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AN EXTRACTION METHOD FOR THE DETERMINATION OF URANIUM ALPHA ACTIVITY IN URINE

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HEALTH AND BIOLOGY

ABSTRACT

To determine uranium in urine the urine is ashed with nitric acid, and the residue is dissolved in 10 ml. of 20% nitric acid and made to 30 ml. with distilled water. This solution is mechanically extracted with di-n-butyl orthophosphoric acid in carbon tetrachloride for 10 minutes. The carbon tetrachloride extract is placed on platinum plates, evaporated, fused, and alpha assayed.

The method given has an accuracy of 84 ± 14% with 1.0 to 10 disintegrations per minute per liter of uranium^{235} in urine. The difficulties encountered in the development of the method are given.

The behavior of di-n-butyl orthophosphoric acid in nitric acid solutions is discussed.

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INTRODUCTION

The determination of uranium alpha activity has been a problem in the field of biological analysis because of the poor reproducibility of the reported methods. The most common methods used for this determination of uranium are electrodeposition,[1-3] and ether extraction of the nitrate.[4] In each method, the final estimation is made by alpha assay. The Industrial Hygiene Laboratory of the Los Alamos Scientific Laboratory has attempted to apply all reported methods for uranium to the determination of this element in urine.

Stewart and Bentley[5] used di-n-butyl orthophosphoric acid in carbon tetrachloride to extract uranium from sea water. Their results appeared practical and the application of this method to urine was studied. They evaporated the extract on platinum and fused the residue. The residue was then submitted to a fission counting technique. Various modifications of this method were necessary to apply the di-n-butyl orthophosphoric acid technique to the extraction of uranium from urine.

EQUIPMENT

Platinum Plates. Platinum foil (2 mil) is cut into 1-1/8 inch squares. These squares are hand-formed into planchets with a 1/2 inch square die (Fig. 1).

Stirring Assembly. Eight Model-1 "Eastern" stirrers are controlled by a 115 V variac and regulators. The stirrer chuck is fitted with a glass rod. A single unit is shown in Fig. 2.

Plate Holder. Alundum rods inserted into a 3/8 inch aluminum rod serve as a convenient plate holder for the flaming process (Figs. 3 and 4).

Digestion Assembly. The digestion assembly consists of a 500 ml. boiling flask fitted with a distilling head, dropping funnel and Friedrichs condenser (Fig. 5).

Instrumentation. The counting instruments used throughout this study were Nuclear Measurement Proportional Alpha Counters, Model PC-2. The chambers were Nuclear Measurement Production Chambers with one bubble of argon gas through the chamber per second. The chambers were operated at 50 V above the knee of the plateau (900 V). The efficiency of the instruments was 49.2 to 49.5% based on the plutonium alpha. The background varied from 0.1 to 0.22 count per minute during this study. In order to reduce the work load of counting technicians, as short a counting time as possible was used. The time a plate was counted was based on the following schedule:

100 to 50 c/m	counted 5 minutes
50 to 20 c/m	counted 15 minutes
less than 20 c/m	counted 30 minutes
all routine samples	counted 30 minutes

REAGENTS

Nitric Acid. Concentrated, analytical reagent, Sp. Gr. 1.42.

Nitric Acid. 20% V/V in distilled water (1 vol. conc. HNO_3 + 4 vol. H_2O).

Carbon Tetrachloride. Analytical reagent.

Di-n-Butyl Orthophosphoric Acid (DBP). Eastman organic chemical, T-5770. (Labeled composition: di-n-butyl orthophosphoric acid 60% and mono-n-butyl orthophosphoric acid 40%).

Stock Di-n-Butyl Orthophosphoric Acid (DBP) 0.6 to 0.8N in Carbon Tetrachloride. In a 1 liter separatory funnel, place 200 ml. of the technical DBP,[6] 300 ml. of carbon tetrachloride, and 500 ml. of distilled water. The mono-n-butyl orthophosphoric acid is removed from the carbon tetrachloride layer by shaking 15 minutes. The layers are allowed to separate and the carbon tetrachloride is drained through cotton into a 500 ml. storage bottle. The solution is kept refrigerated.

Working DBP. Dilute the stock DBP solution 1 + 1 with carbon tetrachloride (0.3 to 0.4N).

PROCEDURE

Place 100 ml. of urine in a round bottom 500 ml. flask and place in digestion assembly. Add 25 ml. of concentrated nitric acid and heat to dryness. An exothermic reaction occurs just prior to the time dryness is reached. Continue heating the flask until oxides of nitrogen are no longer being formed. Remove the flask from the digestion and cool, add 10 ml. of concentrated HNO_3, and evaporate to dryness. The residue should be white. Repeated additions of HNO_3 usually are not necessary; however, incomplete oxidation of the organic matter may cause a loss due to emulsion formation during the extraction process.

