DP - 250

CHEMISTRY - SEPARATION PROCESSES
FOR PLUTONIUM AND URANIUM
(TID-4500, 13th Ed., Suppl.)

THE FORMATION AND EFFECTS OF DIBUTYL PHOSPHATE IN SOLVENT EXTRACTION

by

E. Kenneth Dukes
Separations Chemistry Division

November 1957

E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

Printed for
The United States Atomic Energy Commission
Contract AT(07-2)-1

DISCLAIMER

ABSTRACT

Data are presented for the rates of formation of di-n-butyl phosphate (DBP) from tri-n-butyl phosphate. The effects of DBP on the extraction of zirconium from nitric acid and uranyl nitrate are reported.

CONTENTS

LIST OF FIGURES

THE FORMATION AND EFFECTS OF DIBUTYL PHOSPHATE IN SOLVENT EXTRACTION

INTRODUCTION

It is well known that tributyl phosphate (TBP) undergoes degradation when it is exposed to acids, heat, or radiation. One of the principal products of this degradation is dibutyl phosphate (DBP). This product is a powerful extractant for zirconium; its presence makes the separation of zirconium from other elements more difficult.

The primary objective of this investigation was to obtain quantitative data on the effect of DBP on the extraction of zirconium. It was also desirable to know the rates of formation of DBP in nitric acid and nitric acid - uranyl nitrate systems where the extraction of zirconium could be affected by the presence of DBP. No data were available on rates of formation of DBP in uranyl nitrate - nitric acid systems, and conflicts in the data on nitric acid systems needed to be resolved.

SUMMARY

The extraction of zirconium from solutions of nitric acid into a solution of 30% TBP in dodecane increased greatly when DBP was added. Twenty times as much zirconium was extracted from 3.0M nitric acid at 70°C when 0.10% DBP was present as when no DBP was present.

Uranyl nitrate suppressed significantly the extraction of zirconium by DBP. For example, the quantity of zirconium that was extracted from a solution of 0.47M uranyl nitrate and 3.16M nitric acid was a factor of 15 less than that extracted from 3.0M nitric acid alone.

Exposures of solutions of 30% TBP to nitric acid and uranyl nitrate showed that rates of formation of DBP depended on temperature as well as on the concentration of nitric acid and uranyl nitrate. Greater rates were obtained when the aqueous phase was in contact with the organic phase throughout the period of exposure than were obtained when the aqueous phase was present for only a short time.

Two analytical methods were used to determine the concentration of DBP. In one method, changes in the extraction of zirconium depended on the amount of DBP present. The other procedure made use of the changes in the extraction of uranium-233 caused by the DBP. These methods agreed within ten per cent.

DISCUSSION

COMPARISON WITH OTHER WORK

Rates of formation of DBP from the present work were compared with rates that are reported in the literature. The comparison covered rates of formation of DBP in solutions of TBP that were exposed to nitric acid at temperatures between 25 and 70°C. The concentration of the acid ranged from one to five molar.

In general the values obtained from this investigation are lower than most of the values in the literature. However, these results are in close agreement with results reported by J. Kennedy and S. S. Grimley(1) in which the rates of formation were obtained with 20% TBP in odorless kerosene. These data were extrapolated to 30% TBP and are compared in the following table with those for 30% TBP in n-dodecane. The values below were obtained from experiments in which the organic and aqueous phases were mixed continuously.

EFFECT OF TEMPERATURE AND ACID CONCENTRATION ON FORMATION
(Comparison with Published Data)
DBP per day, %

Temperature, °C	1.0M HNO_3 Present Work	1.0M HNO_3 Kennedy and Grimley	5.0M HNO_3 Present Work	5.0M HNO_3 Kennedy and Grimley
26	0.0003	0.0003	0.0003	0.0005
40	0.0016	0.0014	0.0016	0.0056
70	0.051	0.024	0.090	0.075

EXPERIMENTAL WORK

Formation and Analysis of DBP

DBP was produced experimentally by exposing 30% TBP in dodecane to various aqueous solutions at several temperatures. Two types of exposure were made simultaneously. In one case, equal volumes of an aqueous solution and of a solution of 30% TBP in dodecane were mixed continuously. In the other case, the phases were mixed at the desired temperature, the aqueous phase was discarded, and the organic phase was allowed to stand alone without mixing.

The organic phases were sampled at regular intervals and analyzed for DBP by the U-233 method. A suitable analytical method was not available; therefore such a method was developed and was the principal method used in this work. It is described in detail in Appendix A. The aqueous phase was not analyzed since it contained nitric acid, and DBP was found to extract quantitatively from nitric acid into a solution of 30% TBP in dodecane.

The amount of DBP present in dual-phase exposures was also determined by the use of zirconium tracer. This was done by adding zirconium-95 to the aqueous phase at the beginning of the exposure. The extraction of zirconium was directly related to the amount of DBP present. This analysis was used only when alpha activity could not be counted accurately. The details of this method are given in Appendix B.

Effect of Temperature

The rates of formation of DBP were increased greatly by increases in the temperature of exposure. The following table shows that rates increased by a factor of about five when the temperature was raised from 25 to 40°C. An increase in temperature from 40 to 70°C increased the rate of formation of DBP by a factor of about 25. An exposure of 56 days at 25°C and 21 days at 40°C was required to produce a detectable amount of DBP. Similar results were obtained when the solution of TBP contained either nitric acid or uranyl nitrate and nitric acid. The results shown in the following tables are for exposures of the organic phase alone.

EFFECT OF TEMPERATURE AT VARIOUS CONCENTRATIONS OF NITRIC ACID

Nitric Acid in the Organic Phase, M	DBP Formed in 24 Hours, %		
	25°C	40°C	70°C
0.2	0.0002	0.0010	0.033
0.4	0.0003	0.0017	0.043
0.6	0.0003	0.0015	0.048
0.8	0.0003	0.0015	0.051

EFFECT OF TEMPERATURE AT VARIOUS CONCENTRATIONS OF URANYL NITRATE AND NITRIC ACID

Uranium in the Organic Phase, M	HNO_3 in the Organic Phase, M	DBP Formed in 24 hours, %	
		40°C	70°C
0.357	0.135	0.0014	0.040
0.436	0.110	0.0013	0.024
0.468	0.008	0.0022	0.035
0.029	0.004	0.0010	-----

Effect of Concentration of Nitric Acid

The effect of the concentration of nitric acid on rates of formation of DBP in solutions of 30% TBP was determined at 70°C because long periods of exposure were required at lower temperatures. The results are given in the table below. Rates of formation were proportional to the one-fourth power of the acid concentration.

