CI-R-15
(Declassified Reprint)
SCS-R-163

Ministry of Supply

CHEMICAL INSPECTORATE

# THE REACTION BETWEEN HYDROGEN PEROXIDE AND SOLUTIONS OF PURE URANYL SALTS.
## PART I: THE INTERACTION OF HYDROGEN PEROXIDE AND URANYL NITRATE

by

J. R. SANDERSON, H. E. DIBBEN
and H. MASON
Springfields Works

Date of Manuscript May, 1951

Reprinted by

United Kingdom Atomic Energy Authority, Industrial Group Headquarters
Risley, Warrington, Lancashire

1959

# DISCLAIMER

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or 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 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

## SUMMARY

Potentiometric titration and other experiments indicate that the mechanism of the interaction in solution of pure uranyl nitrate and hydrogen peroxide is governed by the pH and the concentration of the reactants. In absence of free nitric acid the reaction proceeds to completion, as it does when the pH is raised, although hydrolysis then occurs also; in the presence of free nitric acid reaction reversal, i.e. dissolution of uranium peroxide, takes place, thus reducing the precipitation efficiency, but excess hydrogen peroxide, aiding the forward reaction, reduces this effect. At concentrations of 0.05 M and 0.005 M the optimum precipitation pH appears to be that of a solution containing uranyl and nitrate ions in stoichiometric proportions, at which point the reaction is almost quantitative and the rate of settling of the precipitate is the highest.

The progressive addition of ammonium hydroxide to neutral uranyl nitrate in solution results in hydrolysis without precipitation until a compound, perhaps $[(UO_3)_2UO_2OH]\ +NO_3$, exists in the solution which irreversibly slowly hydrolyses with formation of a precipitate which is possibly the trimer of uranyl hydroxide. Further addition of ammonium hydroxide results in the formation of an insoluble uranate, possibly $(UO_3)OH.NH_4$.

CI/R-15

(Seven figures).

# THE REACTION BETWEEN HYDROGEN PEROXIDE AND SOLUTIONS OF PURE URANYL SALTS

## Part I: The Interaction of Hydrogen Peroxide and Uranyl Nitrate

by

H.E.Dibben, H.Mason and J.R.Sanderson

---

The uranium purification process as at present carried out at Springfields involves the step of interacting a solution of uranyl sulphate and hydrogen peroxide with consequent precipitation of impure uranium peroxide. Although the process has been in use for some considerable time it has been unsatisfactory in a number of respects. Slow settling of the precipitate has been encountered at intervals, resulting in inefficient washing and consequent sulphate contamination of the product. Since such contamination has adverse effects on the partition coefficient of the uranyl nitrate/ether/water system, it has been found necessary to reprocess batches of uranium peroxide containing more than 5 per cent sulphate.

In the course of discussions, it transpired that the precipitation conditions had been arrived at by empirical methods, the time available for development work not permitting closer examination of the reactions involved.

In view of the processing difficulties which had been encountered, however, it was felt that some understanding of the reaction was desirable, and accordingly experimental work designed to afford information of the course and nature of the precipitation reaction involved has been carried out.

The problem appears to be complex, and aspects of it which it is intended to deal with in future investigations include:

(i) Production concentration reactions (12-15%U) in the uranyl nitrate - hydrogen peroxide system:
(ii) Reactions between uranyl sulphate and hydrogen peroxide;
(iii) Effect of anions and cations on the reaction when present in varying concentrations;
(iv) Effect of anions and cations on the decomposition of hydrogen peroxide;
(v) Effect of temperature;
(vi) Analytical work on uranium peroxide precipitated under various conditions;
(vii) Rate of settling and particle size and shape.

Other relevant factors may reveal themselves as the work progresses, but experience so far obtained on a production scale indicates that investigation of the above matters is essential.

## INTRODUCTION

There is evidence that the uranyl ion complexes with the sulphate ion. It was felt desirable to avoid complications from this source to start with, and accordingly the preliminary investigation described in this report was confined to the reaction between hydrogen peroxide and uranyl nitrate.

The equation generally ascribed to the reaction between uranyl nitrate and hydrogen peroxide in solutions of pH 2 to 4 is

$$UO_2(NO_3)_2 + H_2O_2 \rightleftharpoons UO_4 + 2HNO_3,$$

the reaction proceeding almost completely to the right under the appropriate conditions of pH and concentration. Free nitric acid, produced in this reaction, causes the pH to fall.

As a first line of attack, it seemed likely that titration of a solution of uranyl nitrate with hydrogen peroxide would yield interesting results if the reaction were followed potentiometrically. When illustrated graphically, such an experiment might possibly give evidence of intermediate products or discontinuities in the reaction.

## TITRATION EXPERIMENTS AND DISCUSSION.

### Potentiometric titration of M/200 uranyl nitrate with hydrogen peroxide (Expts. 1 and 2).

100 ml. of M/100 uranyl nitrate (prepared by dissolving 2.38 grams of uranium metal in minimum amount of nitric acid and diluting to 1 litre) was pipetted into a 400 ml. squat beaker and diluted to 200 ml. with water. Ammonium hydroxide was added until a pH was reached of 3.19 in the first experiment and 4.27 in the second; M/10 hydrogen peroxide (prepared by diluting stock solution and standardising with N/10 potassium permanganate) was then run in from a burette and pH readings were taken during the titration.

A Cambridge pH meter with glass electrode and saturated potassium chloride-calomel (dip type) electrode system was used for pH measurements.

The potentiometric curves obtained are as shown in Fig. 1 and the following features were noted during the experiment:

(a) The appearance of the uranyl nitrate solution at pH 3.19 was no different from that of a similar solution at pH 1.0, while on the other hand the solution at pH 4.27 had acquired a distinctly deeper yellow colouration, indicating hydrolysis of the uranyl nitrate.

(b) On addition of 2 to 3 ml. of hydrogen peroxide, both solutions became a deeper yellow in colour without precipitation, and the pH fell to a lower value. On standing, precipitation occurred; this at first took the form of a turbidity, and then, on further addition of the reagent, flocculation and settling resulted.

(c) From consideration of the two curves in Fig.1 it would seem that the amount of acid liberated on addition of hydrogen peroxide is less than that required by the equation $UO_2^{++} + H_2O_2 \rightleftharpoons UO_4 + 2H^+$. In the two experiments, the liberated hydrogen ion should have reduced the pH to about 2.0 but it was, in actual fact, reduced only to about 2.3 and this apparent discrepancy could perhaps be explained by a back reaction taking place. Further work on these lines is detailed below. The shapes of the two potentiometric curves differ at the beginning of the titration; in Experiment 1 the pH falls rapidly with added peroxide, whilst in Experiment 2 the pH falls slowly, then more quickly after addition of about 0.25 mol. of peroxide. Both curves begin to flatten out in the region of 1 mole of added peroxide. After addition of 2.5 mols they are almost, but not quite, parallel to the horizontal axis.

