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SOME PROPERTIES OF URANOUS PHOSPHATES

Topical Report

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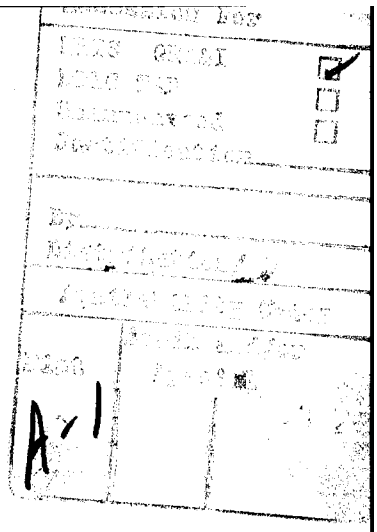


TOPICAL REPORT MITG-245

SOME PROPERTIES OF URANOUS PHOSPHATES

By

James H. Pannell and Emilia M. Rubino

A B S T R A C T

An investigation aimed at characterizing phosphates of tetravalent uranium has shown that these compounds, when formed by precipitation, are gelatinous substances of somewhat variable composition. Their solubilities and behavior on thermal decomposition have been studied in order to obtain data of value in the treatment of uranium ore leach solutions.

I INTRODUCTION

Although the properties of uranyl ammonium phosphates have been known for many years and utilized in analytical chemistry, practically nothing is known about the phosphates of tetravalent uranium. A number of developments in mineral engineering investigations aimed at the separation of uranium finally made a study of uranous phosphates imperative. These developments include the separation of uranium, in low concentrations, from Fe, Mn, Al, and Si present in sulfuric acid leach liquors (MITG-A44, -A62, -A77, -A85, -A90, -A92, -A99) and its separation from commercial-grade phosphoric acid (MITG-216, -217, -218, -221, -228, -229, -238, -241) where the concentration is also low. Information was needed to help explain a removal of uranium from solutions containing traces of phosphate when these solutions are reduced with metals, an effect sometimes referred to as pseudocementation (MITG-A85). Complexing of uranium by phosphate is known to occur and this would be expected to influence, among other things, the degree to which the metal could be precipitated.

This report does not represent a complete study of the vast field of uranium phosphates. It is, rather, an attempt to gather and correlate information which is of some importance to the extraction of uranium from low-grade ores. All of the experiments were carried out on systems whose components were known. In the course of the investigation, new factors arose from time to time which made the interpretation of previous tests less clear and which necessitated reorientations of the program. Such developments, resulting from excursions into entirely new fields, were not unexpected; consequently, the data will be presented approximately in chronological order.

II SUMMARY AND CONCLUSIONS

The uranous phosphates, when precipitated from aqueous solutions, are slimy hydrogels, bulky and green or blue-green in color. Uranous ortho and pyrophosphates are similar in properties although the pyro compound is probably slightly less soluble and more rapidly precipitated. Their compositions are indefinite; they appear to have no crystal structure; they are soluble in strong acids and in Na_2CO_3. When dried, the phosphates are resistant to oxidation and thermal decomposition but can be dissolved in sodium carbonate solutions. The amount dissolved depends on the temperature of ignition, reaching a maximum at about 600°C. The same temperature marks the beginning of detectable crystallinity.

In the absence of other cations, large excesses of pyrophosphate complex uranous ions may form and hinder its precipitation. However, more nearly complete precipitation of the uranium is achieved with pyro than with orthophosphate in such systems when only moderate excess of reagent is used.

III EXPERIMENTAL PROCEDURE AND RESULTS

Preparation of Uranous Phosphates

The phosphates were precipitated from sulfuric or perchloric acid solutions by addition of H_3PO_4 or acidified $Na_4P_2O_7 \cdot 10H_2O$ in approximately stoichiometric amounts. Reduction of uranium, prior to precipitation, was effected electrolytically or with a Jones reductor on solutions of pH about 0.5. Zinc, from the reductor, was not important as its phosphate is highly soluble under the conditions of the tests. After reduction, the solution was diluted considerably to produce a uranium concentration of 1 to 2 grams per liter and to raise its pH to 1.0 to 1.5 and during this dilution color changes showed that all U(III) was oxidized to U(IV).