EFFECT OF CONCENTRATION OF NITRIC ACID

Type of Exposure	Nitric Acid, M		DBP Formed (days), %					
	Organic	Aqueous	1	2	3	4	5	6
Mixed	0.17	1.03	0.053	0.076	0.113	0.149	0.189	0.245
Solvent Alone	0.17	-	0.033	0.065	0.078	0.090	0.110	0.130
Mixed	0.62	2.97	0.063	0.163	0.200	0.293	0.370	0.459
Alone	0.62	-	0.048	0.108	0.163	0.210	0.270	0.295
Mixed	0.86	4.23	0.090	0.163	0.241	0.288	0.360	0.426
Alone	0.86	-	0.051	0.125	0.168	0.245	0.280	0.340

Effect of Concentration of Uranyl Nitrate and Nitric Acid

The combined effects of uranyl nitrate and nitric acid on the rate of formation of DBP were somewhat unusual. The concentration of uranyl nitrate was not important as long as the concentration of nitric acid was high. However, the rate of formation of DBP depended on the concentration of uranyl nitrate in the presence of low concentrations of nitric acid. Two instances of this effect are shown in the table below. High concentrations of uranyl nitrate did not increase the rates appreciably over the rates that were observed in the presence of nitric acid; therefore, experiments with low concentrations of uranyl nitrate were not necessary.

EFFECT OF CONCENTRATION OF URANYL NITRITE AND NITRIC ACID AT 70°C

Nitric Acid, M		Uranyl Nitrate, M		DBP per day, %	
Organic	Aqueous	Organic	Aqueous	Mixed	Solvent Alone
0.006	0.28	0.33	0.47	0.130	0.058
0.03	0.88	0.46	1.06	0.063	0.035
0.04	2.12	0.44	0.94	0.063	0.025
0.05	2.19	0.44	1.00	0.054	0.027
0.058	0.67	0.24	0.23	0.109	0.092
0.06	2.32	0.44	0.67	0.065	0.024
0.11	1.32	0.19	0.15	0.106	0.075
0.11	2.36	0.38	0.37	0.078	0.035
0.11	3.27	0.39	1.05	0.066	0.035
0.15	3.54	0.36	0.38	0.078	0.040
0.15	4.18	0.42	0.81	0.062	0.041
0.50	1.0	0.28	0.25	0.133	0.083

Effect of the Aqueous Phase

In the two preceding tables, rates of formation of DBP were given for mixed phases and for the organic phase alone. Greater rates of formation were obtained in the mixed-phase experiments. Therefore, DBP was apparently formed in the aqueous phase. The solubility of TBP in the aqueous phase was less than 0.3 g/l(2), yet the amount of DBP that was formed in mixed-phase experiments was from 20 to 40% higher than that formed when the organic phase was exposed alone. It was concluded that the rate of formation of DBP was faster in the aqueous phase than it was in the organic phase.

Effect of DBP on Extraction of Zirconium

The presence of DBP increased the extraction of zirconium. This effect was independent of temperature between 60 and 80°C. The effect, shown in the following table, was used as a measure of the concentration of DBP. Values at 60 and 80°C were essentially the same, as shown for 70°C.

EXTRACTION OF ZIRCONIUM FROM 3.0M HNO_3 INTO 30% TBP - DODECANE AT 70°C

DBP Added, %	$E_{O/A}$
0	0.44
0.002	0.52
0.005	0.85
0.02	1.65
0.05	4.76
0.10	10.61

The following table shows the decrease in the extraction of zirconium by DBP when uranyl nitrate is added. The amount of DBP must be very high to extract a significant quantity of zirconium from a uranyl nitrate solution. This is because a large percentage of the DBP is saturated with uranyl nitrate.

EXTRACTION OF ZIRCONIUM FROM 3.16M HNO_3 - 0.47M URANYL NITRATE INTO 30% TBP - DODECANE

DBP Added, %	$E_{O/A}$ 70°C	$E_{O/A}$ 80°C
0.002	0.004	0.004
0.005	0.015	0.014
0.02	0.073	0.060
0.05	0.25	0.25
0.1	0.62	0.61
0.2	--	1.64

In the following table, values are given for rates of formation of DBP which were obtained by determining the extraction coefficient of zirconium and relating it to the amount of DBP by means of a standard curve. These results agreed with results obtained by the analysis with U-233 tracer. The formation of DBP and the extraction of zirconium occurred concurrently in this experiment which is more realistic than experiments in which DBP was added and then the extraction coefficient of zirconium was determined.

FORMATION OF DBP IN MIXED PHASES OF 30% TBP - DODECANE AND 3.16M HNO_3 - 0.47M URANYL NITRATE

Mixing Time, min	DBP Formed, %		
	60°C	70°C	80°C
10	-	-	-
30	-	0.002	0.002
60	-	0.004	0.007
120	0.002	0.007	0.018
240	0.003	0.014	0.044
330	0.006	0.021	0.090
576	0.021	0.10	-

PREPARATION OF MATERIALS

Tributyl Phosphate

Tributyl phosphate was purified before use, by passing the TBP through a column of charcoal followed by a column of alumina, and then by recrystallization. TBP was saturated with uranium and recrystallized from n-hexane three times. The uranium - TBP complex started to crystallize around -20 to -25°C and was filtered at -40°C. After three recrystallizations, uranium was removed from the TBP by washing with Na_2CO_3 and water. Hexane was removed by steam distillation and water was removed by evaporation at reduced pressure. After the treatment, the TBP was made up to 30% by volume in n-dodecane, olefin-free grade, and was scrubbed with caustic and water immediately before use.

The purity of the product was confirmed by ultraviolet spectra, as shown in Figure 1.

A comparison was made to detect any differences in chemical behavior between purified and crude TBP with respect to hydrolysis and extraction of zirconium. Samples of undiluted pure and crude TBP were pre-equilibrated with 3.0M nitric acid and the acid was replaced with a second portion of 3.0M nitric acid. These solutions were exposed at 70°C and mixed continuously. Samples of TBP were taken at intervals and analyzed for DBP by the U-233 method.