## Effect of precipitation pH on the amount of hydrogen ion liberated on addition of hydrogen peroxide.

The apparent discrepancy between the theoretical and actual amount of $H^+$ liberated in the reaction ((c) above) appear to be worth further investigation; obviously it could have a strong bearing on the production precipitation efficiency, i.e. the extent to which the reverse reaction proceeds will determine the uranium content of the mother liquor. Several precipitations were therefore carried out at varying initial pH values.

100 ml. of M/100 $UO_2(NO_3)_2$ solution was diluted to 200 ml. and ammonia was run in until the desired pH was reached. 20 ml. of hydrogen peroxide (M/10) was then added (i.e. 100% excess), and the solution was titrated with N/10 ammonium hydroxide until the initial pH was reached. The results are shown in Table I.

TABLE I

| Experiment | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|
| Precipitation pH | 2.20 | 2.27 | 2.62 | 3.0 | 3.32 | 3.7 | 4.21 | 4.70 | 5.04 | 5.61 |
| % Theoretical acid liberated | 10.5 | 47.7 | 85.0 | 95.0 | 97.0 | 91.5 | 65.5 | 39.5 | 26.0 | 2.95 |

The amount of $H^+$ liberated in the above experiments is shown in the table as the percentage of that required by the equation

$$UO_2(NO_3)_2 + H_2O_2 \longrightarrow UO_4 + 2HNO_3.$$

Alternatively, this may be described as the percentage of the theoretical amount of ammonium hydroxide required to keep the pH constant during the addition of hydrogen peroxide. The results are shown graphically in Fig.2. The shape of this curve is surprising. In the high pH experiments, very little $H^+$ is liberated, e.g. at pH 5.61 only 2.95% appears. As the pH of precipitation is lowered, however, the amount of liberated $H^+$ increases and reaches a maximum of 97% at pH 3.3. It then falls off again at pH values below 3.3. The results for experiments below pH 2.4 cannot be considered very accurate owing to the fact that in this region a fairly large addition of ammonia produces little change in pH, and the end-point is ill-defined.

## Potentiometric titration of M/200 uranyl nitrate with M/10 ammonium hydroxide (experiments 13a and 13b)

It now became apparent that some knowledge of the hydrolysis of uranyl nitrate solutions was desirable. Previous work (3.4) carried out at Springfields, dealing with the potentiometric titration of uranyl nitrate and sulphate with alkali, had shown that the position of the points of inflection varies with uranium concentration. The two reports dealt with more concentrated uranium solutions and it seemed necessary to investigate the hydrolysis at the M/200 level.

For this purpose, 200 ml. of M/200 uranyl nitrate solution were titrated potentiometrically with ammonium hydroxide (N/10), using mechanical stirring. The pH meter assembly was identical with that used in preceding experiments, In Experiment 13a, the titration was completed in about 45 minutes, while in Experiment 13b, the titration was carried out over 24 hours. In the latter experiment the solution and precipitate were finally back-titrated with N/10 nitric acid. This titration was extremely slow, requiring several days to reach completion.

The potentiometric curves obtained appear in Fig.3. It will be seen that both the slow and quick titrations give similar curves up to the point B. Thereafter (B to S) the quick titration curve is similar to that given by Armson (3). As the curve B to S probably does not represent true equilibrium conditions, discussion will be confined to the slow titration.

The first inflexion appears at pH 3.3, and this represents the neutralisation point of the free acid present in solution. As titration proceeds the curve becomes less steep until point B is reached, where another inflexion occurs. After this point, at B', precipitation commences and the pH falls to point C. The fall is very slow and 20 hours, standing is required before a stable state is reached. Precipitation is incomplete at this point and the precipitate is crystalline.

On proceeding further with the titration, the pH again increases slowly until a sudden rise occurs with maximum slope at point E. Back titration of the solution and precipitate from point O with nitric acid produces the curve OE'C'F. This curve follows the forward titration fairly closely to point C'. The precipitate does not dissolve at this point, however, and the pH remains constant until the point F is reached. At this point the last trace of precipitate dissolves. In the forward titration, no precipitate is produced until point B' is reached (pH 5.6), while in the back titration a precipitate exists until the point F (pH4.2) is reached. Thus the slow hydrolysis occurring between B' and C is apparently irreversible and indicates that the solution between points F and B' is metastable.

The inflexion at B occurs after the addition of 5/6 equivalents of ammonium hydroxide per equivalent of the divalent uranyl ion. Thus it may be stated that the greatest degree of hydrolysis which the uranyl ion can undergo without incipient precipitation is reached at this point.

The hydrolysis occurring during the titration from A to B can perhaps be represented by

$$3\,UO_2^{++} + 5OH^- \rightleftharpoons (U_3O_8OH)^+ + 2H_2O \; \ldots\ldots\ldots\ldots (I)$$

Further addition of ammonium hydroxide causes precipitation. Thus at B' a precipitate appears and increases in amount, the pH falling as a result of the continued hydrolysis

$$(U_3O_8\ (OH))^+ + H_2O \rightleftharpoons U_3O_8\ (OH)_2 + H^+ \quad .. \quad .. \quad .. \ (II)$$

The precipitate is possibly a trimer of uranyl hydroxide. It is apparent that at point B the soluble uranium compound is metastable. As soon as the precipitate in (II) is formed the system reverts slowly to the stable state. At point C, the uranyl hydroxide appears to be in equilibrium with a soluble uranium compound, possibly less complex than the $(U_3O_8(OH))^+$ ion, but the degree of polymerisation of the uranyl ion at this point is uncertain. Continuation of the titration results in the sharp inflection at E after the addition of 1 1/6 equivalents of $NH_4OH$. It would appear that, after addition of 1 equivalent of $NH_4OH$, the uranium is completely precipitated as $U_3O_8(OH)_2$, and further addition of 1/6 equivalent results in the formation of an ammonium uranate, usually referred to as ammonium diuranate $(NH_4)_2U_2O_7$. The composition of this precipitate has not been determined during this work, since it is intended to carry out a more detailed investigation later, but it appears possible that the product at this stage could have the composition $(U_3O_8(OH)_3)NH_4$ or $(U_3O_8OH)ONH_4$, containing about 2 per cent of ammonia.