Dissolve the residue in 5 to 10 ml. of 20% nitric acid by warming. Transfer quantitatively to a 40 ml. centrifuge tube and make to approximately 30 ml. with distilled water. Cool the solution to room temperature,

add 1 ml. of the working DBP, and stir mechanically for 10 minutes with the tip of the glass rod just above the carbon tetrachloride layer (Fig. 2).

Remove the DBP layer with the aid of 1/2 ml. transfer pipettes fitted with a syringe and place on a platinum plate. Evaporate the carbon tetrachloride slowly under an infra-red lamp. Repeat the extraction procedure twice, using 1 ml. portions of DBP, and wash once with 1 ml. of carbon tetrachloride. After each extraction, transfer the DBP layer to the plate and evaporate the carbon tetrachloride. Care must be taken not to allow any of the aqueous phase to be placed in the plates as spattering will occur.

Lower the infra-red lamp to 2 inches above the plates and continue heating until the residue is charred and dry; this will require continued strong heat.

Place the plates on the holder and hold at the tip of the oxidizing flame of a Fisher burner (Fig. 3). When boiling ceases, lower the plate to the reducing flame (Fig. 4) and remove as soon as possible after the black residue has disappeared. Excessive heating will cause a loss of the uranium.

Flatten the plate carefully and count by standard counting procedures. The results are reported in disintegrations per minute per liter of uranium (d/m/l).

EXPERIMENTAL

Choice of Plate Material. Preliminary studies using various metals were carried out on the action of hot DBP. Silver and gold obviously are

unsuitable because of their low melting point. Tantalum, nickel, and stainless steel are corroded. For these reasons, platinum was used throughout this study.

Choice of Acid and Ashing Method. Nitric acid is used to acidify the sample prior to extraction. Table I illustrates the effect of various acids. The values shown in this table are based on a stirring time of 15 minutes, using 30 ml. of 20% V/V acid, extracted once with 1 ml. of 0.38N DBP in carbon tetrachloride and plated on platinum plates.

TABLE I

EFFECT OF VARIOUS ACIDS ON URANIUM RECOVERY

Acid	Concentration, % V/V	% Recovery
H_2SO_4	20	37
HCl	20	82
$HClO_4$	20	75
H_3PO_4	20	13
HNO_3	20	100

Only nitric acid appeared to be feasible in ashing the urines, in that both sulfuric and phosphoric acids retarded the extraction of uranium. This excludes the use of digestion mixtures such as perchloric-sulfuric acids or perchloric-phosphoric acids.

Effect of Acid Strength on Uranium Extraction. The strength of the acid appears to have a pronounced effect on the extraction efficiency. A liter of urine containing approximately 20,000 d/m/l of uranium^{235} was

ashed with nitric acid. The residue was washed into a 200 ml. volumetric flask with concentrated nitric acid. Five milliliters of this solution containing solids was placed in each of six 40 ml. centrifuge cones and made to 30 ml. with nitric acid and water equal to 10, 30, 50, 60, 80, and 100% V/V nitric acid. Each was extracted three times for 15 minutes with 1 ml. of 0.38N DBP. Each DBP extract was plated on a platinum plate. The lower nitric acid concentrations gave the best recovery (Table II). The increased recovery per extract exhibited in the strong nitric acid by the 2nd and 3rd extractions is partially explained in the discussion of DBP given below.

TABLE II

EFFECT OF NITRIC ACID CONCENTRATION ON URANIUM RECOVERY FROM URINE

	c/m of $Uranium^{235}$ per Plate from Urines Containing 250 c/m					
% HNO_3	10	30	50	60	80	100
1st extraction	202.3	175.5	133.7	69.3	17.9	3.74
2nd extraction	41.5	27.1	50.0	60.0	83.1	22.1
3rd extraction	5.5	9.1	5.7	35.9	63.1	41.5
Total extraction	249.3	211.7	189.4	165.2	164.1	67.3

Effect of Temperature. Room temperature appeared to be satisfactory for the extraction of uranium with DBP. Three conditions were studied: Ice bath 3°C., room temperature 30°C., and hot water 74°C. The recoveries were 81, 100, and 34%, respectively.

Interfering Elements. Other radioactive elements were placed in a 40 ml. centrifuge cone and made to 30 ml. with 20% nitric acid. Each solution was extracted as described above with 1 ml. 0.38N DBP. Table III shows the amount of interference which may be expected.