Extraction coefficients of zirconium were also measured. No marked difference was found between the samples, as shown in the following table; however, pretreatment of TBP did remove all color and most of the odor.

COMPARISON OF CRUDE AND CRYSTALLIZED TBP AT 70°C

Time, hr	Zr E_O^O/A Pure	Zr E_O^O/A Crude	DBP, % Pure	DBP, % Crude
0	1.45	1.42	0.008	0.009
0.5	2.04	2.40	0.032	0.028
1.0	3.63	3.67	0.048	0.050
2.0	4.58	4.93	0.083	0.086
4.0	6.19	7.22	0.140	0.132
5.0	9.52	9.95	--	--
10.0	13.12	15.17	--	--

Dibutyl Phosphate

Pure DBP was prepared by the dealkylation of purified TBP. Fifty milliliters of TBP were refluxed with 150 ml of 20% NaOH. At the end of eight hours the aqueous layer contained the bulk of the sodium salt of dibutyl phosphate.

A purification method was used that was similar to the one described by R. M. Wagner(3). Unreacted TBP was removed from the sodium salt of DBP with carbon tetrachloride; then the sodium salt was acidified with concentrated HCl to release the DBP that was extracted into benzene. Azeotropic distillation removed most of the water. The remaining water was evaporated at reduced pressure. The final yield was 31.2 grams of DBP. A curve of the analysis for DBP by potentiometric titration is shown in Figure 2. The product contained 97.7% DBP, 0.8% MBP, and 1.5% inert material.

Monobutyl Phosphate

Monobutyl phosphate was separated from a mixture of DBP and MBP, which contained 40% MBP. The method that was used was described by R. M. Wagner(3) and was similar to the method of T. E. Hicks and D. C. Stewart(4). Equal volumes of the DBP - MBP mixture, water, and dibutyl ether were mixed in a separatory funnel. MBP was extracted into the aqueous layer and DBP stayed in the dibutyl ether. Ethyl ether was used to extract MBP from the aqueous phase. The ether was removed and the MBP was dried by azeotropic distillation with benzene. The titration curve in Figure 3 showed the product was 95% MBP and 5% DBP.

N-Dodecane

N-dodecane, olefin-free grade, was used as the diluent for all TBP dilutions. Earlier tests showed dodecane to be more stable than other diluents. This stability was desirable so that degradation products of the diluent would not mask the effects of DBP. Dodecane was obtained from Humphrey-Wilkinson and was used without further treatment.

Zirconium Tracer

Zirconium-95 tracer was separated from a mixture of zirconium - niobium and other fission products. The method of separation was essentially the same as was described by F. L. Moore(5). Glassware that was treated with

"Dri-Film" was used to reduce the loss of zirconium to glassware by plating out.

Zirconium was extracted from 1.0M nitric acid by mixing for 15 minutes with a 0.05M solution of 2-thenoyltrifluoroacetone (TTA) in benzene. The solution of TTA and zirconium was washed with equal volumes of 1.0M nitric acid. The second wash with 1.0M acid was left in contact with the TTA. Immediately before use, the TTA and 1.0M acid were mixed and an aliquot of TTA was transferred to a dri-filmed bottle and diluted tenfold with benzene. An equal volume of 8.0M nitric acid was added and the solutions were mixed for 15 minutes. The 8.0M acid extracted the zirconium and some TTA. The extracted TTA was removed from the acid by a benzene wash and zirconium was deposited on the walls of a dri-filmed beaker by evaporating the acid to dryness. Solutions were pipetted into the beaker to redissolve the zirconium. This technique permitted zirconium to be added to a solution without changing the concentration of that solution.

Uranium-233 Tracer

The U-233 tracer that was used in DBP analyses was obtained from a dilute solution of U-233 which was contaminated with various fission products. Diethyl ether was used to extract U-233 from the solution which was first saturated with ammonium nitrate. The ether was allowed to evaporate to a small volume to concentrate U-233. Water was used to extract the U-233 from the ether. This solution of U-233 contained 1 x 10^8 c/m-ml alpha activity. A small aliquot of this stock solution was diluted with 0.01M nitric acid for use as tracer in the DBP analysis. It contained 5.9 x 10^4 c/m-ml of alpha activity.

E. K. Dukes

E. K. Dukes
Separations Chemistry Division

BIBLIOGRAPHY

1. Kennedy, J. and Grimley, S. S. Radiometric Studies with Phosphorous-32 Labelled Tri-n-butyl Phosphate. Part II: Acid-Alkali Hydrolysis. Harwell, Berks., England, AERE-CE/R-1284, December 1953.

2. Burger, L. L. and Forsman, R. C. The Solubility of Tributyl Phosphate in Aqueous Solutions. Hanford Works, HW-20936, April 1951 (Declassified).

3. Wagner, R. M. Hanford Works, HW-19959, April 1951 (Classified).

4. Stewart, D. C. and Hicks, T. E. Alkyl Phosphoric Acid Extractions. Univ. of California·Radiation Lab., UCRL-861, August 1950.

5. Moore, F. L. "Separation of Zirconium from Other Elements by Liquid-Liquid Extraction." Anal. Chem. 28 997-1001 (1956).

6. Rider, B. F. Selected Analytical Methods for Purex Process Control. Knolls Atomic Power Lab., KAPL-890 Rev., April 1953 (Declassified).

7. Pietri, C. E. Dibutyl and Monobutyl Phosphate Studies: The Determination of Micro-Quantities of Dibutyl Phosphate in Tributyl Phosphate - Amsco Solutions. Oak Ridge National Lab., ORNL-CF-53-6-166, June 1953 (Declassified).

APPENDIX A

ANALYSIS FOR DBP WITH URANIUM-233 TRACER

Dibutyl phosphate is known to be a good complexing agent and advantage is taken of this fact in the analysis of DBP. A method of DBP analysis by uranium complexing is reported by B. F. Rider(6). In this DBP analysis the fluorometric method is used to analyze for uranium. This uranium analysis has a standard deviation of 20%. DBP analyses depend directly on the uranium analyses, so DBP analyses have a 20% deviation also.