The above conclusions are in agreement with the reactions suggested by Sutton (5), who gives the following ion species as occurring during the titration of uranyl perchlorate with sodium hydroxide:-

$$U_2O_5^{++},\ U_3O_8^{++},\ U_3O_8(OH)_2,\ (U_3O_8(OH)_3)^-$$

on the basis of oxyoscopic measurements, potentiometric, conductometric and absorption spectra data. Arden and Harbutt (6) found that the course of the reaction between uranyl sulphate and calcium hydroxide differed in some respects from that between uranyl perchlorate and sodium hydroxide, e.g. the first precipitate formed was believed to be the tetramer of uranyl hydroxide, $[UO_2(OH)_2.U_3O_8(OH)_2]$. They attribute this difference to complex formation between the uranyl and sulphate ions. Tanford, Tichenor and Young (7) have studied the hydrolysis of uranyl nitrate with calcium hydroxide and have suggested that the first precipitate is the trimer of uranyl hydroxide. It would seem, therefore, that the hydrolysis of uranyl nitrate with ammonium hydroxide may be similar to that of uranyl nitrate or perchlorate with calcium hydroxide and sodium hydroxide, at least as far as the formation of the first precipitate, while with uranyl sulphate and calcium hydroxide the course of the reaction is modified by the sulphate/uranyl ion complex formation.

As the present Springfields process entails precipitation of uranium peroxide from sulphate solutions, this complex formation may possibly effect precipitation, and it must not be assumed that any conclusions drawn from the present work (precipitation from nitrate solutions) are necessarily applicable to precipitation from sulphate solutions.

## Discussion of results of Experiments 1-13

The point of maximum acid liberation on addition of hydrogen peroxide to uranyl nitrate solution occurs when the addition is made to a solution containing no free acid. Thus the maximum of the curve in Fig. 2 (Experiments 3 and 2) occurs at the same pH as that of the free acid end point shown in Fig. 3 (Experiment

13). However, the coincidence of the free acid end point pH and the pH of maximum acid liberation could be fortuitous, and a further check appeared to be desirable. This was achieved by utilising the fact that an increase in the uranium concentration results in the lowering of the free acid end point pH (4). Thus, with M/20 uranyl nitrate solutions the curve obtained in Fig. 2 should be displaced to the left, the maximum occurring at a pH corresponding to that of the new free acid end point pH. A repetition of Experiments 3-13 using higher uranyl nitrate concentrations is, therefore, capable of confirming whether this coincidence is fortuitous or not.

### Potentiometric titration of M/20 uranyl nitrate with N ammonium hydroxide solution (Experiment 21)

The experimental details are identical with those for Experiment 13 except that a M/20 solution of uranyl nitrate and a N solution of ammonium hydroxide were used. The titration curve is shown in Fig. 6.

### Effect of precipitation pH on the amount of hydrogen ion liberated on addition of hydrogen peroxide (Expts. 22/34)

The experimental details are identical with those for Experiments 3-12 but with tenfold increase in the concentration of all solutions used. The results are shown in Table II and illustrated in Fig. 5.

TABLE II

| Expt. | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pptn.pH. | 1.7 | 1.90 | 2.0 | 2.3 | 2.6 | 3.0 | 3.4 | 3.82 | 3.48 | 4.4 | 4.8 | 5.0 | 2.47 |
| % acid liberated | 89.5 | 92.5 | 93.3 | 95.9 | 97.0 | 92.5 | 82.5 | 60.0 | 45.3 | 33.4 | 24.7 | 20.0 | 95.8 |

Comparison of Figs. 6 and 5 shows that, as anticipated, the point of maximum acid liberation occurs at the pH of the free acid end point. It is not intended to deal with concentrated (o.5 molar) solutions in this part of the investigation, but it may be mentioned here that there is some indication that the same effect is observed with solutions of this concentration. Again, in the curve in Fig.5 the amounts of acid liberated at pH values below 2 are approximate only. Equilibrium in these experiments is attained slowly, and this, together with the insensitiveness of the pH meter to small pH changes at high $H^+$ concentration, makes the titration inaccurate.

### Potentiometric titration of M/200 uranyl nitrate solutions with M/10 hydrogen peroxide commencing at various pH values (Experiments 14-20)

The two curves for experiments 1 and 2 differed essentially in form, and it appeared probable that titrations over a wider range of initial pH values would yield useful information. The curves obtained in such experiments are to be found in Figure 4. It will be seen that the curves for experiments which commenced above the pH of the free acid end point have the same form as that for Experiment 2, whilst those commencing below the free curves, except those for Experiments 14 and 15, the pH was still falling slightly, even after addition of 100% excess (i.e. 2

mols) of hydrogen peroxide. In Experiments 14 and 15, the pH became constant just after addition of the theoretical amount of hydrogen peroxide, and remained so up to the addition of a further one and a half mols, when the addition was discontinued.

## SUGGESTED MECHANISM FOR THE HYDROGEN PEROXIDE-URANYL NITRATE REACTION

From the preceding results the following mechanism may be suggested for the interaction of hydrogen peroxide and uranyl nitrate. Below the pH of the free acid end point a solution of uranyl nitrate contains free nitric acid. On addition of ammonium hydroxide the pH rises until the free acid is neutralised, when an inflexion occurs. This is followed by hydrolysis of the uranyl nitrate, the degree of which is determined by the volume of ammonium hydroxide added.

Addition of a small amount of hydrogen peroxide to a solution of uranyl nitrate, the pH of which is higher than that of the free acid end point. produces a characteristic potentiometric titration curve of the form given by experiments 14, 15, 16 and 17. In such solutions the following equilibrium may exist:-

$$3UO_2^{++} + 5OH^- \rightleftharpoons (U_3O_8OH)^+ + 2H_2O \quad \ldots\ldots\ldots\ldots \quad \text{(III)}$$

The addition of a small amount of hydrogen peroxide results in the removal of some $UO_2^{++}$ ions from the left hand side with the production of hydrogen ion and precipitation of $UO_4$:

$$UO_2^{++} + H_2O_2 \rightarrow UO_4 \downarrow + \quad 2H^+ \quad \therefore \ldots\ldots\ldots\ldots \quad \text{(IV)}$$

followed by

$$2H^+ + 2OH^- \rightarrow 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(V)}$$

The net effect is to remove both uranyl and hydroxide ions, and the equilibrium is moved towards the left in III, with the production of $UO_4$ at the expense of the hydrolysis product. Thus, continued titration will result in the ultimate disappearance of the compound $U_3O_8(OH)^+$, which, while it is present, acts as a buffer, removing hydrogen ions as they are formed. The potentiometric curves therefore have a gently sloping portion at the beginning of the titration. When all the hydrolysis form has disappeared the only uranium-containing ions left in solution are uranyl ions, and at this stage reaction IV only takes place, the pH falling rapidly. Completion of the reaction is shown by a flattening of the curve after addition of 1 mol. of hydrogen peroxide.

In neutral solutions the uranium exists almost completely as the uran ion. Precipitation at this pH occurs according to the equation IV and the amount of acid liberated approaches the theoretical.

