



TREATMENT OF TRIBUTYL PHOSPHATE WASTES
BY EXTRACTION CUM PYROLYSIS PROCESS

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ABSTRACT

For the treatment of spent tri n-butyl phosphate (TBP) wastes from Purex process, a method involving extraction of TBP with phosphoric acid followed by pyrolysis of TBP - phosphoric acid phase was investigated. The process was examined with respect to simulated waste, process solvent wastes and aged organic waste samples.

In the extraction experiments, about 1 to 8 moles of phosphoric acid per mole of TBP were used. At acid : TBP mole ratio of 3:1 and above, quantitative disengagement of diluent (top phase) was achieved. Under these conditions, formation of 2:1 complex of acid to solvent in the middle phase was confirmed. The separated diluent retained about 2 to 7 % of ruthenium feed activity. Further treatment of the diluent phase with fresh phosphoric acid resulted in little reduction of ruthenium activity. Purity of the diluent was also examined by subjecting it to plutonium retention test and the results indicated that even after several strippings with dilute nitric acid, significant quantity of plutonium activity remained in the organic phase.

In pyrolysis experiments with TBP - phosphoric acid phase obtained from simulated waste, it was found that about 95 percent of TBP could be decomposed in about 2 hours at temperatures in the range of 175 to 200 degrees centigrade. During pyrolysis, less than 0.1 percent of ruthenium activity was found to escape with the off - gas.

These studies seem to offer a simple treatment method for the separation of bulk of diluent from spent solvent wastes. The diluent phase needs further purification for reuse in reprocessing plant; otherwise it can be incinerated.

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1 INTRODUCTION

In the fuel reprocessing plants, 30 % tri n-butyl phosphate (TBP) in kerosene or n-dodecane diluent is used for recovery of plutonium and uranium from spent fuel by Purex process. Due to the exposure to high radiation, TBP and diluent get degraded resulting in decrease of selectivity towards plutonium and uranium. When TBP - kerosene can no longer be repurified to desired quality, it is discarded as organic liquid waste.

For the treatment of organic liquid wastes, various types of incinerators have been developed [1, 2, 3]. Elevated temperature pyrolysis of alkyl phosphates including TBP in the range of 180 to 1000 degrees centigrade has also been studied [4 to 9]. In some of these processes, calcium or sodium carbonates or calcium oxide were used to retain phosphorus pentoxide vapours inside the furnace. The quantities of secondary wastes generated are large and off-gases are highly corrosive. Cementation of TBP - kerosene has also been tried [10] with some success. The activity is just retained in a solid matrix and not immobilised. This is not a desired mode of treatment for actinide bearing wastes. Also TBP- kerosene incorporated is about 30 to 40 volume percent leading to considerable increase in

volume of the end product. Fractional distillation of diluent from TBP is feasible [11], if pure dodecane is used as diluent, due to the large difference in the boiling points. Kerosene or dodecane containing higher alkanes are obviously not separable to large extent by this method.

It is well known that mineral acids like nitric acid and phosphoric acid form polar adducts [12, 13] with TBP. Based on this, Eurochemic has developed [14] a process for the treatment of organic liquid wastes. In this process, TBP is extracted at ambient temperature with phosphoric acid in first step and in the next step, TBP - acid phase is pyrolysed at around 200 degrees centigrade to destroy organics and generate phosphoric acid (about 20 volume % of the TBP pyrolysed) for recycle. During pyrolysis butene is a major non-condensable product in the off-gases and it may be discharged to environment after proper dilution or burnt. The excess phosphoric acid generated can be either neutralised and then bituminised or converted into phosphate glass. This process has been cold tested using a four stage mixer - settler for extraction and wiped - film evaporator for pyrolysis. Subsequently, Eurochemic has tested [15] this process for the treatment of actual TBP - kerosene wastes of Purex process.

In view of the obvious advantages and proven viability, it was decided to investigate this process in detail on laboratory scale. The results obtained using simulated wastes, process solvents and aged actual wastes are reported here.

2 EXPERIMENTAL

2.1 Extraction Experiments

For extraction experiments, commercially available LR grade

phosphoric acid having a concentration in the range of 14.7 to 15.6 M was used. A partially dehydrated phosphoric acid was prepared by heating LR grade acid to 205 degrees centigrade for 5 minutes. The concentration of this acid was estimated to be 17.6 M.

2.1.1 Experiments With Simulated Wastes

(i) Preparation of simulated wastes

Commercially available kerosene was decolourised and deodourised by contacting with pre - dried activated charcoal and filtration. LR grade TBP was used without further purification. A 30 volume % solution of TBP in kerosene was prepared as and when required. It was used as such for inactive experiments. The TBP - kerosene was contacted with neutral 2 to 5 M sodium nitrate solutions spiked with Ce-141, Ru-103 and Sb-124 in order to load it with desired tracer. This loaded TBP - kerosene was used for radioactive experiments.

(ii) Separation of phases

To about 5 ml of 15.6 or 17.6 M phosphoric acid, appropriate quantities of 30 % TBP - kerosene with or without tracer were added to vary acid : TBP mole ratio from 1:1 to 8:1. The mixture was shaken vigorously and allowed to stand for sufficient time for complete disengagement of phases. In order to estimate the volumes of phases accurately, a reverse calibrated burette (100 X 0.2 ml) was used. The volumes of different phases were recorded. The experiments with tracers were performed in the separating funnel and the activity left in the top diluent phase was analysed using sodium iodide detector and single channel analyser.

(iii) Settling time for phases

About 5 ml of LR grade 15.6 M phosphoric acid was taken in a

separating funnel. To this, appropriate quantity of 30 % TBP - kerosene tagged with ruthenium-103 was added to achieve phosphoric acid : TBP mole ratio of 4:1. The funnels were shaken vigorously by hand for 10 minutes and allowed to stand for different time intervals. The kerosene phase of each experiment was analysed for Ru-103 activity.