TABLE III

EFFECT OF INTERFERING ELEMENTS

Element Added	d/m/Sample Added	d/m/Sample Recovered
Thorium	204	62.6
Plutonium	40	27.2
Radium	188	0
Americium	80	0.5
Actinium	308	7.0
Curium	54	8.6
Americium) mixture Curium)	400	2.8
Fission products	5000 (β-α)	0

Di-n-Butyl Orthophosphoric Acid (DBP). The di-n-butyl orthophosphoric acid as purchased contains some 40% mono-n-butyl orthophosphoric acid. Since the latter material does not participate in the extraction process, and indeed hinders the final preparation of the plate, it is removed from a carbon tetrachloride solution of the original material by extraction in water as described. The washed carbon tetrachloride solution is approximately 0.68N DBP. Figure 6 demonstrates the completeness of purification. The curves were obtained by titrating the mixed

acids and fractions (0.11N NaOH) after the indicated purification procedure. The absence of any clearly defined inflection point on Curve C at pH 7 demonstrates the complete removal of the mono-ester (Curve B) from the carbon tetrachloride solution of the original (Curve A).

Other possible organic solvents were investigated, including chloroform; 1,2-dichloroethane; 1,1,1-trichloroethane; 1,1,2-trichloroethane; β,β'-dichloroethyl ether. None appeared superior to carbon tetrachloride in this application.

The results in Table II suggest an interaction between DBP and strong acid (greater than 60% nitric acid). Accordingly, 1 ml. portions of DBP (0.38N) were extracted with 30 ml. of nitric acid of varying concentrations. The DBP concentration in the carbon tetrachloride phase was measured by titration. The results in Table IV indicate that the strong nitric acid, by some means, removed DBP from the carbon tetrachloride. An increased contact time caused further removal of DBP from the carbon tetrachloride phase.

TABLE IV

CONCENTRATION OF DBP IN 1 ML. CCl_4 AFTER EXTRACTION WITH NITRIC ACID

30 ml. of HNO_3	Normality of DBP
20%	0.022
40%	0.022
60%	0.022
80%	0.0178
100%	0.0062

Effect of DBP Concentration on Uranium Recovery. When excess DBP is added to a plate, the flaming time must be increased. Therefore,

higher concentrations of DBP have not proven beneficial. The losses observed in Table V cannot be attributed to ineffective extraction but to excessive heating during the removal of DBP.

TABLE V

EFFECT OF DBP CONCENTRATION ON URANIUM RECOVERY

DBP	d/m/Sample Added	d/m/Sample Recovered
0.16	200	200
0.32	200	200
0.63	200	196.2
1.62	200	177.4
1.89	200	176.5

Effect of Sample Treatment on Recovery. To insure transfer of the uranium from sample containers to digestion flasks, either all of the urine samples should be washed into the ashing flask with acid or the urines should be acidified with nitric acid prior to removal of an aliquot.

The analysis of urine samples larger than 100 ml. is difficult because of the increased amount of salts handled. With appropriate modifications and technique, samples as large as 2 liters have been analyzed with moderate success. Regardless of the ashing technique used the recovery was always within the range given. Urines ashed with nitric acid and heated to dryness several times were equal in recovery to those urines ashed with nitric acid and removed from the heat immediately after the exothermic reaction. Losses were not attributed, in all cases, to unoxidized organic matter.

Comparison of Electrodeposition and Extraction Methods. The method used routinely in this laboratory has been the electrodeposition of the uranium on silver, as modified by T. C. Whitson and T. K. Kwasnoski.[2]

Four 100 ml. urine aliquots were spiked with 24 d/m uranium^{235} and analyzed according to the electrodeposition procedure. The amounts recovered were 12.2, 4.6, 212, and 8.7 d/m/sample. A comparison of the analytical methods on routine samples is given in Table VI.

TABLE VI

COMPARISON OF ELECTROPLATING AND EXTRACTION METHOD OF ANALYSIS

Sample No.	Electroplating, d/m/l	Extraction, d/m/l
1	0	17.2
2	6	12
3	92	370
4	0	98
5	13	28
6	13	216
7	27	86
8	10	618
9	10	16.8
10	22	105

It is obvious from these analyses that a loss occurred because of poor electrodeposition or alpha absorption by the precipitated urine salts on the plate. Four plates, having been processed in the usual manner of electroplating, were dissolved in HNO_3 until the surface of the silver plate was clear of most of the blacking. Each plate was recounted and the acid wash was analyzed by the extraction method. Table VII gives the results of this test.