The mechanism in acid uranyl nitrate solutions is similar to that in neutral solutions, but the reverse reaction operates to an extent determined by the amount of free acid in the uranyl nitrate solution, so that the uranium is incompletely precipitated and less than the theoretical quantity of acid from nitrate ion in combination is liberated. Reaction IV can be made to move further to the right under these conditions, if excess hydrogen peroxide is added. Thus, the reason for the sloping portion of the curves at the end of titration in experiments 16-20 inclusive can be explained.

It will be noted that in all these experiments the final pH was below the free acid end point pH, and hence on addition of one mol of hydrogen peroxide the reactions were not completed. Addition of excess $H_2O_2$ resulted in precipitation of a little more $UO_4.2H_2O$ and liberation of an equivalent amount of nitric acid. In Experiments 14 and 15, the final pH was higher than the free acid end point pH, and hence the reactions were complete on addition of one mol of $H_2O_2$. Further addition therefore had no effect on the system except that of dilution.

## EFFICIENCY OF PRECIPITATION AT VARIOUS pH VALUES

From considerations outlined above, it is apparent that if a solution of uranyl nitrate is precipitated with hydrogen peroxide at a pH equal to, or greater than, the free acid end-point pH complete precipitation must take place, while at lower pH values precipitation is incomplete due to the occurrence of a reversible reaction. Experiments 35 and 40 were carried out to confirm these points.

In these experiments 200 mls. of M/20 $UO_2(NO_3)_2$ solution were treated with ammonium hydroxide to give a solution of definite pH. Slightly more than 1 mol. of hydrogen peroxide was added, and the solution titrated with ammonia until the initial pH was reached. The contents of the beaker were then transferred to a 250 ml measuring cylinder and the rate of settling was observed. The solution and precipitate were allowed to stand overnight in an aliquot of the filtrate was then used for the determination of soluble uranium and excess hydrogen peroxide.

TABLE III

| Expt. | Ppt. pH | Conc. of U in filtrate mols/litre | Conc. of $H_2C_2$ in filt. mols/litre | Pptn. eff. % | Settling* | Amt. of $H_2O_2$ added mls. M |
|---|---|---|---|---|---|---|
| 35 | 3.97 | .000004 | .0100 | 100- | 25 mins. | 11.0 |
| 36 | 2.93 | .000004 | .0095 | 100- | 13 mins. | 11.0 |
| 37 | 2.26 | .000006 | .0110 | 100- | 11 mins. | 11.0 |
| 38 | 1.54 | .0004 | .0121 | 99 | 20 mins. | 11.0 |
| 39 | 1.09 | .0146 | .0146 | 93 | 30 mins. | 11.0 |
| 40 | 0.83 | .0278 | .0278 | 62.5 | Several hours | 11.0 |

*Settling is expressed as the time for the level of the precipitate to fall 10 cms. from the surface of the solution.

The results are recorded in Table III and plotted in graphical form in Fig. 7. As anticipated, complete precipitation occurs at pH values above the free acid end-point pH. Below this point, the efficiency falls off with increasing rapidity. The point at which precipitation just ceases to occur was determined in the following manner:- 200 ml. of M/20 $UO_2(NO_3)_2$ were made strongly acid (pH 0.0) with nitric acid, 11.0 mls of M/1 $H_2O_2$ were added, and ammonia was run in until a turbidity just appeared; the pH at this point was noted and is, presumably, approximately the point at which the reaction is completely reversed under the conditions of the experiment. The settling times show great variability, settling being most efficient in the region of the free acid end-point pH. In all cases, however, the mother liquor was turbid, containing fine particles which did not settle for some hours.

## CONCLUSIONS

The reaction of hydrogen peroxide with uranyl nitrate has been shown to follow a course which is dependent on the hydrogen ion and uranium concentrations of the solution. If precipitation is carried out at or above the pH of the free acid end point of the uranyl nitrate solution, the extent to which precipitation occurs is almost 100%. Below this pH value, the precipitation is incomplete owing to the operation of the reverse reaction, and the extent to which the precipitation is affected is dependent upon both pH and the excess of hydrogen peroxide. It also seems clear that the settling properties of the precipitate from solutions at the M/20 level is affected to some extent by the pH at which the precipitation is carried out, best conditions apparently obtaining at the pH of the free acid end-point. Such low concentration of uranium would be encountered perhaps in the treatment of low grade ore.

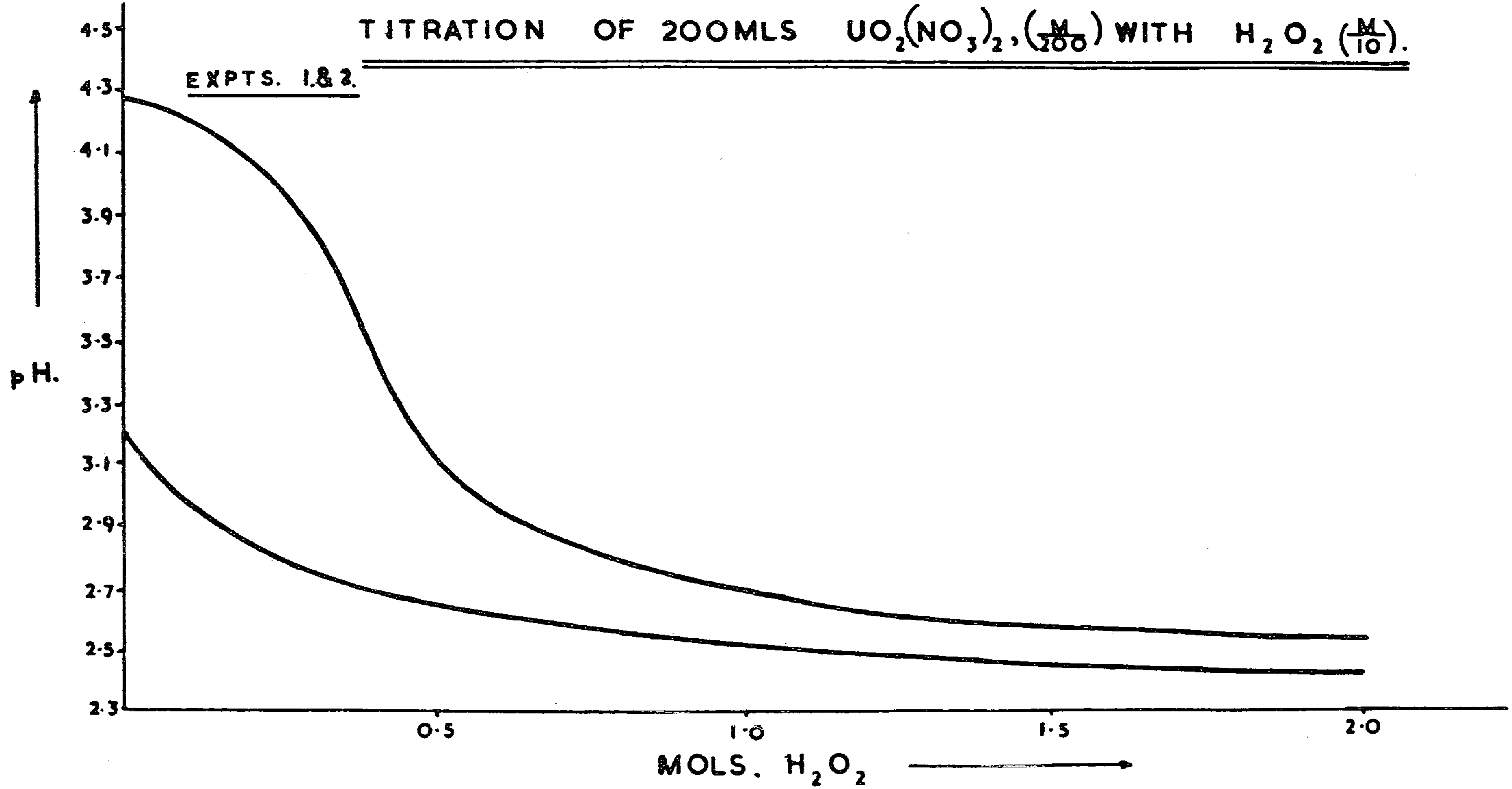
From preliminary work on the hydrolysis of uranyl nitrate with ammonium hydroxide, it has been shown that the uranyl ion polymerises to $(U_3O_8(OH))^+$ before hydrolysis to the trimer of uranyl hydroxide occurs. A possible formula for ammonium uranate is suggested, viz. $U_3O_8\ (OH)_3NH_4$, or $(UO_3)_3(OH)MH_4$. Since uranium is quantitatively precipitated by $H_2O_2$ at pH values above the free acid end-point, a possible separation from ions which do not precipitate above this pH is suggested and methods for the determination of certain elements, normally impracticable in the presence of uranium may by this means be made applicable.