2.1.2 Experiments with Process Solvents and Aged Wastes

30 percent TBP in shell sol T (SST) is used as a process solvent in plants. Two samples of this were taken for experiments. They were designated as PS - 1 and PS - 2. They were washed with water (1:1) in order to make them acid free and then analysed for activity contents. Besides, two samples of aged organic solvent wastes were also investigated. They were designated as AW - 1 and AW - 2.

(i) Separation of phases

About 50 ml of waste samples were taken in conical flasks and different quantities of 15.2 M phosphoric acid were added to achieve acid : TBP mole ratios between the ranges 2:1 and 5:1. The mixture was stirred by a magnetic stirrer unit for one hour and then transferred to a measuring cylinder. After allowing one hour for settling of phases, the volumes of different phases were noted.

In few experiments, the separated diluent phases obtained from PS - 2, AW - 1 and AW - 2 were taken for second contact with fresh phosphoric acid keeping the same volume ratio in all experiments. After this contact, the organic phases were taken for fission product assay and plutonium loading and stripping experiments, to check their quality.

(ii) Assay of radioactivity and TBP content of phases

(a) Fission product analysis

The samples from separated phases were analysed by gamma spectrometry using a large volume high purity germanium detector coupled to 4 K analyser.

(b) Plutonium analysis

Plutonium in feed samples was estimated by stripping with ascorbic acid followed by radiometry. Plutonium in the aqueous samples was directly taken for plancheting and then counted on an alpha proportional counter. The aqueous samples were mainly from diluent quality test mentioned below.

(c) TBP analysis in the diluent phase

A suitable aliquot of the sample was taken and fumed with perchloric acid 3 to 4 times. The inorganic phosphate thus formed was estimated by spectrophotometry following the ammonium vanado molybdate method. TBP content of diluent phases from AW- 1 and AW - 2 were analysed using Shimadzu gas chromatographic analyser.

(iii) Diluent quality test by plutonium extraction and stripping

The separated diluent phases from above experiments were taken for these tests after washing with water. A Plutonium stock solution of about 0.1 mg per ml was prepared in 2 M nitric acid and was conditioned to Pu (IV) state. 3 ml of this solution was shaken with equal volume of separated diluent phase for 10 minutes. After phase separation, plutonium in both the layers was analysed by direct plancheting and alpha counting.

Diluent layer from the above experiments were taken for stripping experiments. It was contacted with 0.1 M nitric acid in 1:2 volume ratio. Four stripping contacts were given. Plutonium in the diluent phases after strippings was estimated by direct planchetting.

2.2 Pyrolysis Experiments

These experiments were conducted only with simulated waste samples.

(i) Time required for pyrolysis

14.7 and 17.6 M phosphoric acids were used for these experiments. About 10 ml of acid was taken in different conical flasks. Appropriate quantity of 100 % TBP was added to each of them in order to achieve acid : TBP mole ratio of 3:1 or 4:1. The contents of the flasks were thoroughly shaken for 10 minutes. Air inside the flasks was replaced by nitrogen. The flasks were dipped for different time intervals in glycerol bath kept at 175 or 200 degrees centigrade. Subsequently, the contents of the flasks were diluted to a known volume and an aliquot of it was titrated potentiometrically with standard sodium hydroxide solution. From the initial and final quantities of phosphoric acid, the percent TBP pyrolysed was estimated.

A few experiments were conducted to determine the rate of pyrolysis of TBP in phosphoric acid by following the evolution of non-condensable gases during pyrolysis at acid : TBP mole ratio of 4:1. Butene gas was collected by downward displacement of water in inverted measuring cylinder. The effect of nitric acid on the rate of pyrolysis was also studied using this setup.

(ii) Distribution of activity during pyrolysis

These experiments were conducted to estimate the fraction of antimony-124, cerium-141 and ruthenium-103 activity released to the off - gases during pyrolysis. About 5 ml of 15.6 M phosphoric acid was taken in different conical flasks. Appropriate quantity of 30 % TBP - kerosene spiked with one of the above radioactive tracers was added to each of these flasks in order to achieve phosphoric acid : TBP mole ratio of 3:1 or 4:1. The mixture was shaken for 10 minutes and allowed to stand for 1 hour. The kerosene phase was pipetted out almost completely. The flask was then connected to a phosphoric acid scrubber and condenser. For experiments with ruthenium-103, silica gel bed was used after the condenser in order to trap any ruthenium escaping to the off-gas. The flask was dipped in glycerol bath at 175 degrees centigrade for 2 hours 15 minutes. At the end of this period, the setup was dismantled and distribution of radioactivity was estimated.

(iii) Use of pyrolysed acid for further extraction

These experiments were performed using simulated waste tagged with ruthenium - 103 at acid : TBP mole ratio of 4:1. After completion of one batch of extraction and pyrolysis as described above, required quantity of fresh simulated waste tagged with ruthenium - 103 was added to the flask in order to maintain mole ratio at 4:1 and experiment was repeated. After completion of 10 batches in this way, distribution of ruthenium - 103 was estimated.

3 RESULTS AND DISCUSSIONS

3.1 Extraction Experiments

(i) Experiments with simulated wastes

The graph indicating volume of kerosene phase separable at different acid : TBP mole ratios is shown in Fig. 1. At the mole ratio of 1:1, there is no clear separation of phases. This is probably due to insufficient quantity of phosphoric acid available for formation of phosphoric acid - TBP adduct. The volume of the kerosene phase separated rises rapidly with increase in the acid : TBP mole ratio upto 3:1. For mole ratios higher than 3:1, the volume of the kerosene phase separated stabilises at around 92 to 94 % of expected volume for both 15.6 and 17.6 M phosphoric acids studied. Hence, it is desirable to use acid : TBP mole ratios greater than 3:1 for separation of diluent kerosene in large-scale work. The presence of TBP in the kerosene separated in these experiments was tested qualitatively using congo red paper test [16]. The tests were positive in all the cases. One hour settling time was allowed in these experiments for reasons which are discussed below.