The precipitant in dilute solution was added slowly with stirring in order to obtain uniform conditions of precipitation throughout the solution. The precipitates were allowed to settle at room temperature for periods of 3 to 20 hours. Settling was rapid, but the settled material was of large volume, one observation indicating that it contained less than 1 per cent solids on a dry basis. Filtration of the orthophosphates was not difficult, but the pyrophosphates were finer grained and more colloidal. A comparative test showed that the latter took 3 times as long to filter as the former. Moreover, the fineness of the pyro compound necessitated the use of tight filter papers such as Whatman #42. The precipitates were washed by repulping with water, although this operation resulted in dispersion of the pyrophosphate so that it no longer settled completely unless the solution was heated. Although rapid flocculation could be induced by the addition of aluminum sulfate, the introduction of this or any other cations was generally avoided.

Evidence for distinction between pyro and orthophosphates was clear from the beginning and was supported on theoretical grounds. Thus it was determined (MITG-A99) that a solution of pyrophosphate at pH 1.5 hydrolyzes to only a very slight extent at room temperature, the rate being about 1 per cent per day. Hence, it is hardly possible for an orthophosphate to be formed when a stoichiometric amount of pyrophosphate is added and precipitation occurs immediately. The substances differ even in color, the ortho compound being a forest green and the pyro somewhat turquoise. As will be seen later, many properties distinguish them.

Composition of Uranous Phosphates

The washed precipitates were dried at 110°C for a minimum of 16 hours before being ground to -100 mesh and submitted for chemical analysis for U_3O_8 and P_2O_5. Conversion of the analyses to the appropriate molecular constitution showed that only about 90 per cent of the weight was accounted for so analyses for zinc and sulfate were requested. The former was found to be present in some samples to the extent of 0.5 per cent while the latter was a major impurity and frequently constituted several per cent of the weight. Discrepancies between the total assays of a sample and 100 per cent were attributable to water which was not lost at 110°C.

The development of methods for producing reliable chemical analysis on these materials proved to be difficult, particularly in the determination of P_2O_5. After suitable methods were developed, many early tests were rerun to obtain reliable analyses. Therefore, it is believed that no gross errors are present in the analytical data presented in this report.

Examination of the analytical results for any one type of phosphate showed a wider dispersion in the ratio $U:P_2O_7$ or $U:PO_4$ than would ordinarily be attributed to errors in analysis and in general there appeared to be a 10 to 20 per cent excess of phosphate. This point is illustrated by the data in Table 1 pertaining to some phosphates prepared in the early stages of the investigation.

Roasting tests, the results of which will be presented later in this report, indicated that the excess phosphate was chemically combined and not merely adsorbed as free acid for it was not removed by heating to 900°C. By analogy with other heavy metal phosphates, e.g. $BiPO_4$, it had been assumed that the normal phosphate would be formed upon precipitation because of the dominant electrostatic effect. However, the excess phosphate found by analysis suggests that an acid compound or mixture of acid and normal compounds was being precipitated. Therefore, one might expect the pH of the solution to affect the composition of the substance precipitated as it controls the degree to which the phosphoric acid is dissociated. Therefore, at high acidities, where dissociation is inhibited, the precipitate would be expected to contain a larger per cent of phosphate. In order to check this hypothesis, a series of tests was made in which the phosphates were precipitated at various acidities between pH 0.5 and 2.0. The pH was measured before and after precipitation by means of a Beckman model H2 pH meter calibrated with buffer solutions at pH 1.0 and 2.0 so the readings are believed to be within

0.05 units. No appreciable change in pH occurred on precipitation except at pH 2.0 where it dropped about 0.1. The results of this experiment are shown graphically in Figure 1. It can be seen that a definite variation in composition with pH occurs for the orthophosphates, but not for the pyrophosphates. The latter were not only of more constant composition, but they contained less sulfate and less water.