## REFERENCES

1. C.I. Technical Report R.S.2335
2. R.H.Betts and Miss R.K.Michels. Chemical Society Symposium on the Chemistry of Heavy Elements. March, 1949.
3. Armson. Springfields Report No.30.
4. Worthington. Springfields Report No.146.
5. J.Sutton. Chemical Society Symposium on the Chemistry of the Heavy Elements. March, 1949.
6. T. V. Arden and Jeanette Harbutt. C.R.L./A.E.38.
7. B. Tanford, R.L.Tichenor, H.A.Young. A.E.C.D.-2653.

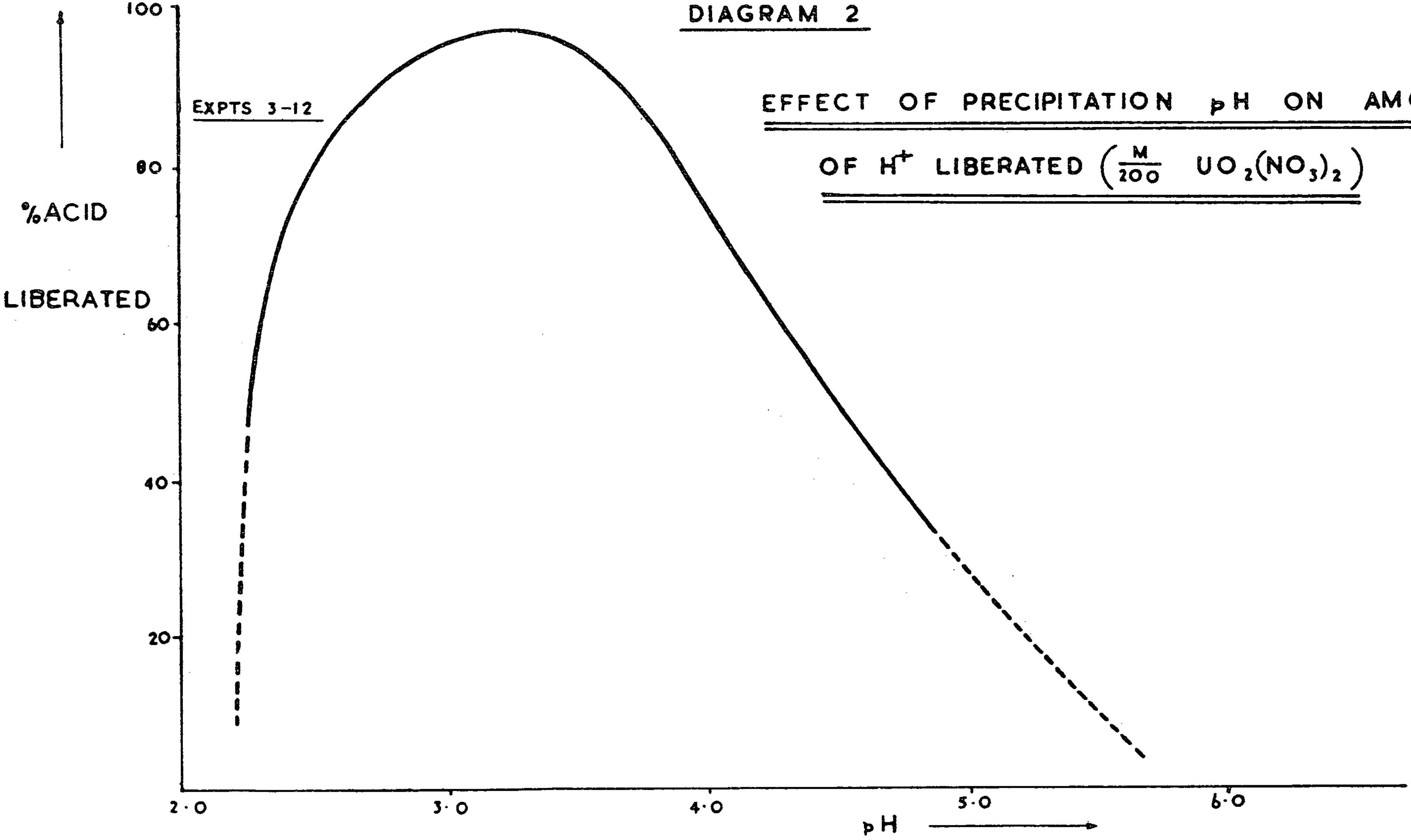
# DIAGRAM 1.

