in general, the trivalent and quadrivalent ions did. An interesting exception to this behavior was lanthanum, in view of the fact that precipitates did form with the other rare earths (cerium and praseodynium) studied on a macro scale. The solvent had very little extractive power for prometheum tracer as shown.

A preliminary experiment was made to study the possibilities of uranium recovery and purification by means of the solvent. A volume of U^{233} labeled 0.1M uranyl nitrate solution was mixed with an equal volume of the "mixed nitrate" stock previously described. This aqueous solution was then extracted with one volume of 20 percent n-butyl phosphoric acid in dibutyl ether. The uranium was recovered from the organic layer with 30 percent sodium carbonate solution. This alkaline solution was neutralized with HCl, but a small amount of organic phase reformed, carrying the uranium as a suspended precipitate. This was not destroyed by heating with acid, but was broken up by treatment with 40 percent NaOH. The precipitate thus formed was centrifuged out, washed twice with water, and dissolved up in 1 percent HCl. Samples were taken for alpha-count assay and for spectrographic analysis. The uranium recovery was 100 percent (within the counting error) and the spectrographic analysis showed good separation from most of the cations originally present (Table VII).[8]

A small amount of "Hanford dissolver" (pile-irradiated) uranium solution was available, and a cursory check was also made of its behavior towards the 20 percent n-butyl phosphoric acid in dibutyl ether mixture. The dissolver solution was diluted by a factor of two, after adding enough HNO_3 to make the final acidity 0.34M. It was then heated with $KBrO_3$ to convert the plutonium present to the plutonyl form. After cooling, the solution was contacted with an equal volume of the solvent. About 96 percent of the alpha-activity and one-half of the Geiger activity was removed. Subsequent washing of this organic layer with an equal volume of water removed essentially none of the activity, either alpha or Geiger.

---

[8] M. Moore and J. Conway, personal communication, plate 456.

TABLE VII

Spectrographic Analysis of Purified Uranium

Species	γ with 48 γ U	Approximate U Decontamination
Al	0.05	10
Fe	0.1	10
Ca	<0.01	>60
Th	<0.1	>40
Ce, Co, Cr, La, Mn, Pb, Zn	not detected	--
Cu	Could not determine	--

It should be emphasized that all of the qualitative observations made above might be quite different with different carrier solvents, concentrations, pH conditions, etc. Above all, it seems quite probable that the use of pure HBu_2PO_4 as compared to the commercial acid mixture would change the precipitation behavior quite radically. This might well be particularly true if the latter contains free phosphoric acid as well as the mono and dialkyl forms.

CONCLUSION

The alkyl phosphoric acids can be used as extractants for uranium from non-salted solutions if an appropriate organic solvent is used as a carrier. Some of the more general properties of these acids as commercially prepared have been presented, as well as preliminary observations of their behavior towards uranium and other cations.

January 27, 1950

CONFIDENTIAL

CONFIDENTIAL

DECLASSIFIED

CONFIDENTIAL