Variation of percent ruthenium- 103 activity carried to the separated kerosene phase with time after mixing is shown in Fig. 2. It is seen that the ruthenium - 103 activity decreases rapidly with time for about 15 minutes due to rapid settling of droplets of

heavier phosphoric acid - TBP adducts from the topmost kerosene phase. After about one hour, satisfactory disengagement of phases was observed and kerosene phase was clear. Also after this, there was no significant decrease in the ruthenium- 103 activity in the kerosene phase. Hence one hour settling time was adopted in all these experiments.

The quantity of antimony -124, ruthenium -103 and cerium - 141 remaining in the kerosene phase during extraction of TBP at different acid : TBP mole ratios is presented in Fig. 3 and Fig. 4 for 15.6 and 17.6 M phosphoric acids respectively. It is seen that the activity decreases very fast initially and then stabilises at near constant value for acid : TBP mole ratios higher than 3:1 for both the phosphoric acids studied.

In the extraction with 15.6 M phosphoric acid about 3.8 % antimony, 1.9 % ruthenium and 0.03 % cerium are left in the kerosene phase at acid : TBP mole ratio of 4:1. In extraction with 17.6 M phosphoric acid, 0.7 % antimony, 1.2 % ruthenium and 0.03 % cerium are left in the kerosene phase at acid : TBP mole ratio of 4:1. It may be noted from the above that by increasing the phosphoric acid concentration from 15.6 to 17.6 M, antimony and ruthenium activities carried over decrease by 5.4 and 1.2 times respectively, whereas there is no change in case of cerium. This behaviour is advantageous because ruthenium activity is most significant in actual wastes and the recycled acid in actual operation is expected to have concentration higher than 17.6 M.

(ii) Experiments with process solvents and aged wastes

Process solvents PS - 1 and PS - 2 were estimated to contain TBP around 30 percent V/V, whereas the values obtained for aged wastes AW - 1 and AW - 2 were 32 and 35 percent respectively. Besides, the aged waste samples also contained 0.15 to 0.25 gm per litre of dibutyl phosphate (DBP). Ruthenium- 106 was the major activity in all the 4 samples (10 to 8000 micro Ci per litre). Although other radionuclides like cerium - 144, cesium - 137 and zirconium - 95 were also detected in these samples, their concentrations were very low (less than 1 micro Ci per litre) and hence were not reported.

Results of the extraction experiments carried out with PS - 1 are reported in Table 1. It may be seen that volume of top diluent phase remains constant at all the four acid : TBP mole ratios, the value being about 92 percent of the expected volume of the diluent. This compares very well with 92 to 94 percent observed in case of simulated waste. From the values of TBP content in top diluent phase and the volume of middle phase, it appears that the complexation of TBP with phosphoric acid is complete at acid : TBP mole ratio of 3:1 or more. In order to verify this, the acid : TBP ratios in the middle phase were determined and the ratios were found to be in the range 2.0:1 to 2.6:1. These ratios were also calculated based on the findings of Higgins and Baldwin [13]. As may be seen from the Table, the calculated values are comparable with the experimental values. These results suggest that for complete complexation of TBP, a minimum of 4 moles of phosphoric acid should be available for every mole of TBP in large scale extraction work.

Results of the ruthenium and plutonium activities retained in the diluent phase after extraction of the solvent waste samples with phosphoric acid are presented in Table 2. Data obtained using simulated wastes are also included for comparison. It may be seen that in case of simulated waste and PS - 1, the quantity of ruthenium carried to the diluent phase at mole ratios of 3:1 and above is nearly constant irrespective of the quantity of phosphoric acid taken for extraction. Although the extraction was carried out at only one mole ratio in the case of PS - 2, AW - 1 and AW - 2, the ruthenium carried to the diluent phase is much larger being 4.2 to 6.8 percent. This might be partly due to the greater degree of degradation of these samples. Besides, the peculiar chemistry of ruthenium with multiplicity of oxidation states and complexes may also be a factor operating under these experimental conditions.

In regard to plutonium, it can be seen that its carry-over to diluent phase is 0.1 % in the case of process solvent PS - 2 and 0.5 to 1.1 % in the cases of aged wastes AW - 1 and AW - 2 even though the plutonium feed concentrations are not much different. Greater degradation of aged wastes might account for these observations.

With a view to improve the quality of the separated diluent phase, subsequent treatment with fresh phosphoric acid by way of second contact was tried in the cases of PS - 2, AW - 1 and AW - 2 wastes. Although this procedure resulted in substantial reduction of activities of other fission products, in case of

ruthenium the reduction was not significant. This behaviour seems to suggest that in multistage extractions using mixer - settlers, one has to put up with significant quantity of ruthenium at the end of final stage. Since the residual plutonium concentration after first contact itself was low (about 4 micro g per litre), second contact values were not estimated.

Results of the plutonium retention tests with separated diluent are given in Table 3. These tests were conducted to get information on the purity of these diluents with respect to degradation products. It may be seen that in case of the diluent from PS - 1, the forward extraction of plutonium decreases with increasing acid : TBP mole ratios, i.e. mole ratios greater than 3 yield better diluents. In regard to diluents from the remaining waste streams, forward extraction values are much higher than those in corresponding samples from PS - 1. However, there is a general decrease in plutonium concentration in samples subjected to second contact with phosphoric acid. Although small quantity of TBP is present in all these samples, it appears that the degradation products of diluents also contribute to the observed behaviour.

Although as noted above, the forward extraction of plutonium was less for diluent phases obtained after 2 successive contacts with phosphoric acid, there was no significant difference in the concentration levels of residual plutonium left in the diluent phase after 4 strip contacts with 0.1 M nitric acid. When a fresh n-dodecane

sample was subjected to the same test, the residual plutonium concentration in the diluent phase was found to be less than 0.01 mg per litre. This value is much lower than those obtained in case of diluents separated from PS - 1, PS - 2, AW - 1 and AW - 2. There was no improvement in the separated diluent quality even after washing it with 1.0 M sodium hydroxide, 0.5 M nitric acid and water successively. These steps would have removed the degradation products of TBP like DBP and MBP, if present, from the organic phase. Apparently these are not the impurities responsible for the plutonium retention observed in case of separated diluents. Thus the separated diluents will have to undergo further purification steps such as treatment with alumina and silica gel [17] before it can be reused as diluent for TBP in Purex process.