## TITRATION OF 200MLS $UO_2(NO_3)_2$, $(\frac{M}{200})$ WITH $H_2O_2$ $(\frac{M}{10})$.



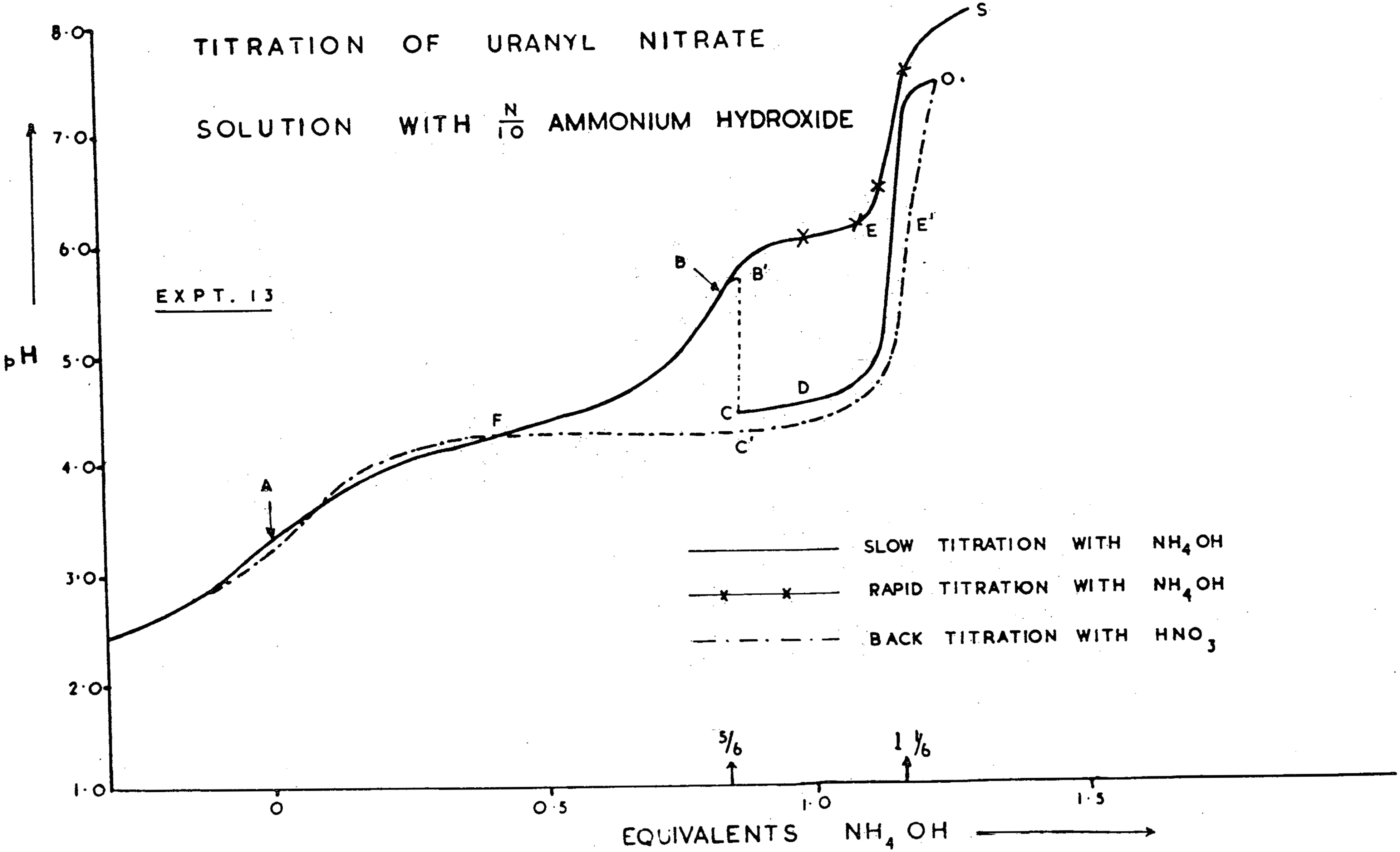
## DIAGRAM 2

### EFFECT OF PRECIPITATION pH ON AMOUNT OF $H^+$ LIBERATED $\left(\frac{M}{200}\ UO_2(NO_3)_2\right)$



## DIAGRAM 3.

### TITRATION OF URANYL NITRATE SOLUTION WITH $\frac{N}{10}$ AMMONIUM HYDROXIDE



## DIAGRAM 4.