TABLE VII

CAUSE OF LOSSES IN ELECTRODEPOSITION OF URANIUM FROM URINE

20 ml. of Urine Ashed and Uranium Electroplated on Silver, d/m/plate					d/m/l Calc.
Direct Count of Plate	Plate Count after 20% Nitric Acid Wash	DBP Extract of Acid Wash	d/m/l Calc. on Total Counts	d/m/l Calc. from Direct Count of Plate	from DBP Extract of 100 ml. of Urine
0.00	0.20	0.60	45	0	6
0.08	0.34	0.46	45	8	138
0.34	0.06	0.74	45	34	86
0.34	0.00	0.26	13	34	105

Accuracy of the Method. The sensitivity and accuracy of the method is dependent upon the total d/m/plate. A low concentration of uranium which approaches the counts per minute of the background introduces large errors in accuracy. Samples over 10 d/m/sample are well above the counter background and approach 100% recovery in spiked urines. Using 100 ml. urine samples spiked at various levels, from 1 to 10 d/m/sample, gave an accuracy of 84 ± 14%. Duplicate urine samples received on a routine basis were reproducible if the total was over 100 d/m/l of urine. Analyses of urines below 25 d/m/l of urine were not duplicated. However, analysis of 4 or 5 aliquots of urine showed that the higher values were above 85% recovery. Urines to be analyzed for uranium should be acidified as soon as possible so that a more accurate aliquot can be taken. Old urines left neutral or alkaline have shown that the uranium is bound in the precipitate.

Volatility of Uranium during Heating. Uranyl phosphate has a vapor pressure at elevated temperatures which may cause a loss during the flaming of the plates. The following was a study to determine the effect of frequency and length of flaming time on this loss.

The addition of 0.6 ml. of phosphoric acid to a precounted plate and flaming to white heat caused no loss in uranium. Also, no loss was observed using 0.2 ml. of phosphoric acid, then flaming and counting the plate between each addition until a total of 0.6 ml. had been added. Precounted plates were warmed with phosphoric acid and a carbon tetrachloride solution of DBP; the liquids were transferred to new plates and

flamed in the usual manner. Phosphoric acid and DBP both reacted with the uranium and transferred to the new plate. This shows that the uranium was actually in solution and did not remain on the surface of the platinum during the evaporation and prior flaming.

Two milliliters of DBP was added to platinum plates containing a previously determined amount of uranium. After evaporation, heating, and flaming slowly until clear of ash, the plates were flamed for 0, 1, 2, and 3 additional minutes at red heat. Table VIII gives the results of this study. Table IX shows the effect of flaming after the addition of each half milliliter of the DBP.

TABLE VIII

EFFECT OF FLAMING TIME ON URANIUM RECOVERY WITH SINGLE APPLICATION OF DBP

Conditions of Flaming after Evaporation	% Loss
Flamed to red heat and removed immediately	0
Flamed to red heat for 1 min. after clearing	10
Flamed to red heat for 2 min. after clearing	12
Flamed to red heat for 3 min. after clearing	55

It is a matter of choice whether the plates are flamed after the addition of each extract or after the addition and evaporation of all extracts, as long as the length of time the plate is flamed at red heat is kept at a minimum. A trace of phosphoric acid on the plate did not exhibit too great an alpha absorption.

TABLE IX

EFFECT OF FLAMING TIME ON URANIUM RECOVERY WITH MULTIPLE APPLICATION OF DBP

Conditions of Heating after Evaporation	% of Original Count Lost by Evaporation and Flaming with Each 1/2 ml. of DBP			
	1st Add.	2nd Add.	3rd Add.	4th Add.
Flamed to red heat and removed immediately	0	0	0	3
Flamed to red heat for 1 min. after clearing	24	59	73	79
Flamed to red heat for 2 min. after clearing	33	65	82	89
Flamed to red heat for 3 min. after clearing	43	89	92	94

SUMMARY

Uranium is successfully extracted from ashed urine by di-n-butyl orthophosphoric acid (0.38N in CCl_4). The extraction efficiency depends on the acid concentration of the dissolved urine salts; optimum conditions were found to be 5% V/V nitric acid. The major cause of error in the determination is the final preparation of the plates for radiometric analysis.