3.2 Pyrolysis Experiments

Data on the pyrolysis of TBP as a function of time in 14.7 and 17.6 M phosphoric acids at 175 and 200 degrees centigrade are presented in Fig. 5 and Fig. 6. respectively. In determining the percent pyrolysis completed a sample of the pyrolysis product was tested for pyrophosphoric acid by using colorimetric method [18]. The pyrophosphoric acid content was found to be low, as time of heating during pyrolysis was short and temperature low. Hence titration values were taken as ortho phosphoric acid.

From Fig. 5 and Fig. 6, it is seen that the initial rates of pyrolysis of TBP were faster in 17.6 M phosphoric acid when compared with the data on 14.7 M. However, the time required for 95 % completion of pyrolysis is about 2 hours in both the cases.

Effect of nitric acid on the rate of pyrolysis of TBP was studied to see whether there is any unusual catalytic effect during pyrolysis. In experiments without nitric acid the gas generation rate was found to rise steeply and then fall rapidly as pyrolysis was nearing completion. The peak gas generation rate in these experiments at 175 degrees centigrade and acid : TBP mole ratio of 4:1 using 15.6 M acid was around 150 ml per minute. It was found that the peak gas generation rate remained almost unchanged for nitric acid : TBP mole ratio upto 0.1:1.0 indicating negligible effect on rate of pyrolysis at the corresponding nitrate ion concentrations.

The results of experiments on pyrolysis of simulated waste tagged with antimony - 124, cerium - 141 and ruthenium - 103 at 175 degrees centigrade indicated that activity carried over to off-gases during pyrolysis was low. It was observed that about 0.5 % antimony and less than 0.1 % of cerium and ruthenium were carried over to off-gases at acid : TBP mole ratios of 3:1 and 4:1. The activity balance in these experiments was very good. The silica gel bed used in experiments with ruthenium- 103 showed traces of activity. This indicates that ruthenium volatilisation in the gaseous form during pyrolysis is low and it can be retained in silica gel bed effectively.

In order to study the effect of residual organic matter in the pyrolysed phosphoric acid on its efficiency, extraction cum pyrolysis cycle was repeated 10 times using the acid obtained from one cycle after pyrolysis for extraction in subsequent cycle. In this way, with an initial charge of 5 ml of phosphoric acid, it was possible to

treat nearly 600 ml of simulated wastes tagged with ruthenium - 103. The amount of ruthenium retained in the diluent phase was estimated at each cycle and was found to increase only slightly, i.e. from 1.7 to 2.4 percent at the end of the tenth cycle. The carry-over of ruthenium during pyrolysis was less than 0.1 percent. It appears from the above that a few percent of organic matter left in the acid after incomplete pyrolysis of TBP does not affect its performance.

4 CONCLUSIONS

These studies seem to offer a simple method for the separation of bulk of diluent from spent solvent wastes. As the major activity in the separated diluent is ruthenium (with only traces of plutonium) it can be safely incinerated. However it needs further purification for reuse in reprocessing plants.

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Table 1

EXTRACTION EXPERIMENTS WITH PROCESS SOLVENT PS - 1

Volume of Process Solvent PS-1 = 50.0 ml

Concentration of phosphoric acid = 15.2 M

Description	Phosphoric acid : TBP mole ratio			
	2:1	3:1	4:1	5:1
Volume of acid added (ml)	7.0	10.6	14.1	17.6
Volume of top diluent phase (ml)	32.0	32.0	32.0	32.0
TBP in diluent phase (% V/V)	2.4	1.2	0.5	0.5
Volume of middle phase (ml)	20.0	22.0	22.0	22.0
Acid : TBP in middle phase				
Experimental (± 5%)	1.6:1	2.0:1	2.4:1	2.6:1
Calculated	1.8:1	2.3:1	2.2:1	2.2:1

Table 2

RUTHENIUM AND PLUTONIUM ACTIVITIES RETAINED (IN %) IN THE TOP
DILUENT PHASES AT DIFFERENT ACID :TBP MOLE RATIOS

Type of waste	Phosphoric acid : TBP mole ratio			
	2:1	3:1	4:1	5:1
Simulated Waste				
Ruthenium	3.6	2.0	1.9	1.8
Process Solvent PS - 1				
Ruthenium	11.9	2.7	2.4	2.9
Process Solvent PS - 2				
Ruthenium				
after first contact	----	----	----	6.8
after second contact	----	----	----	4.2
Plutonium				
after first contact	----	----	----	0.1
Aged Waste AW - 1				
Ruthenium				
after first contact	----	----	5.2	----
after second contact	----	----	4.6	----
Plutonium				
after first contact	----	----	0.5	----
Aged Waste AW - 2				
Ruthenium				
after first contact	----	----	6.7	----
after second contact	----	----	5.7	----
Plutonium				
after first contact	----	----	1.1	----

TABLE 3
PLUTONIUM RETENTION TESTS WITH SEPARATED DILUENTS

Sr. No.	Diluent	Acid: TBP mole ratio	TBP concn. in diluent (% V/V)	Pu concn. in diluent in (mg/ l)	
				after Loading	4 Strippings
1	Fresh dodecane	----	-----	< 0.01	----
2	PS - 1	2:1	2.4	-----	-----
		3:1	1.2	3.18	0.43
		4:1	0.5	0.81	0.43
		5:1	0.5	0.71	0.04
3	PS - 2	5:1	----	10.30	0.81
		5:1	-----	2.78*	1.07
4	AW - 1	4:1	0.73	2.37	0.57
		4:1	----	2.57*	0.59
5	AW - 2	4:1	0.52	4.25	1.32
		4:1	0.18	1.13*	0.75

* second contact samples.