Table 1. Uranium : Phosphate Ratios in some Uranous Phosphates

Test No.	Type	% U	% PO_4	Mole Ratio
189	Ortho	53.2	36.4	1 : 1.71
196	Ortho	47.5	36.2	1 : 1.90
281	Ortho	54.4	32.2	1 : 1.49
384	Ortho	57.8	35.5	1 : 1.53
400	Ortho	55.0	30.8	1 : 1.40
Theoretical $U_3(PO_4)_4$				1 : 1.33
			% P_2O_7	
338	Pyro	50.5	42.7	1 : 1.16
401	Pyro	50.7	40.2	1 : 1.08
Theoretical UP_2O_7				1 : 1.00

The presence of sulfate is believed to be due to a uranous sulfate sol which itself precipitates at a pH of 2.0 under certain conditions. Some work of Barnard, reported in MITG-A75, showed that raising the pH of uranous sulfate solutions resulted in the precipitation of a hydrated sulfate rather than a hydroxide. Attempts were made to prevent inclusion of sulfate by carrying out reduction and precipitation in perchloric acid, but it was discovered that such solutions were unstable towards hydrolysis at pH 1.4. Even during the electrolytic reduction, at pH 1.0, a slimy film of uranous hydroxide formed on the lead cathode and on the diaphragm. Evidently sulfate complexes uranous ion and protects it from hydrolyzing between pH 1.4 and 2.0. It should be remembered, in connection with these hydrogen ion activities, that hydrolysis occurs more rapidly in hot solutions and at high uranium concentrations. The per cent SO_4 in uranous orthophosphates precipitated from sulfuric acid ranged from 0.9 to 7.4 but was not a function of any of the variables studied and could not be decreased by washing or repulping. In the pyrophosphates the range was from 0.0 to 2.7. Allowance was made for the uranium which was present as a sulfate in computing uranium : phosphate ratios discussed in this report.

Totalization of assays for U, PO_4 or P_2O_7, SO_4 and Zn gave figures averaging 89.4 per cent for the ortho and 93 per cent for the pyrophosphates. Roasting experiments showed that a weight loss of 6 to 10 per cent took place at about 300°C. The relative proportions of the constituents did not change, however,

and there were no visible signs of oxidation so the loss may be attributed to water. It was thought that these substances, which resemble hydroxides in many respects, might respond to Willstätter's method for dehydrating hydroxides, that is washing with acetone to restore the normal vapor pressure of water in the capillaries. In spite of thorough repulping in acetone or alcohol, no decrease in the water content of the dried material was observed.

No crystal structure, as determined by X-ray diffraction patterns, was found in uranous phosphates as prepared and dried. Patterns were obtained on phosphates heated to at least 600°C and these will be discussed under roasting experiments.

Solubility of Uranous Phosphates

A knowledge of the solubilities of the uranous phosphates was of obvious need because of its application to the separation of uranium. Discordant results from various laboratories (MITG-A90) left the relative merits of ortho and pyrophosphate as precipitants for uranium in ore leach solutions undetermined so it appeared that a systematic investigation was in order. At the outset, information concerning the variations in composition of the phosphates was not available and it was assumed that each type had inherent distinguishable characteristics and, moreover, was a definite compound. Data on previous pages indicate how this concept should be modified.

Determinations of solubility were carried out in pure solutions, with limited or negligible access to air. Because of the susceptibility of uranium to complexing, approach to saturation from the low-concentration side was favored over precipitation by mixing solutions. However, data were obtained by both methods and proved to be quite discordant but of some value in shedding light on the properties of the substances concerned. For each test, a range of pH values was covered by altering the concentration of the acid. Several grams of dried phosphate were added to each 100 ml of the de-aerated solution in a 150-ml flask which was stoppered and shaken mechanically for 4.5 hours. It was expected that this period would give almost, if not quite, a saturated solution and longer periods would have retarded the investigation excessively. Solvents included in these tests were aqueous solutions of nitric, hydrochloric, sulfuric, phosphoric, perchloric, and acetic acids in the pH range 0.5 to 2.5. The filtered solutions were assayed for uranium and phosphate with the results shown graphically in Figures 2 through 7.