Work described by C. E. Pietri(7) using the technique of B. F. Rider(6) indicates that the degree of DBP - uranium complexing depends on the uranium concentration. This complication is eliminated when very low concentrations of uranium are used.

In the present work U-233 was substituted for natural uranium, so that the analysis could be made by measuring alpha activity. This procedure was faster and more precise than the fluorometric method.

Analysis in the Presence of Nitric Acid

It was known that the extraction of uranium was affected by the concentration of acid; therefore, it was necessary to make all extractions at the same pH. Samples were adjusted to a pH of 2 which gave the highest degree of sensitivity to changes in concentration of DBP. Samples of solvent which contained DBP and acid were scrubbed with a 5.0M solution of sodium hydroxide. The phases were separated and the aqueous phase which contained all of the DBP was adjusted to a pH of 2 by adding nitric acid. DBP was extracted from this solution back into a fresh solution of 30% TBP in dodecane. This technique gave versatility to the analysis since it was possible to analyze for DBP that was present in samples of solvent other than 30% TBP in dodecane.

A typical analysis was performed in the following manner: A one-milliliter sample of organic solution that contained DBP and some extracted acid was pipetted into a 15-ml centrifuge tube that contained two milliliters of 5.0M sodium hydroxide. The solutions were mixed and DBP was removed from the organic phase as the sodium salt of DBP. Phases were separated by centrifugation and the sodium salt of DBP was transferred to a 20-ml beaker. To ensure good recovery the organic phase was washed again with one milliliter of 5.0M NaOH.

The sodium salt of DBP was adjusted to a pH of 2 with nitric acid and the volume of the solution was measured and recorded. DBP was extracted from the solution of sodium nitrate with two one-milliliter portions of a fresh solution of 30% TBP in dodecane.

One milliliter of the solvent that contained the DBP was equilibrated with one milliliter of a tracer solution of U-233 in 0.01M nitric acid. Extraction coefficients were obtained by counting alpha activity in each phase. The percentage of DBP was read from a standard curve in which the extraction coefficient of uranium was proportional to the concentration of DBP. The calculations took into consideration the amount of DBP that was recovered, as well as the increase in volume that was incurred at the pH adjustment step.

Preparation of Standard Curve

A typical standard curve was prepared by plotting the extraction coefficient of U-233 against the percentage of DBP added. Such a curve is shown in Figure 4. The extraction coefficients of U-233 were determined by the following procedure. A solution of 30% TBP in dodecane was equilibrated twice with a solution of sodium nitrate which had been adjusted to a pH of 2. Two volumes of sodium nitrate were used for each volume of TBP - dodecane so the TBP - dodecane was similar to that which was used to extract DBP in the analysis. DBP was added to a one-milliliter sample of the TBP - dodecane and an equal volume equilibration was made with the solution of U-233 in 0.01M nitric acid. The phases were mixed for 30 seconds at 30°C with an air-powered stirrer, and were separated by centrifuging for three minutes. The extraction coefficients were determined from the amount of alpha activity in each phase.

Recovery of DBP

The percentage of DBP that was recovered was determined by pipetting DBP into a sample of 30% TBP - dodecane which was then treated as a regular sample. Several samples that contained known amounts of DBP were analyzed with each group of samples that contained unknown amounts of DBP. The percentage of DBP that was recovered was calculated from the following table. The average amount recovered was 80.7% for the analysis of DBP in the presence of nitric acid.

EFFECT OF CONCENTRATION OF DBP ON RECOVERY

DBP Added, %	DBP by Analysis, %	Recovered, %
0.075	0.06	80
0.05	0.046	92
0.05	0.044	88
0.25	0.19	74
0.25	0.18	76
0.50	0.37	74

Precision

The precision was determined for the analysis for DBP in the presence of acid. Seven samples of 30% TBP - dodecane that contained 0.10% DBP and 0.1M HNO_3 were analyzed. The average yield was 68%. The standard deviation for this series was ±0.0038 or 5.6%. A yield of 68% for samples containing 0.10% DBP was inconsistent with the results that are given in the table in the section on recovery of DBP. The percentage of DBP that was recovered was very sensitive to changes in pH; therefore, slight variations in the standardization of the pH meter caused variations in the percentage yield.

Sensitivity

The sensitivity of the method was decreased by volume increases in the caustic scrub and by the addition of nitric acid in the pH adjustment step. Instead of a lower limit of 0.002% DBP, which the standard curve in Figure 4 indicates, the lower limit was 0.008%. Determinations were made on organic solutions that contained as much as 1.0% DBP without initial dilution.

Interference

Experiments were performed to determine possible interference from MBP and phosphoric acid. These compounds may be present in samples that contain DBP. MBP was added to samples of 30% TBP in dodecane. Extraction coefficients for U-233 were determined and are shown with the percentage of DBP in the table below. Interference by phosphoric acid was tested in a similar manner and the results are also given below. No interference was caused by MBP or phosphoric acid at concentrations that were present in this study.

EFFECT OF MBP ON THE ANALYSIS OF DBP

DBP Added, %	MBP Added, %	U-233 EO/A	DBP by Analysis, %*
0.0	0.125	0.17	- -
0.0	1.0	2.45	0.05
0.1	0.01	6.57	0.10
0.1	0.05	6.83	0.103
0.1	0.10	8.20	0.110
0.1	1.0	13.10	0.140

---

*The MBP contained 5% DBP and the amount of DBP in the aliquots of MBP that were added corresponded to the increase in percentage of DBP found by analysis.

EFFECT OF PHOSPHORIC ACID ON ANALYSIS OF DBP

Phosphoric Acid Added*	U-233 EO/A
0.15	0.008
2.0	0.004
0.0	0.007

---

*Samples were adjusted to pH of 2 after phosphoric acid was added.

Analysis in the Presence of Uranyl Nitrate and Nitric Acid

Analyses of DBP in the presence of large concentrations of natural uranium were made by a modification of the procedure just described. Several steps were introduced to eliminate interference by natural uranium.

Samples of 30% TBP - dodecane that contained DBP, uranium, and acid were scrubbed with two volumes of 5.0M NaOH and the phases were separated by centrifugation. NaOH extracted DBP from the organic phase and precipitated some of the uranium. Both phases were transferred to another centrifuge cone and the precipitate of sodium uranate was discarded. The phases were remixed and centrifuged to remove any remaining precipitate. The aqueous phase was transferred to another cone and the organic phase was scrubbed again with an equal volume of 5.0M NaOH which was added to the first scrub. The combined scrubs were centrifuged and poured into a 20-ml beaker.