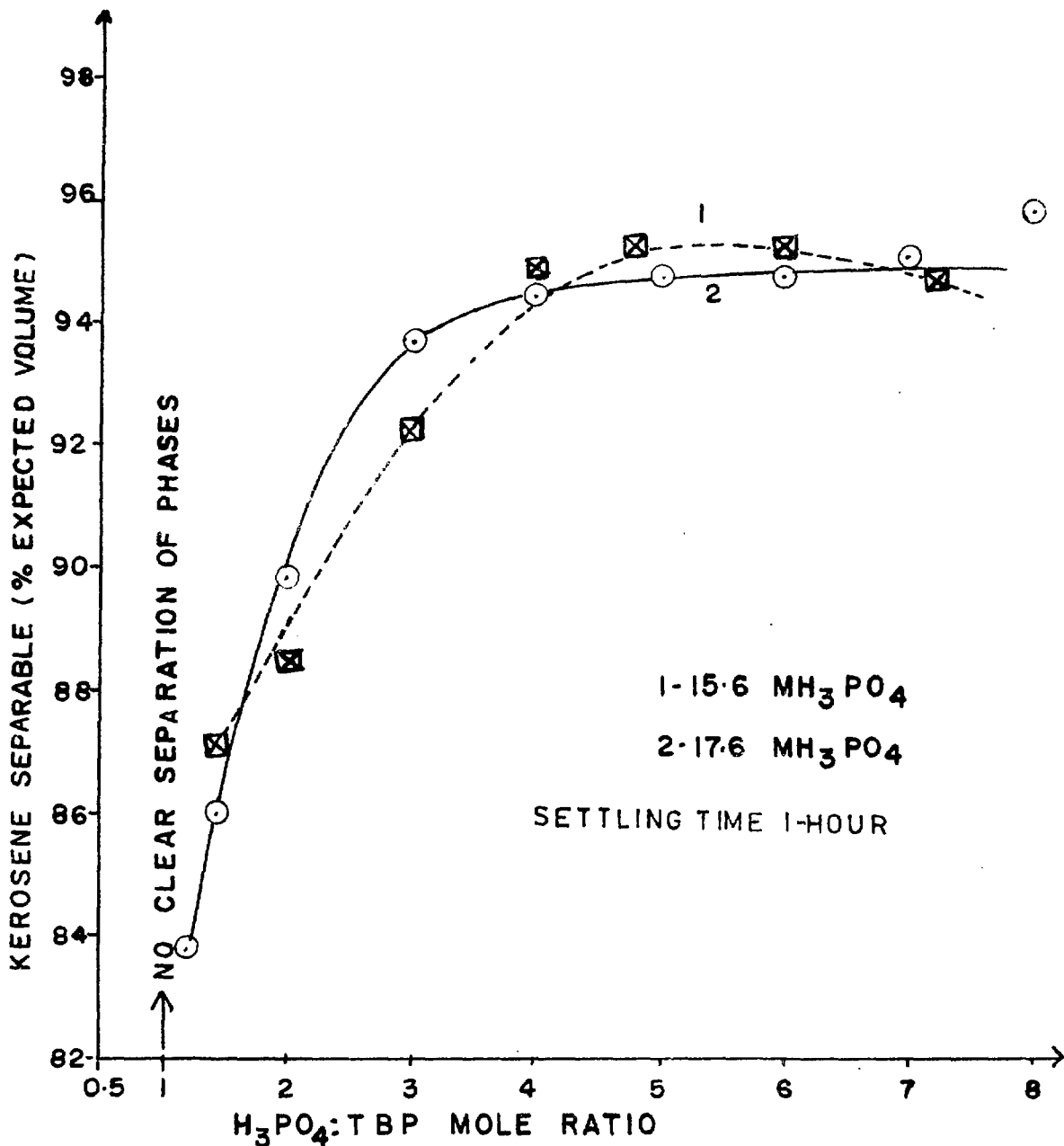


FIG:1 KEROSENE SEPARABLE FROM 30% TBP-KEROSENE BY EXTRACTION WITH H_3PO_4

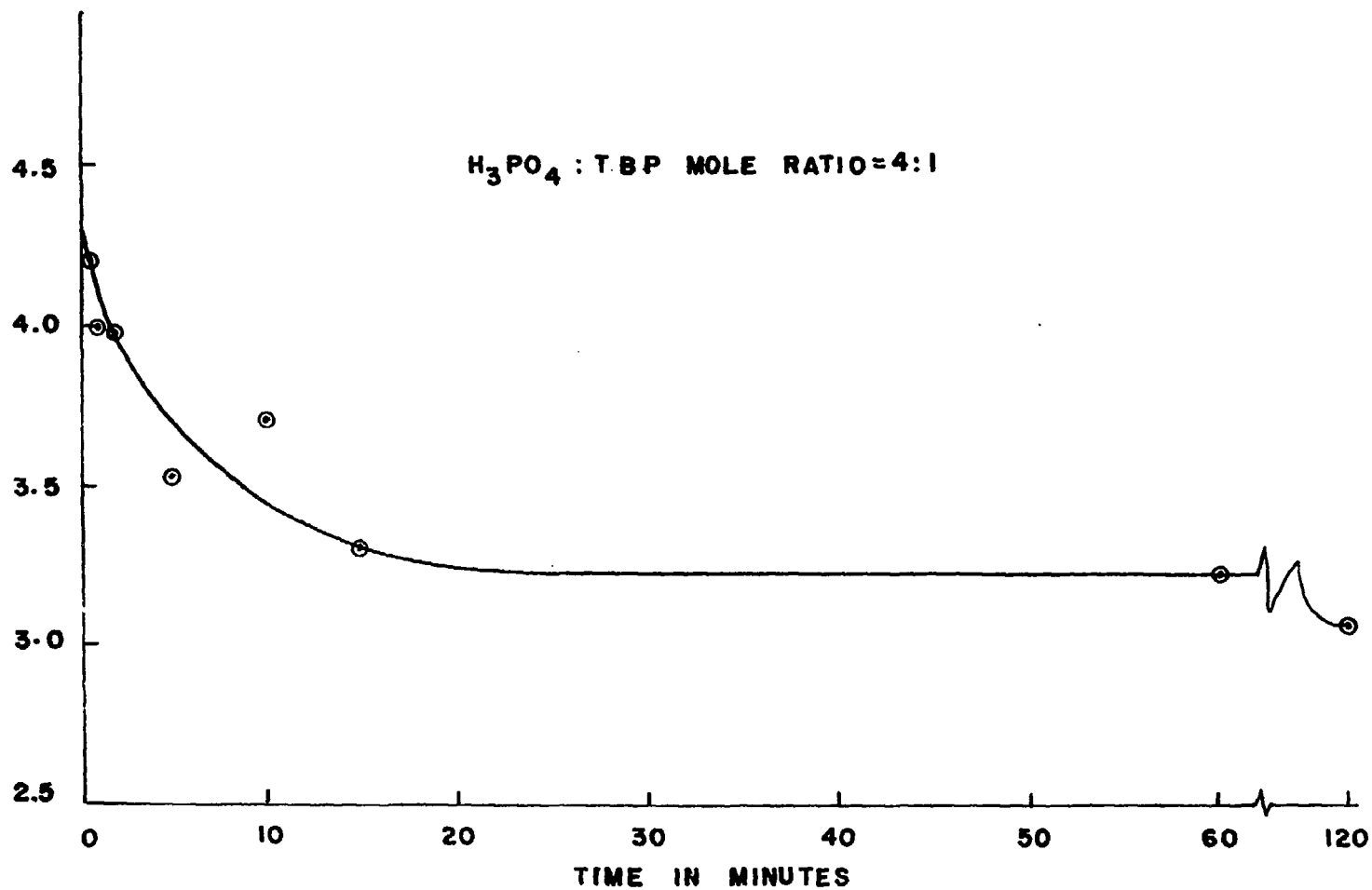


FIG. 2 :- AMOUNT OF Ru. TRACER CARRIED TO KEROSENE PHASE DURING EXTRACTION