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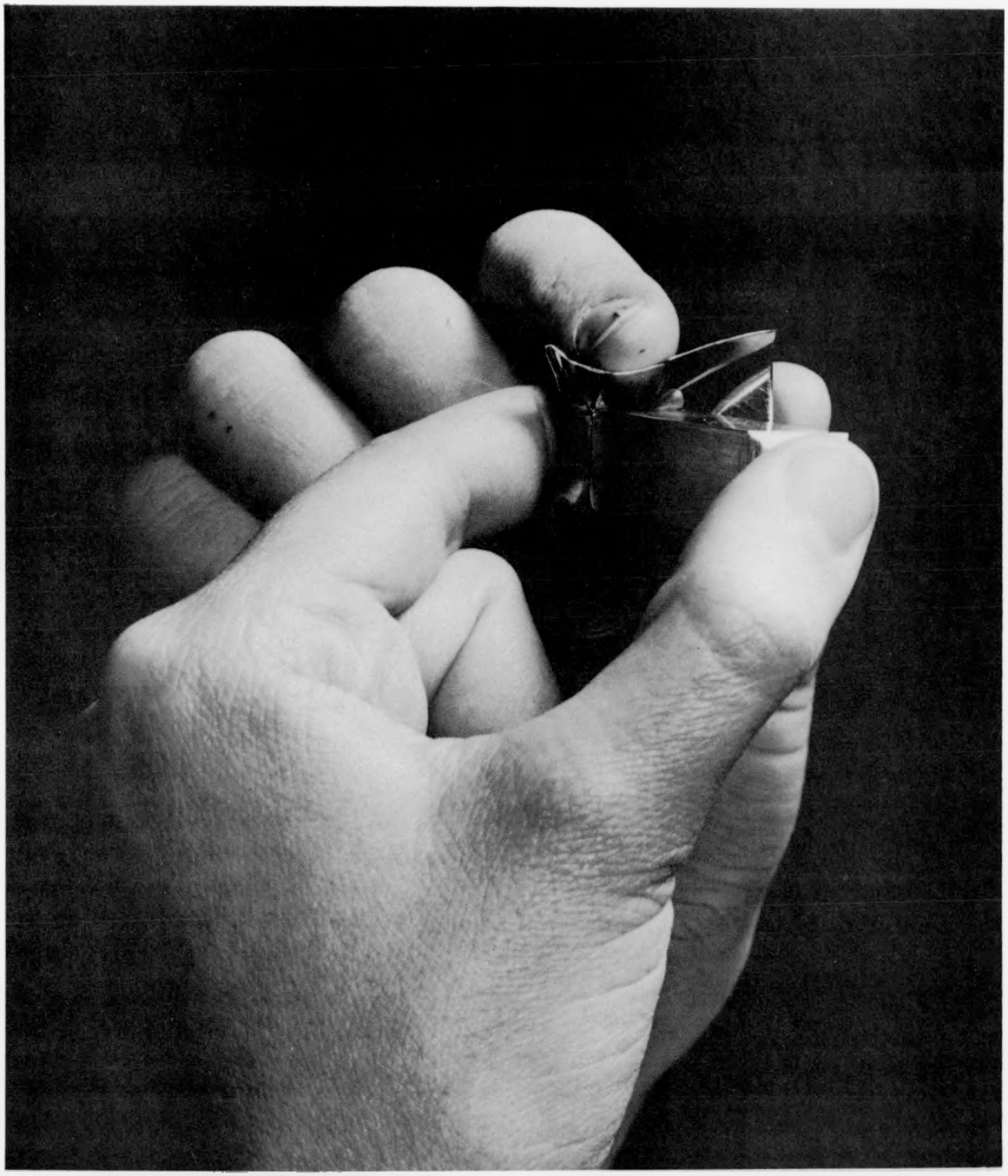