The procedure that was described for the analysis of DBP in the presence of acid alone was followed to the point at which DBP was extracted from sodium nitrate into two milliliters of a fresh solution of 30% TBP in dodecane. At this point the solution of 30% TBP in dodecane was mixed with a half volume of a phosphate scrub solution. This solution was prepared by adding KOH to a 1.0M solution of H_3PO_4 until a pH of 2 was reached. Precipitation of natural uranium as sodium uranate reduced the concentration of natural uranium to 10^{-5}M. The phosphate scrub further reduced the concentration of natural uranium in the TBP - dodecane from 10^{-5}M to 10^{-7}M. Since the concentration of the U-233 tracer was 10^{-5}M, which was well above the concentration of the natural uranium, no interference from macro-uranium was experienced. From this point on, the analysis proceeded just as the analysis for DBP in the presence of acid.

Standard Curve

The standard curve for the analysis of DBP in the presence of uranyl nitrate was similar to the curve for the analysis in the presence of nitric acid. TBP - dodecane for use in preparation of the standard curve was scrubbed with one-half its volume of a phosphate solution just before the equilibration with U-233. This was done because a phosphate scrub was used as a step in the analysis to remove traces of natural uranium from the TBP - dodecane. Figure 4 shows that the curve was displaced downward by the phosphate treatment.

Recovery of DBP in the Presence of Uranyl Nitrate

The percentage of DBP that was recovered was decreased when the sample contained uranyl nitrate. This was mainly due to the loss of DBP in the precipitation of sodium uranate. Losses of DBP to the sodium uranate were reproducible if the uranium concentration of the samples did not vary greatly. Determinations were made by mixing equal volumes of a solution of 30% TBP in dodecane and an aqueous solution of uranyl nitrate with about the same concentration as was used in the actual experiments. The average amount of DBP that was recovered in this analysis was 61% and was calculated from the table below.

EFFECT OF CONCENTRATION OF URANIUM ON RECOVERY

Uranium	DBP Added, %	DBP Found, %	DBP Recovered, %
0.39M	0.0625	0.040	64.0
0.38	0.0625	0.040	64.0
0.33	0.0625	0.041	65.0
0.43	0.0625	0.035	56.0
0.28	0.0625	0.039	62.0
0.44	0.0625	0.031	50.0
0.24	0.0625	0.044	70 0

Precision

The precision of this method was calculated from the results that were obtained in the determinations of the percentage of DBP recovery as shown in the last table. The standard deviation was 11%.

Calculations for Percentage DBP

$$\text{DBP, \%} = \frac{D \times V}{R}$$

where

D = DBP from standard curve, %
V = dilution factor obtained after pH adjustment
R = DBP recovery, %

APPENDIX B

ANALYSIS FOR DBP WITH ZIRCONIUM-95 TRACER

DBP is a powerful extractant for zirconium. Changes in extraction coefficients of zirconium were also used to analyze for DBP. This procedure gave a direct method of analysis which eliminated the determination of the percentage of DBP recovered. The results that were obtained by the zirconium and uranium methods agreed within ten per cent.

The analysis was done in the following manner. Zirconium was deposited on the walls of a beaker by evaporating a solution of zirconium to dryness. The zirconium was redissolved by adding the desired aqueous solution and agitating, and no change occurred in the concentration of the solution. Equal volumes of this solution and a solution of 30% TBP in dodecane were mixed by magnetic stirrers at the proper temperature. Samples of each phase were taken at regular intervals and extraction coefficients of zirconium were determined by counting gamma activity. The percentage of DBP was read from a standard curve in which the percentage of DBP was plotted against the extraction coefficient of zirconium.

STANDARD CURVE

A standard curve had to be run for each aqueous solution, since the distribution coefficients of zirconium changed with changes in the aqueous solution.

An aqueous solution was prepared which contained zirconium. One-milliliter aliquots of 30% TBP - dodecane and the aqueous solution were combined. Each sample contained a known amount of DBP. The samples are mixed by magnetic stirrers for five minutes at the desired temperature. Gamma activity is counted in each phase and the zirconium extraction coefficient is plotted against the percentage of DBP added. The zirconium extraction coefficient due to 30% TBP - dodecane is subtracted so that the extraction coefficient that was plotted was for the change in DBP only. Typical curves are shown in Figure 5.

Precision

Precision was determined by fitting the experimental points to a straight line by the least squares method. The standard deviation was 11%.