OF TBP FROM 30% TBP - KEROSENE INTO 15.6 M H_3PO_4

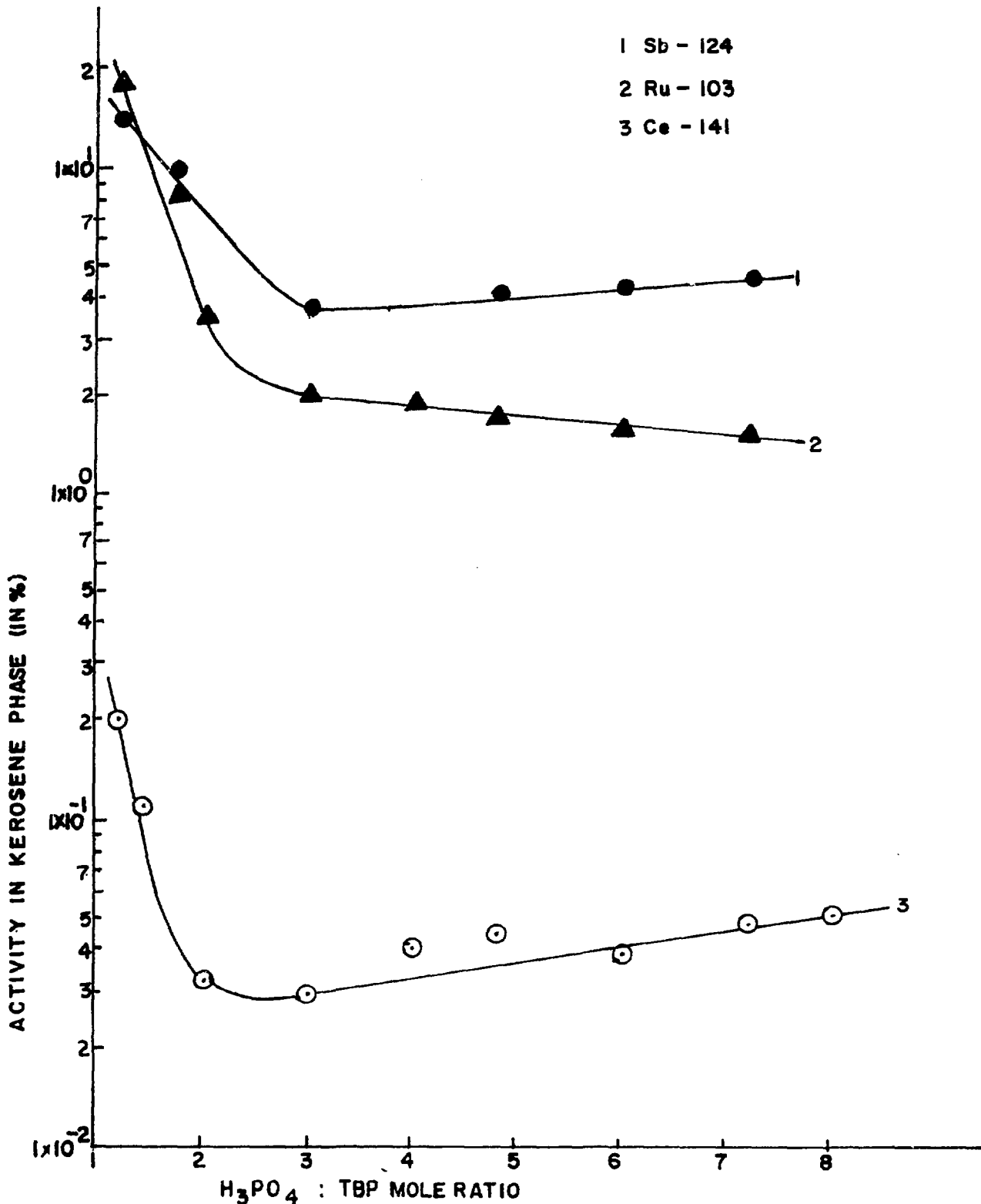


FIG-3 AMOUNT OF Sb, Ru AND Ce TRACERS CARRIED TO KEROSENE PHASE DURING THE EXTRACTION OF TBP FROM 30% TBP-KEROSENE INTO 15.6 M H_3PO_4