Fig. 1. Preparation of platinum plates

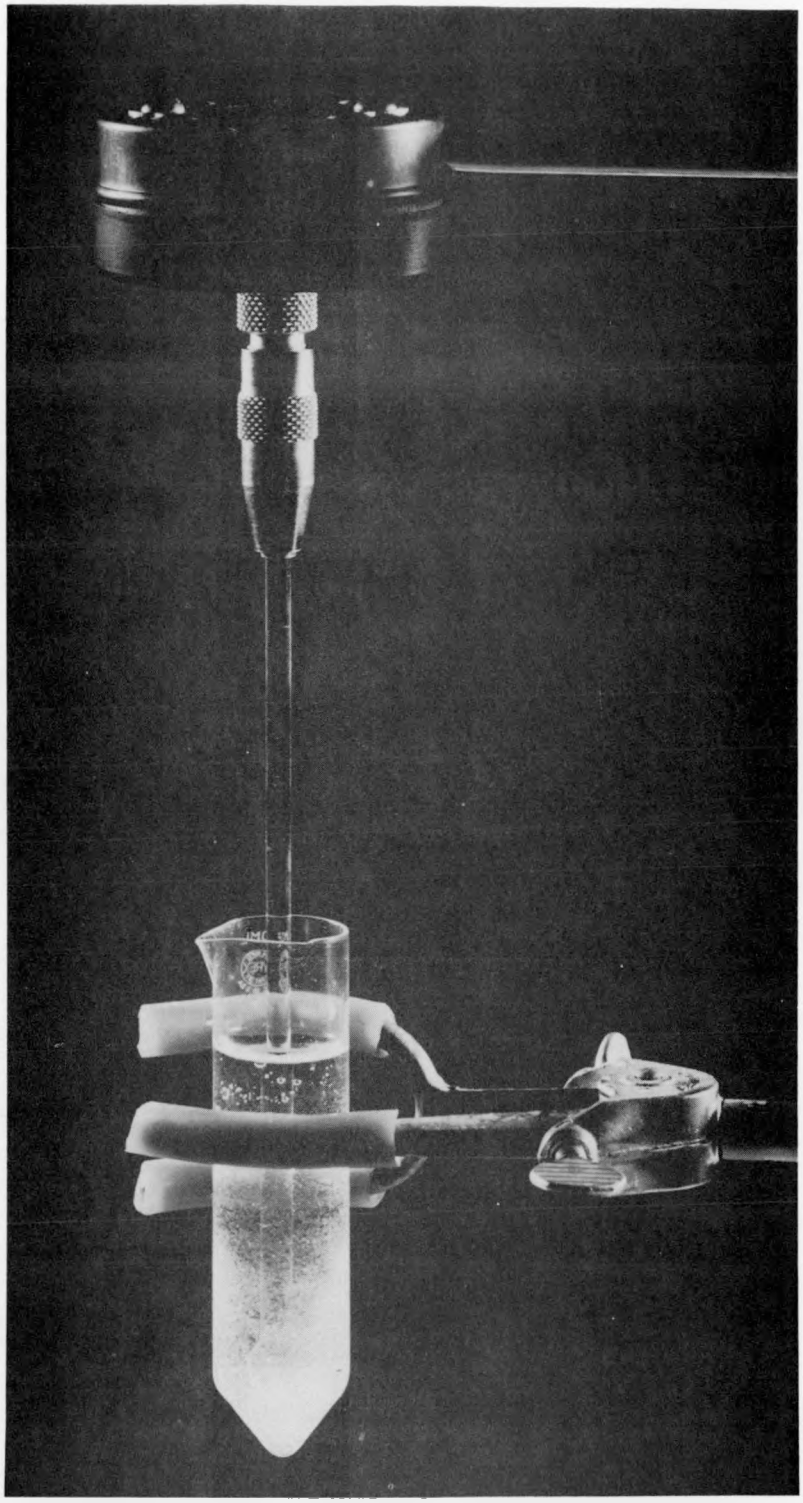

Fig. 2. Stirring assembly

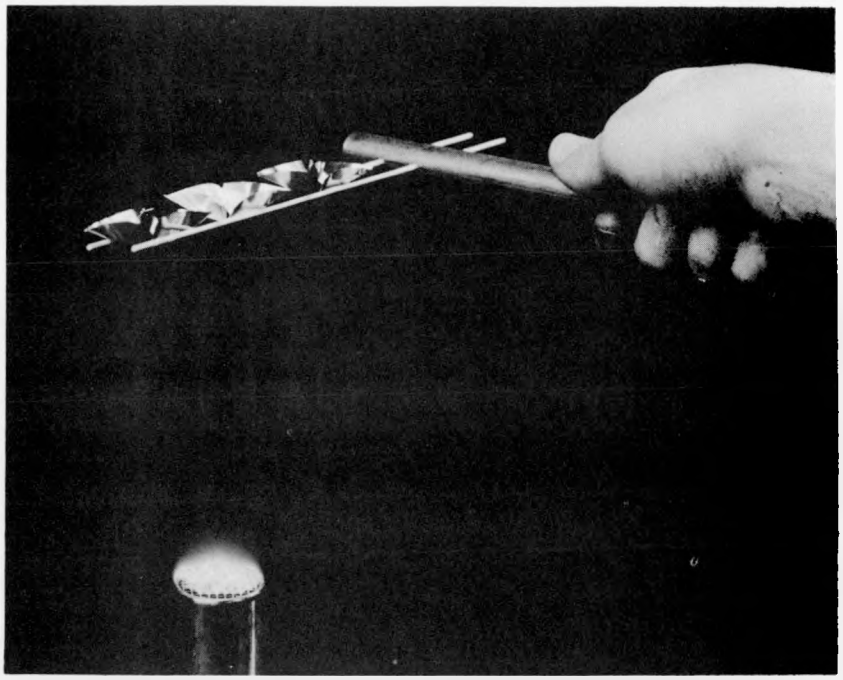

Fig. 3. Flaming of plates at low heat