EFFECT OF DBP ON EXTRACTION OF ZIRCONIUM AT 70°C

DBP, %	Zr $E_{O/A}$
0	0.44
0.002	0.52
0.005	0.85
0.02	1.65
0.05	4.76
0.1	10.61

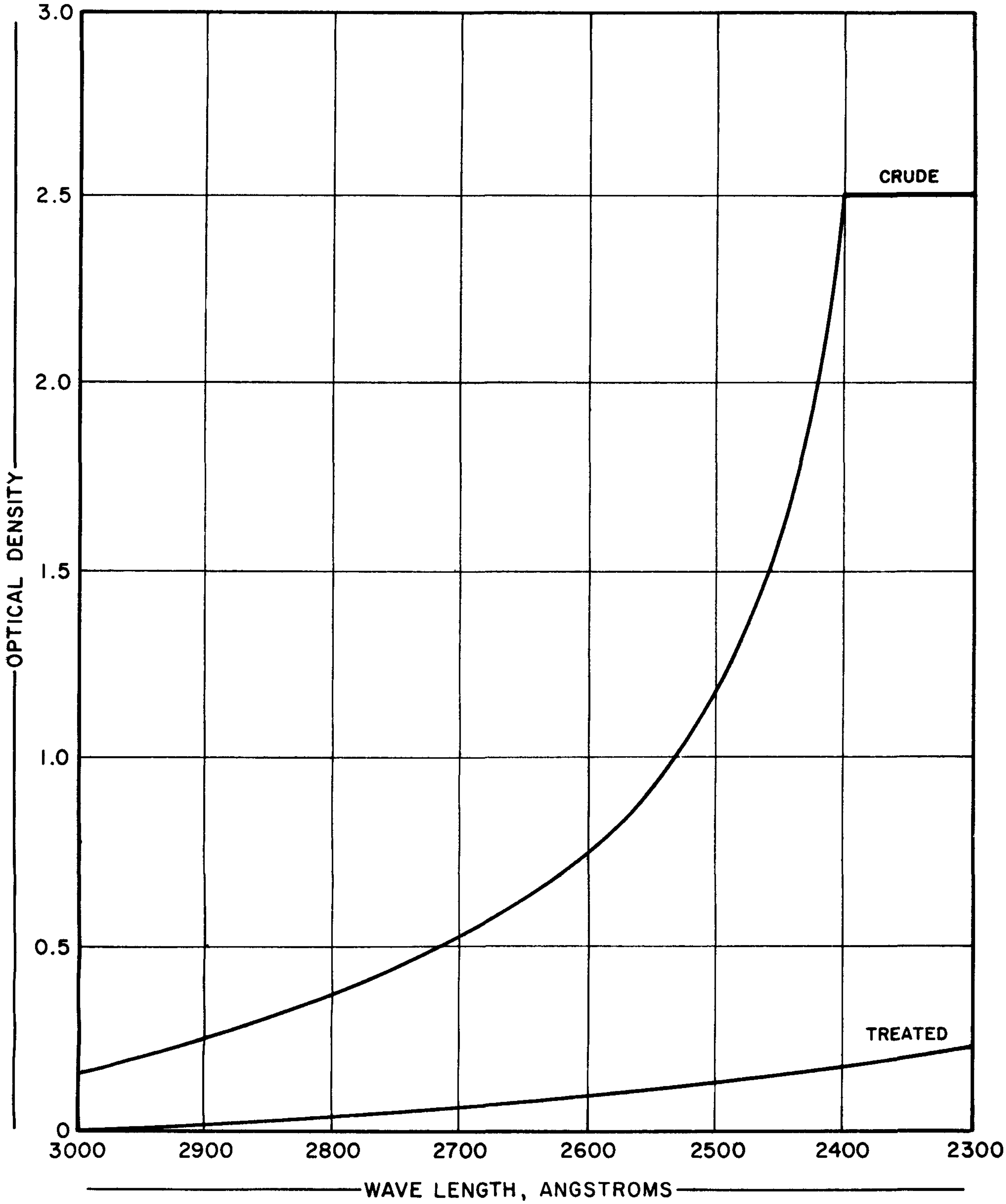
Calculations for Percentage of DBP by Zirconium-95 Method

T - P = DBP on standard curve, %

where

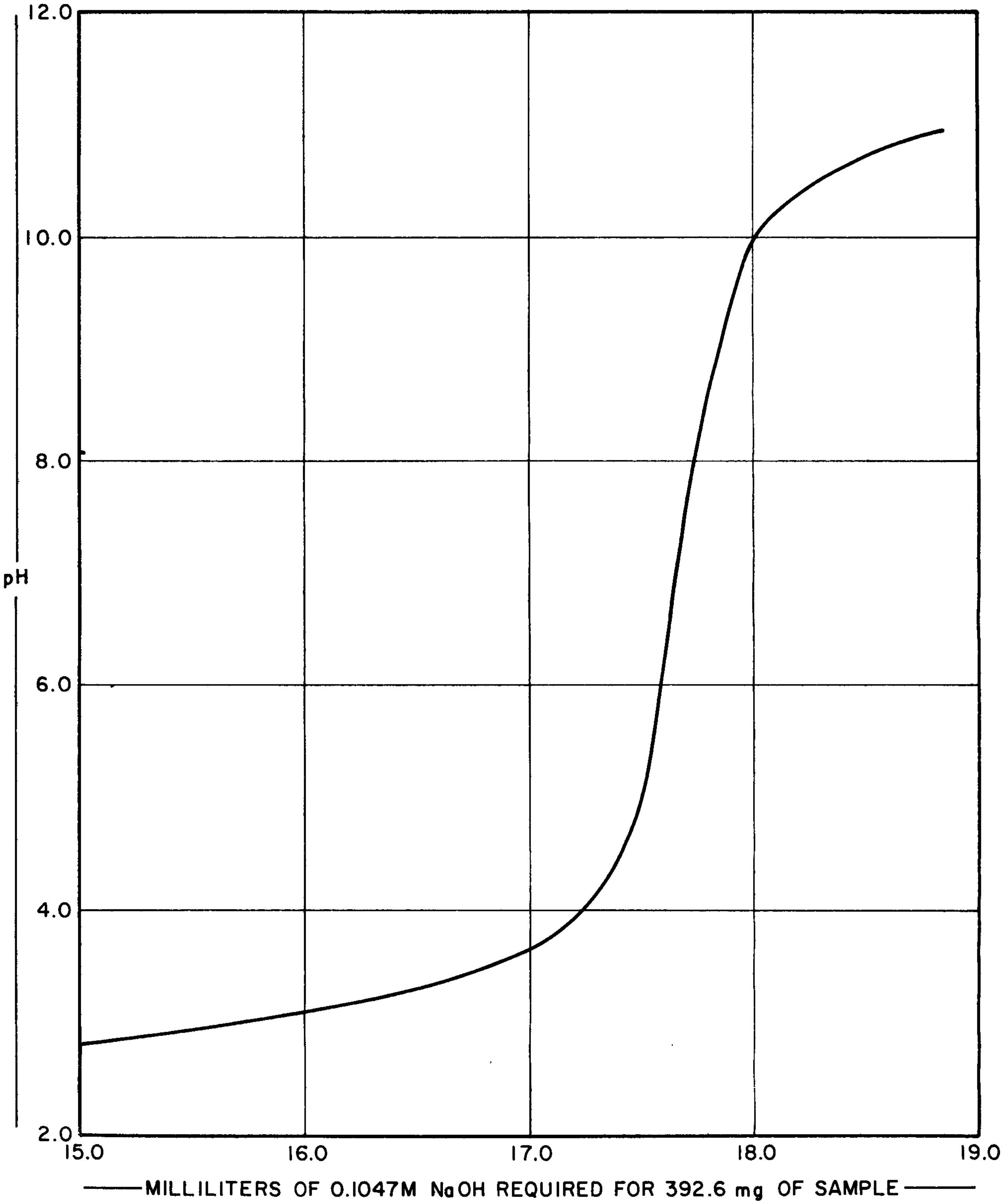
T = extraction coefficient of zirconium by sample
P = extraction coefficient of zirconium by 30% TBP