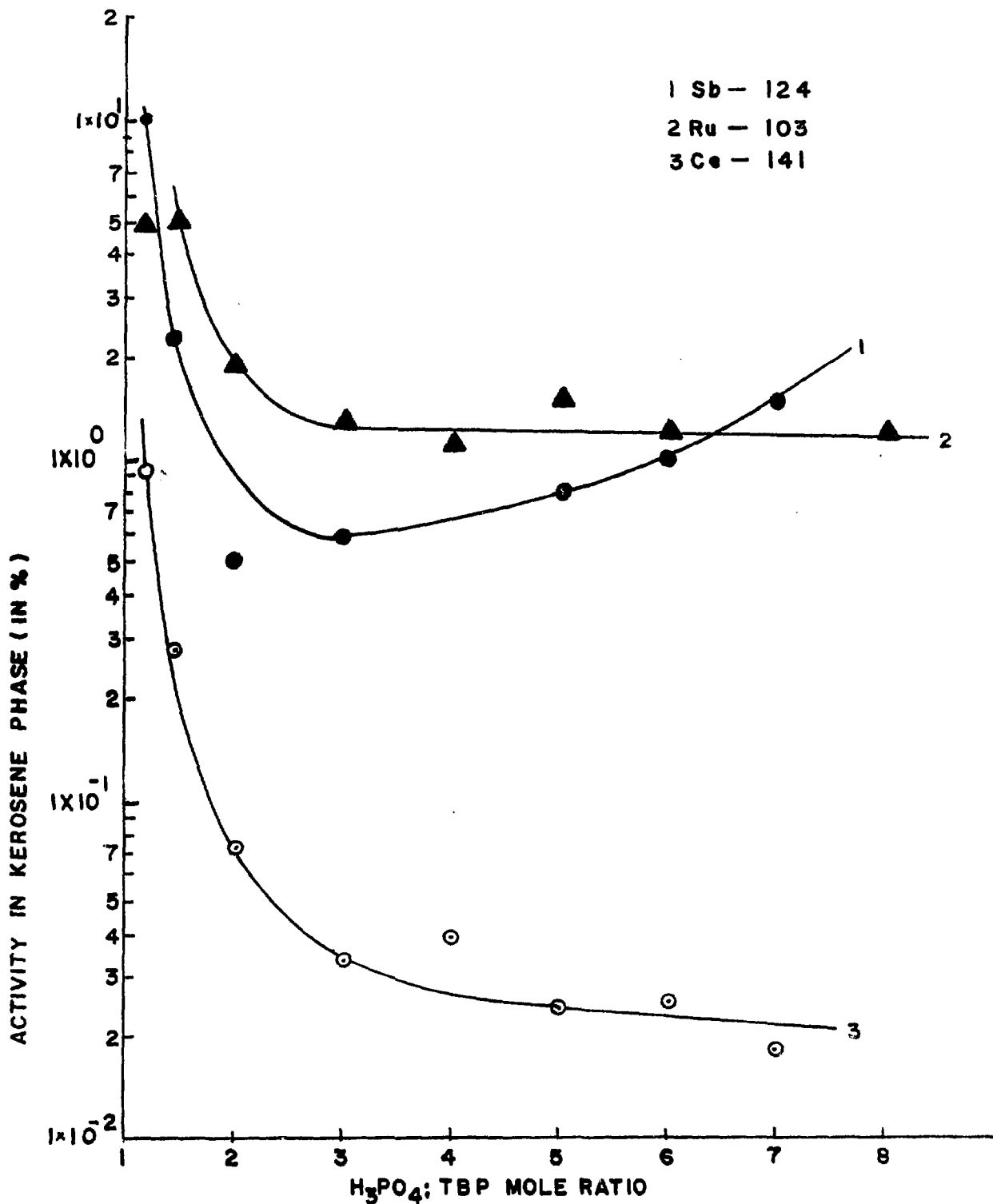


FIG-4 AMOUNT OF Sb, Ru AND Ce TRACERS CARRIED TO KEROSENE PHASE DURING THE EXTRACTION OF T B P FROM 30% T B P-KEROSENE INTO 17.6 M H_3PO_4