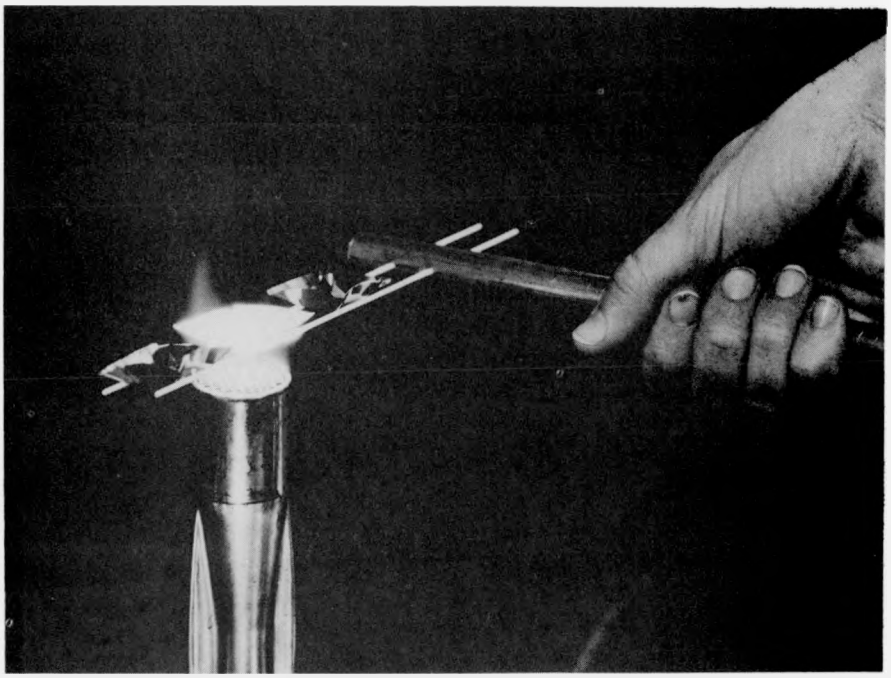

Fig. 4. Flaming of plates at red heat

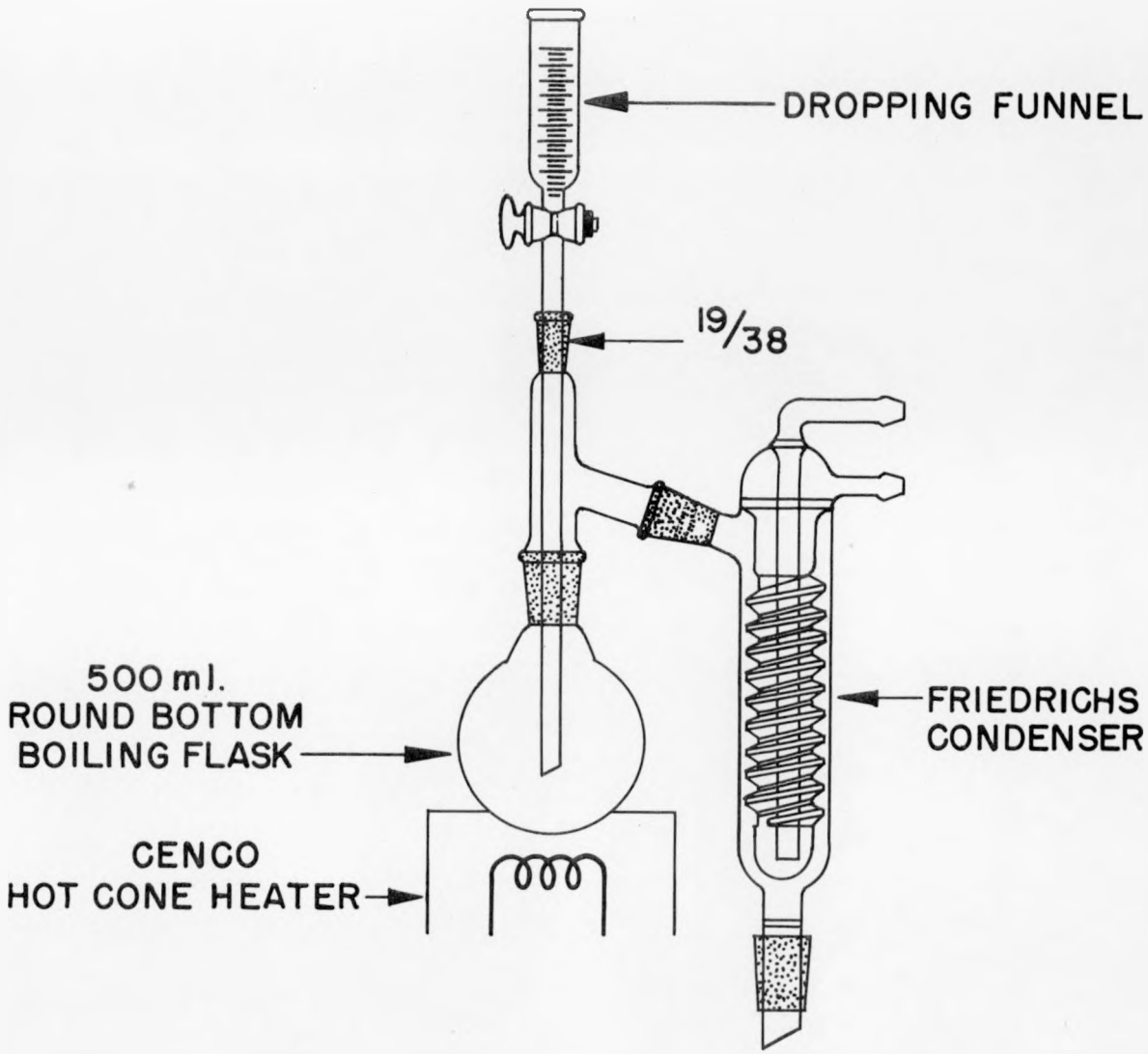

Fig. 5. Digestion assembly

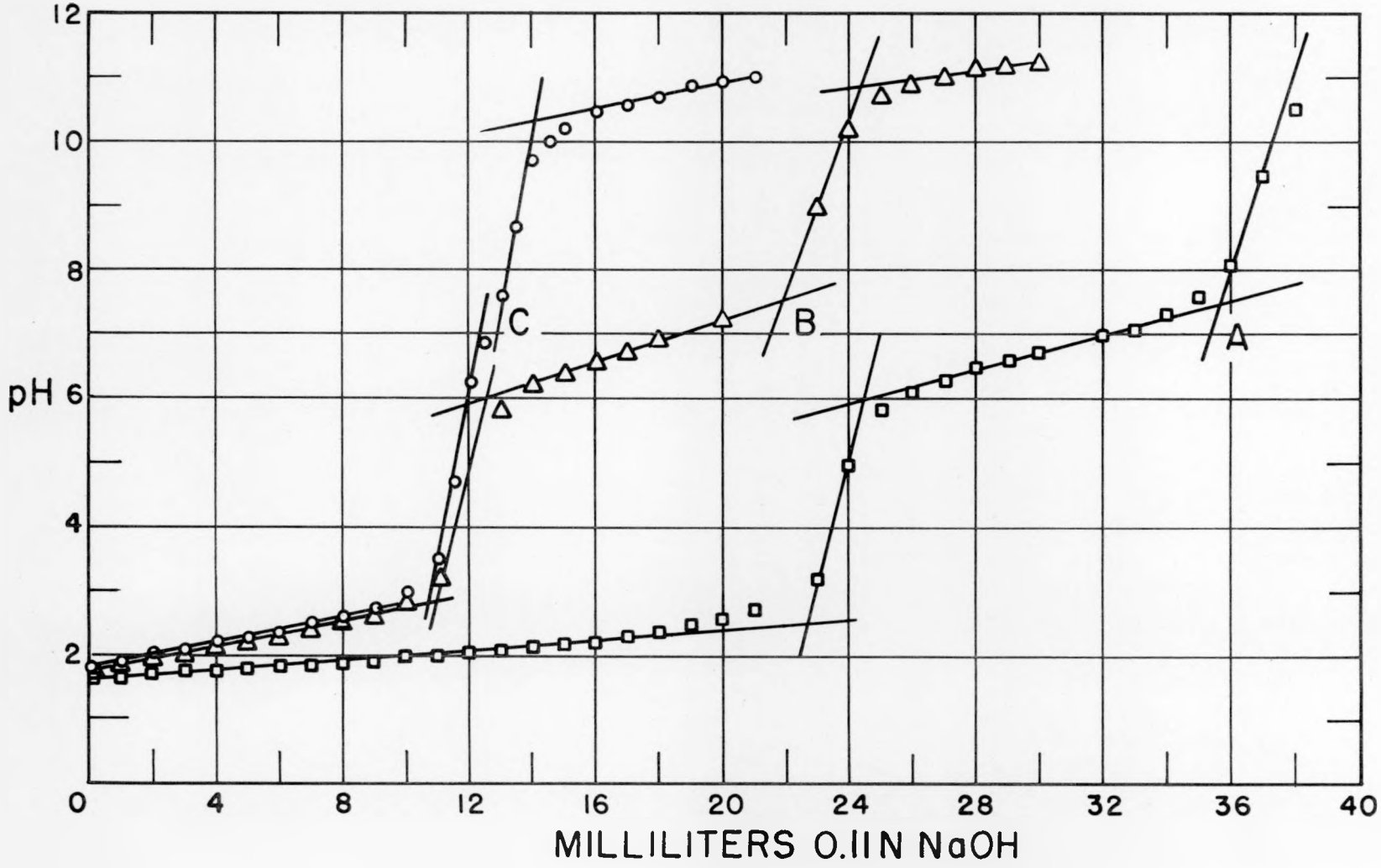

Fig. 6. pH Titration curves of DBP

□ Curve A for 2 ml. of the DBP in CCl_4
△ Curve B for 2 ml. of the aqueous extract of Curve A
o Curve C for 2 ml. of the CCl_4 after extraction