FIGURE 1



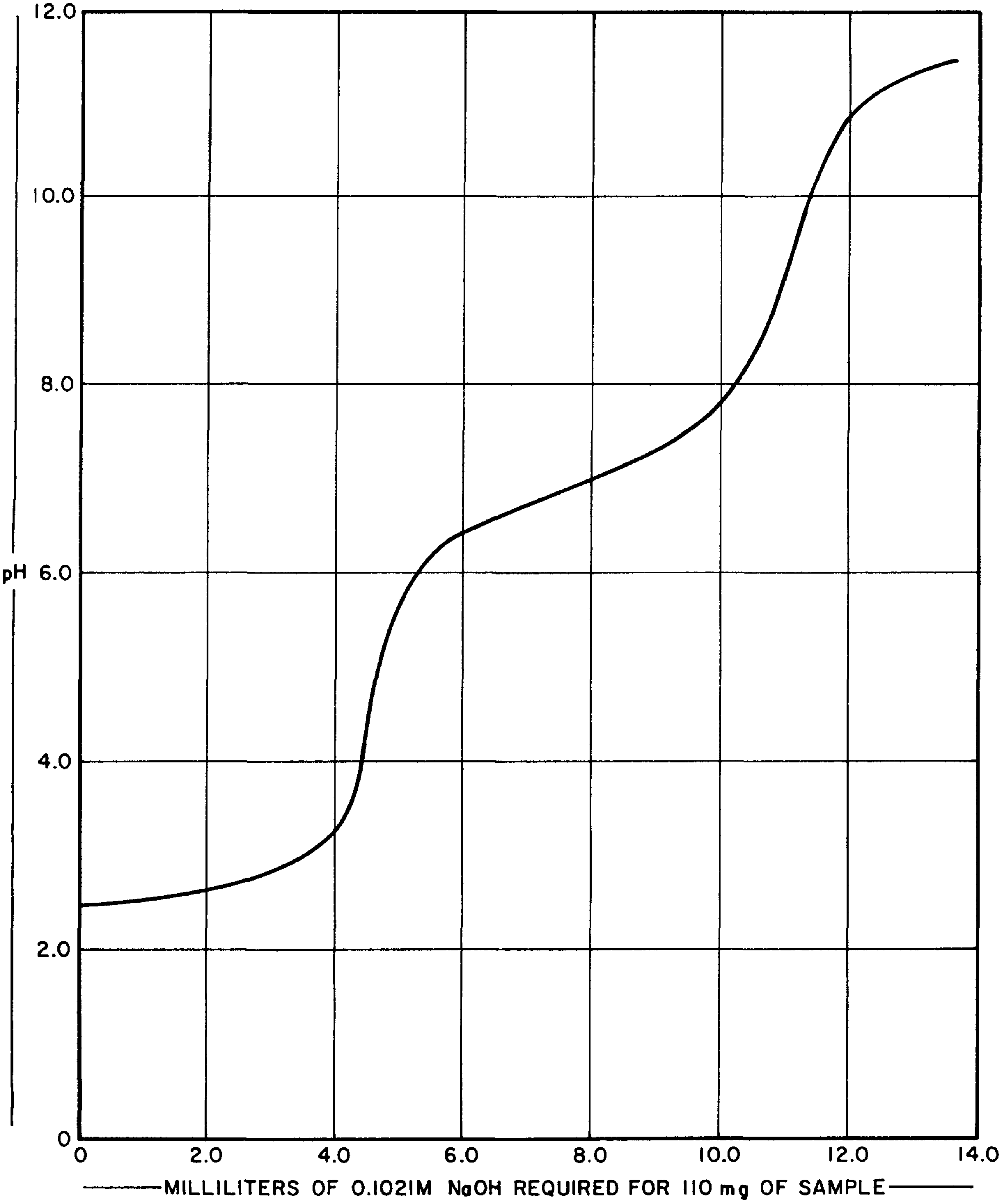
COMPARISON OF ULTRAVIOLET SPECTRA
OF CRUDE AND TREATED 100 % TRI-N-BUTYL PHOSPHATE