## POTENTIOMETRIC TITRATIONS OF 200MLS. $UO_2(NO_3)_2$ $\frac{M}{200}$ WITH $H_2O_2$ $\frac{M}{10}$.

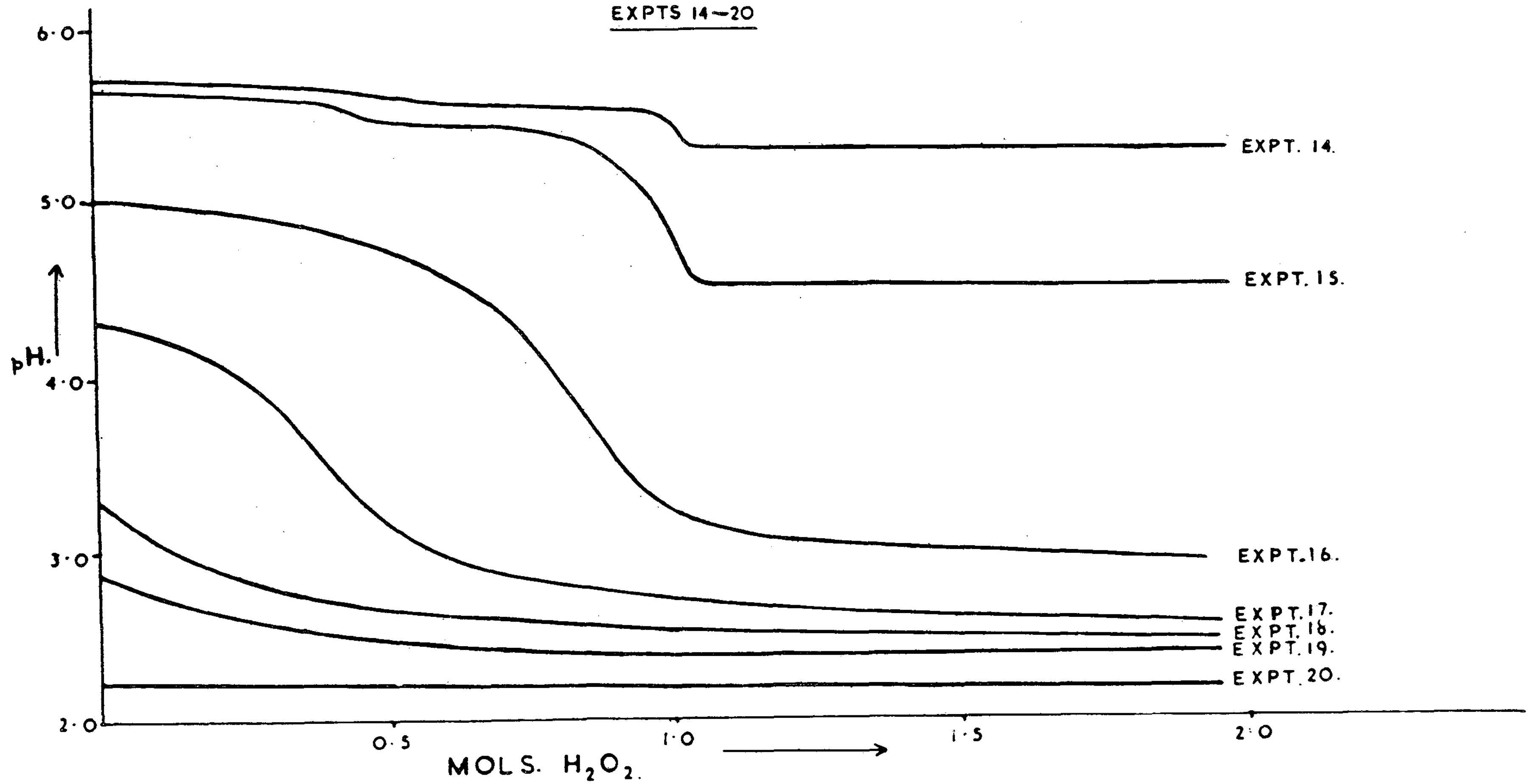
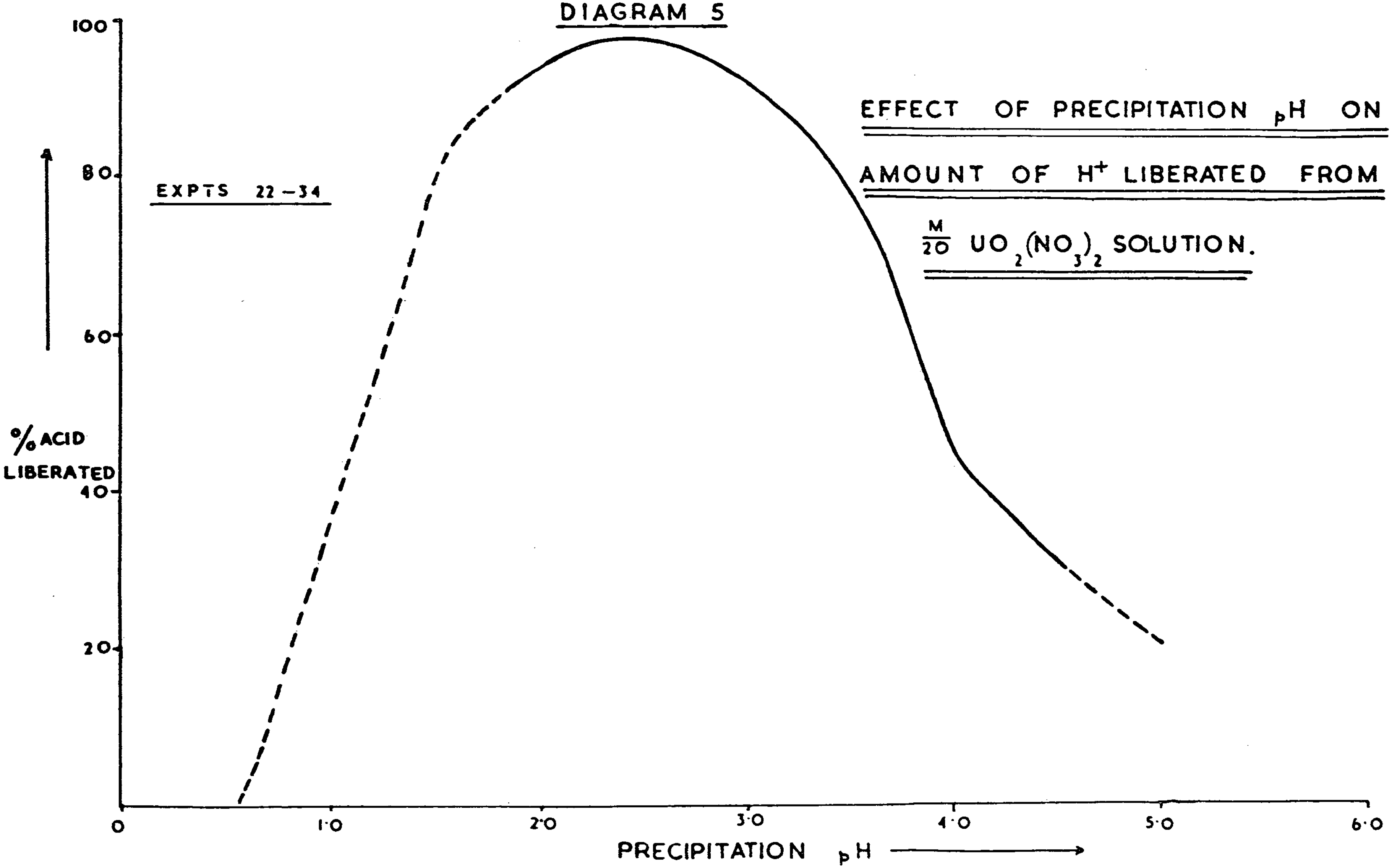


DIAGRAM 5



EFFECT OF PRECIPITATION pH ON AMOUNT OF $H^+$ LIBERATED FROM $\frac{M}{20}$ $UO_2(NO_3)_2$ SOLUTION.