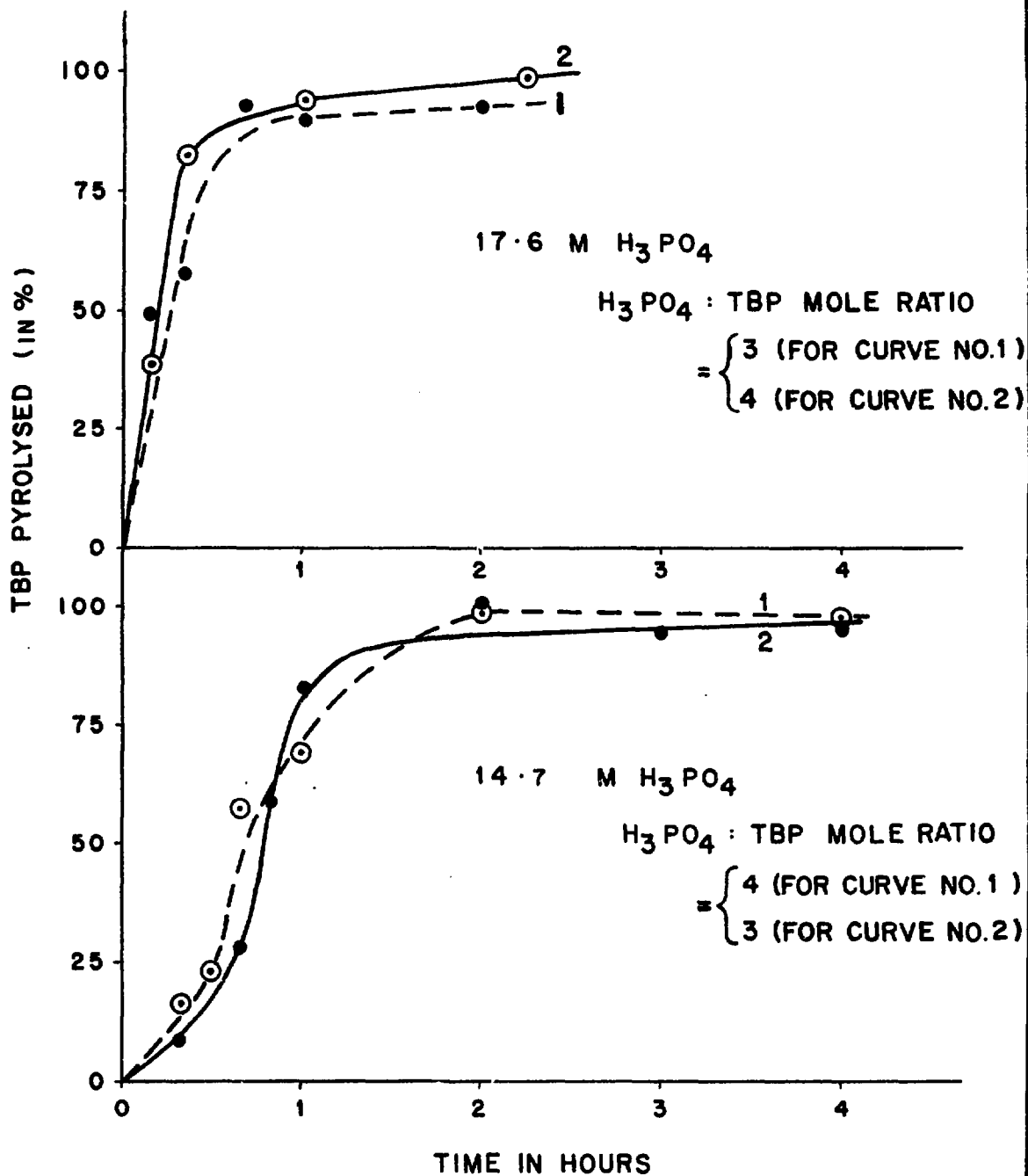


FIG. 5 . PYROLYSIS OF TBP IN H_3PO_4 AT $175^\circ \pm 5^\circ C$

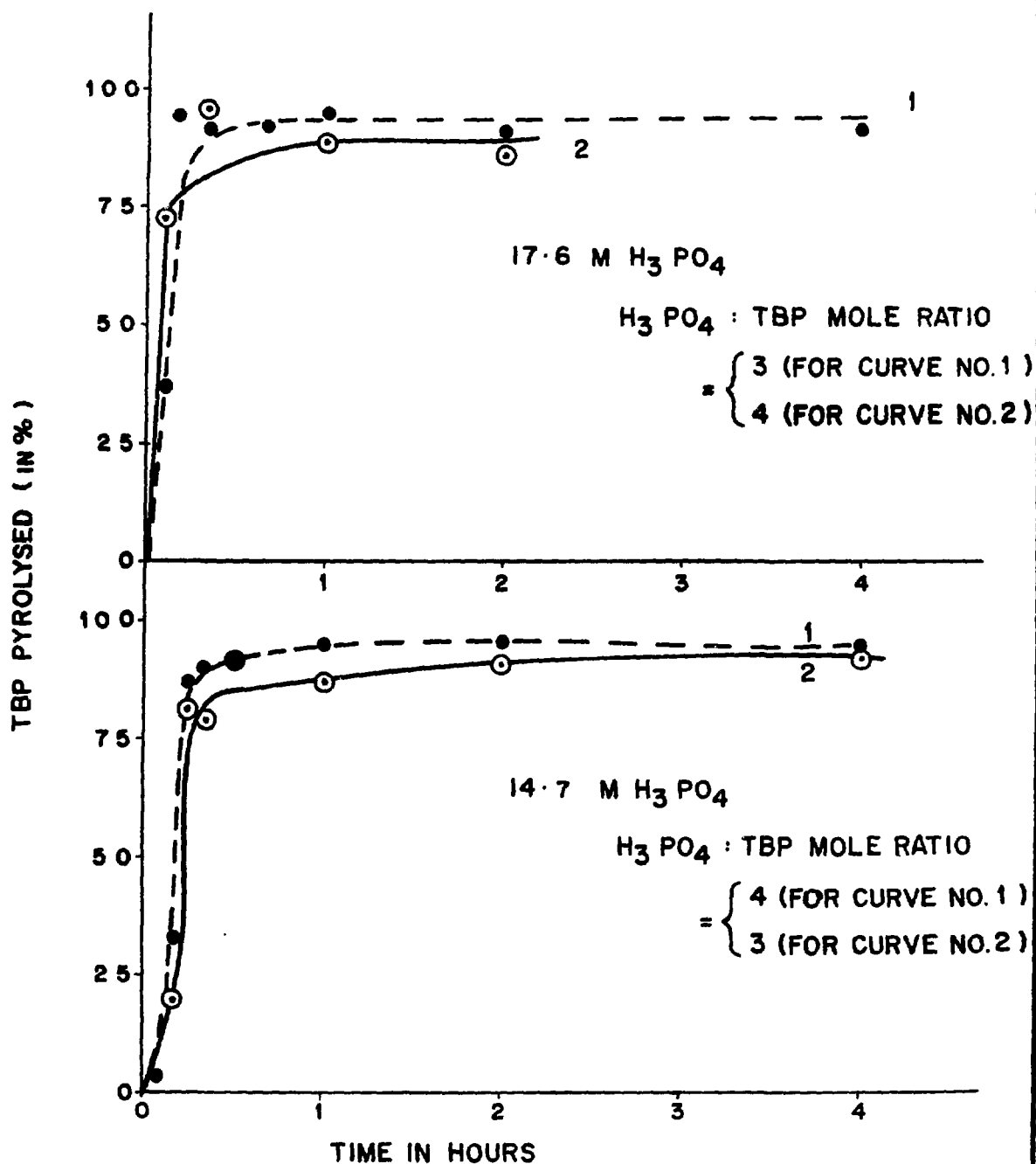


FIG. 6. PYROLYSIS OF TBP IN H₃PO₄ AT 200° ± 5° C