FIGURE 2



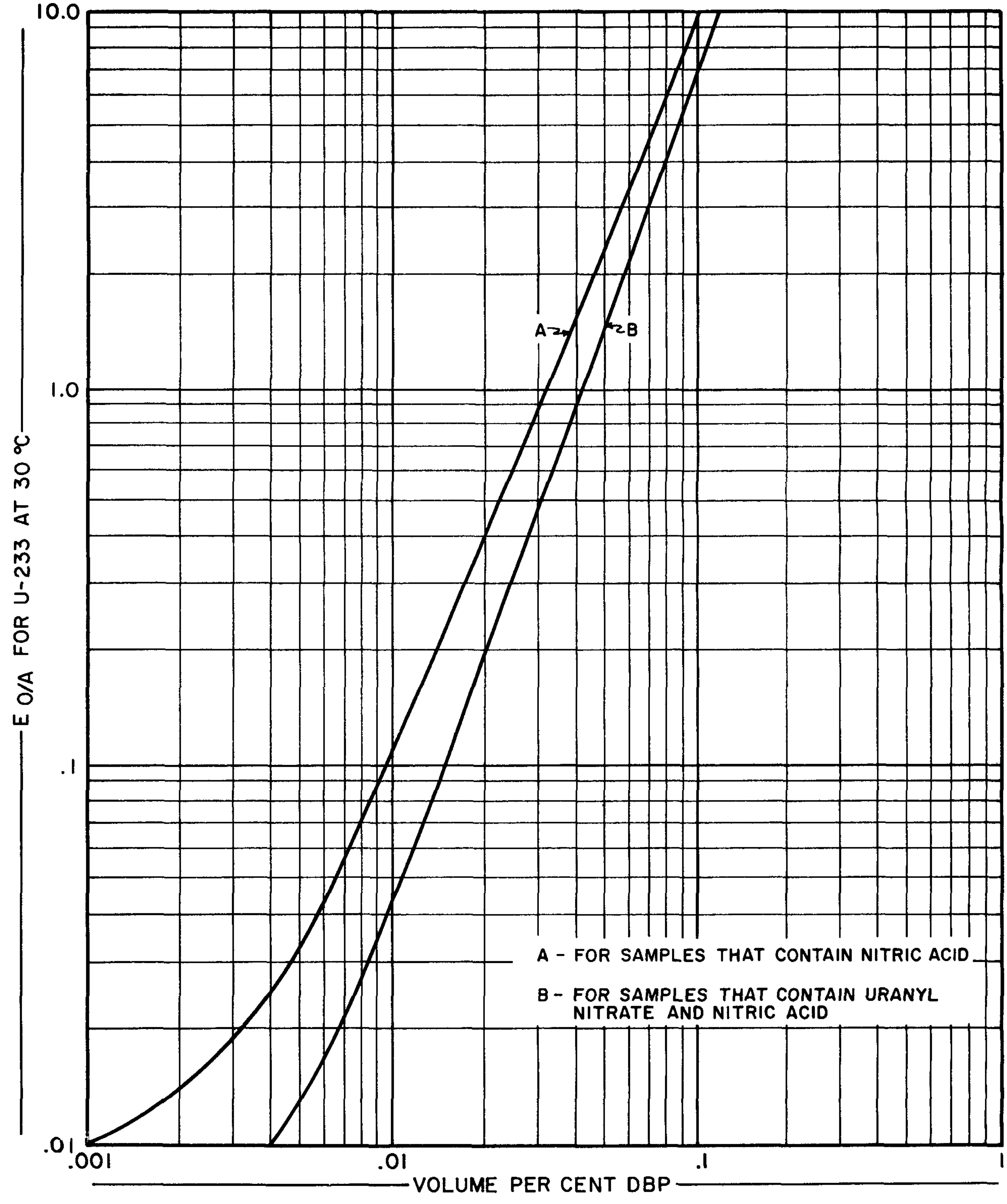
TITRATION CURVE FOR DIBUTYL PHOSPHATE

FIGURE 3



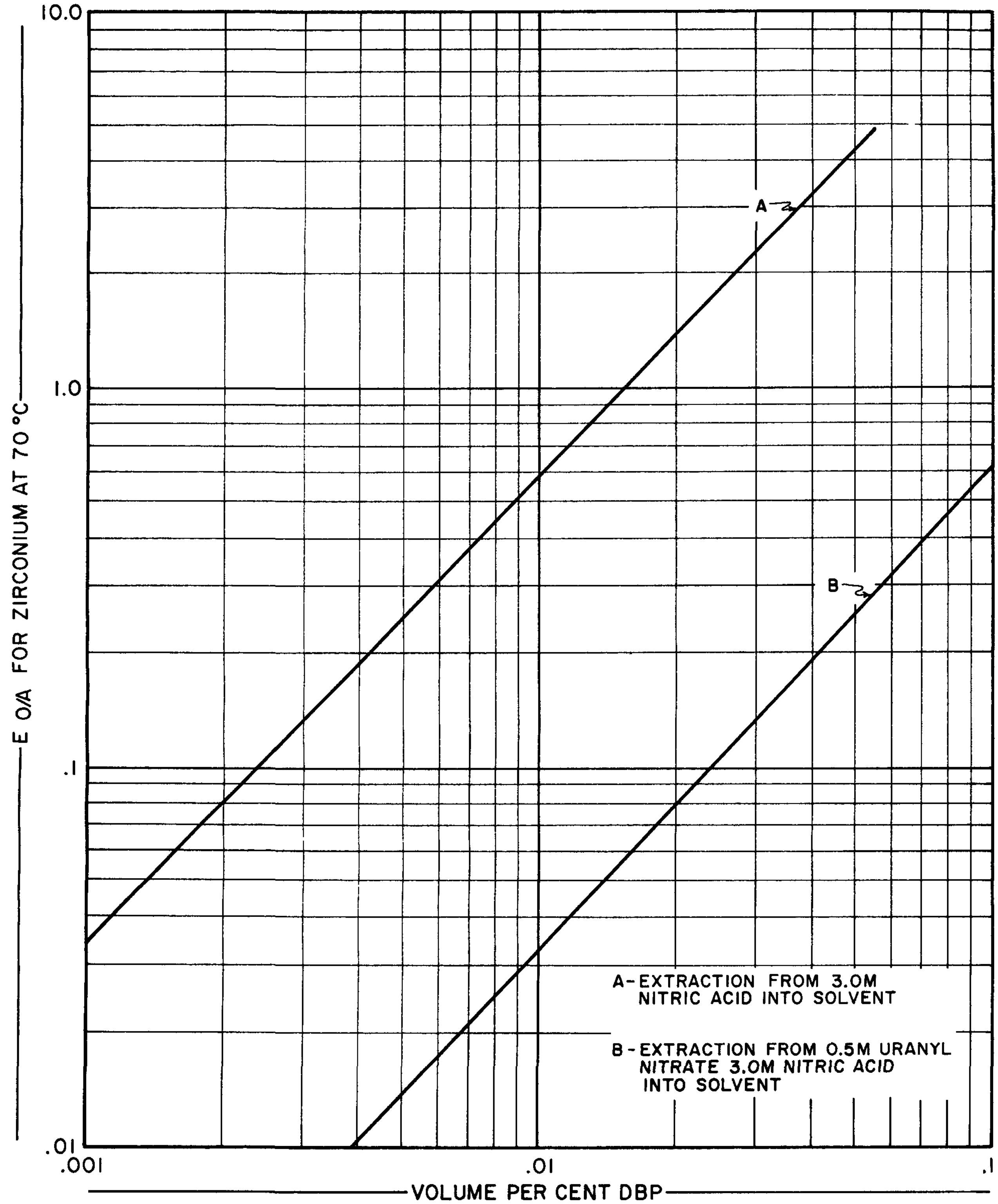
TITRATION CURVE FOR N-BUTYL PHOSPHATE

FIGURE 4



TYPICAL STANDARD CURVES FOR ANALYSIS OF DBP BY U-233 METHOD

FIGURE 5



TYPICAL STANDARD CURVES FOR ANALYSIS OF DBP BY THE ZIRCONIUM METHOD