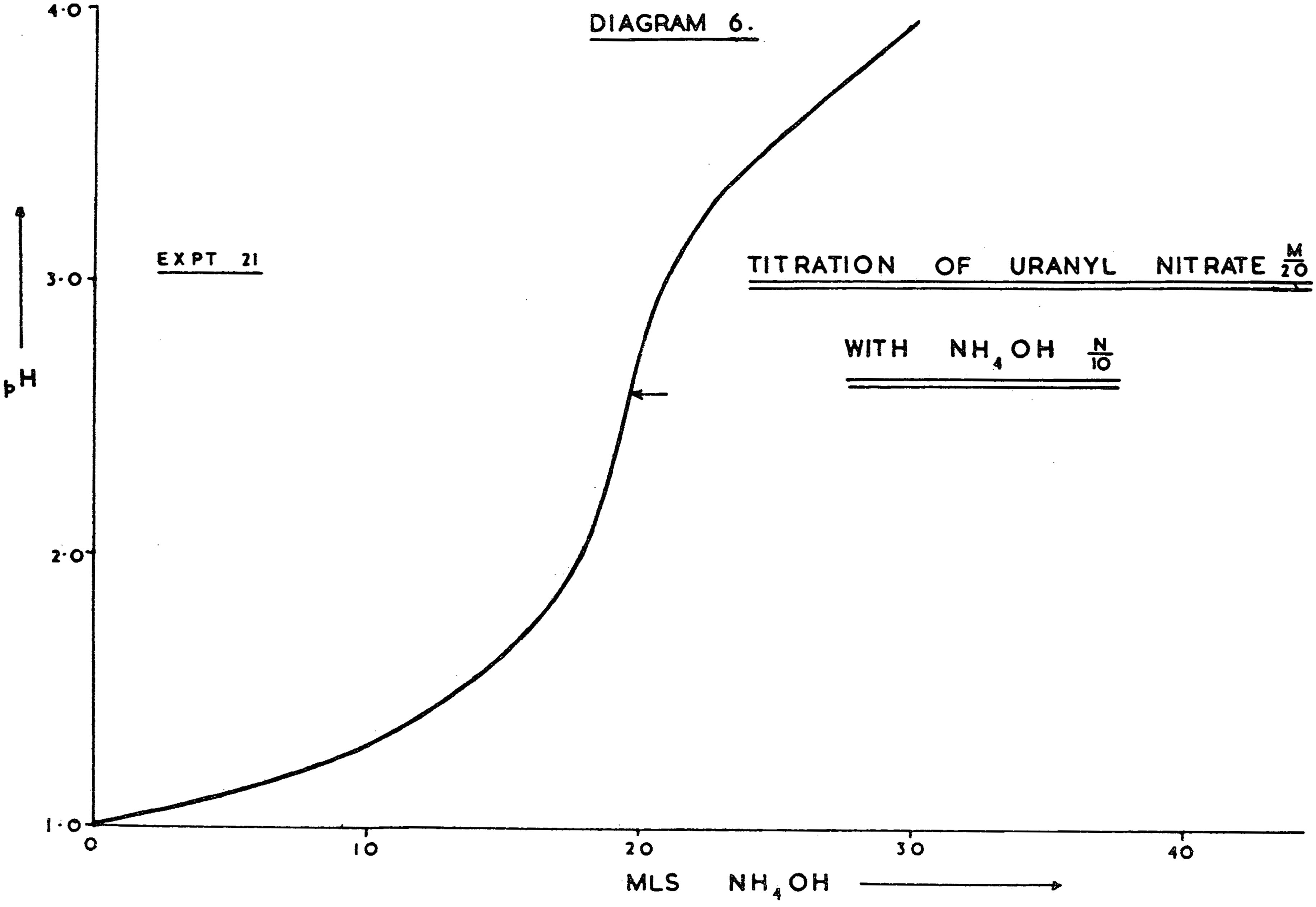
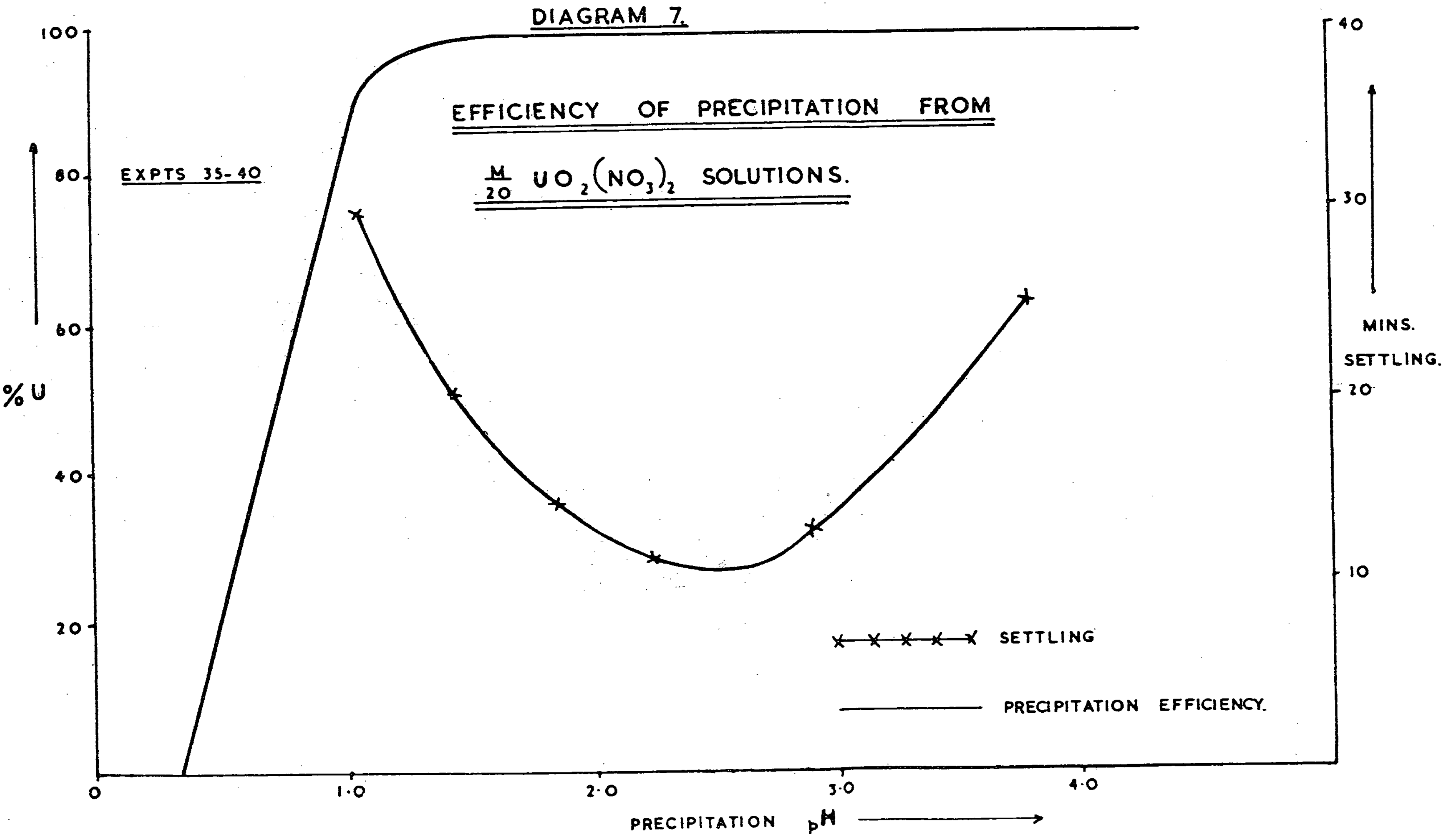


DIAGRAM 6.
EXPT 21
TITRATION OF URANYL NITRATE $\frac{M}{20}$
WITH $NH_4OH$ $\frac{N}{10}$
pH
4·0
3·0
2·0
1·0
0
10
20
30
40
MLS $NH_4OH$



# DIAGRAM 7.

## EFFICIENCY OF PRECIPITATION FROM $\frac{M}{20}$ $UO_2(NO_3)_2$ SOLUTIONS.

C.I. REPORT No.15

SERIAL No.2004/7