In the acid solutions solubility increased in proportion to the hydrogen ion activity with the exception of acetic acid. As the concentration of this acid was very high at a pH of 1.0 or below, the system was not aqueous in the same sense as the others. The results peculiar to acetic acid are believed to be due to that cause. A comparison of ortho and pyrophosphate results shows that while in the ortho there was no marked difference between the compositions of the solid and solute phases, in the pyro the solute phase contained a dispro-

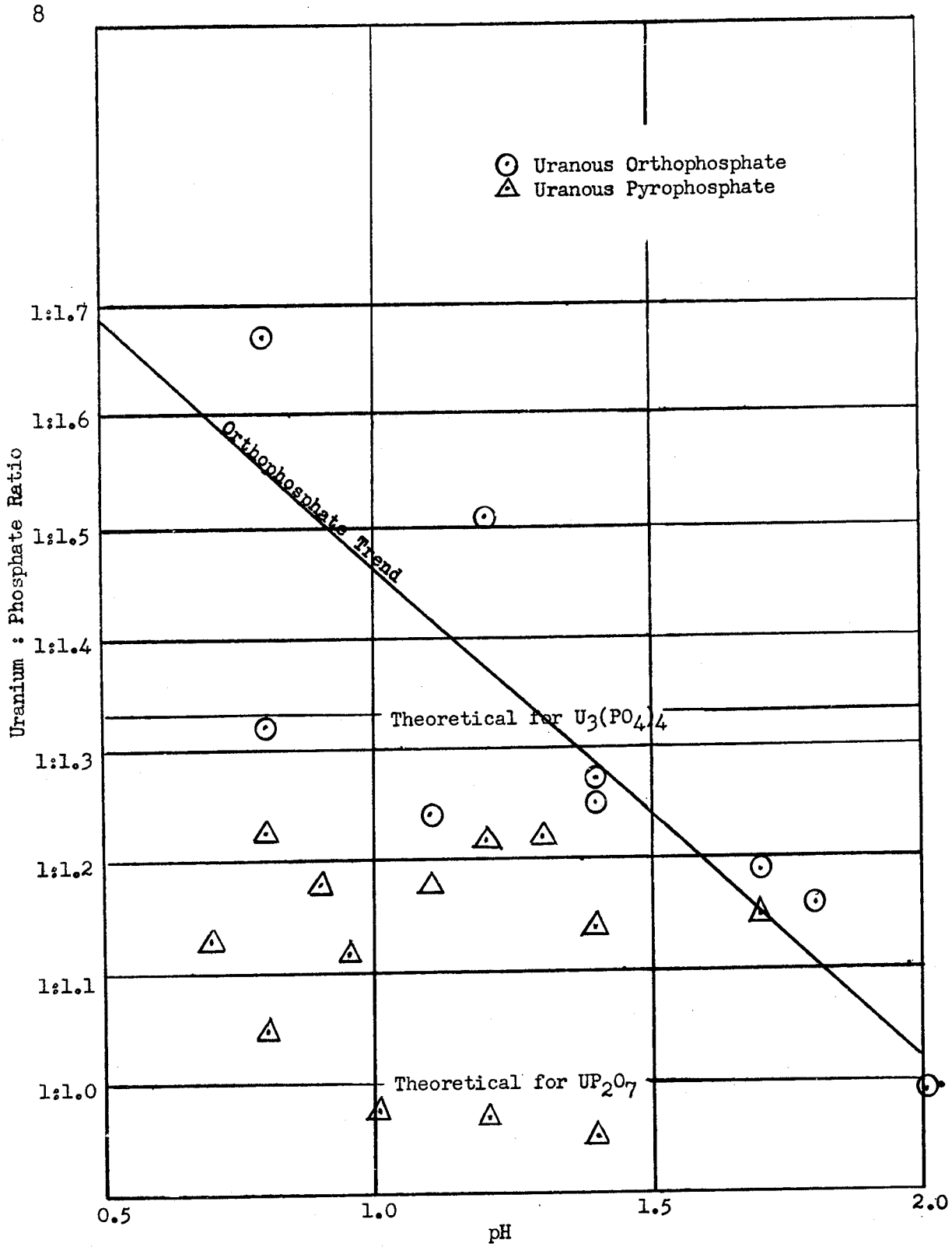


Figure 1. Effect of pH at Precipitation on Composition of Phosphates

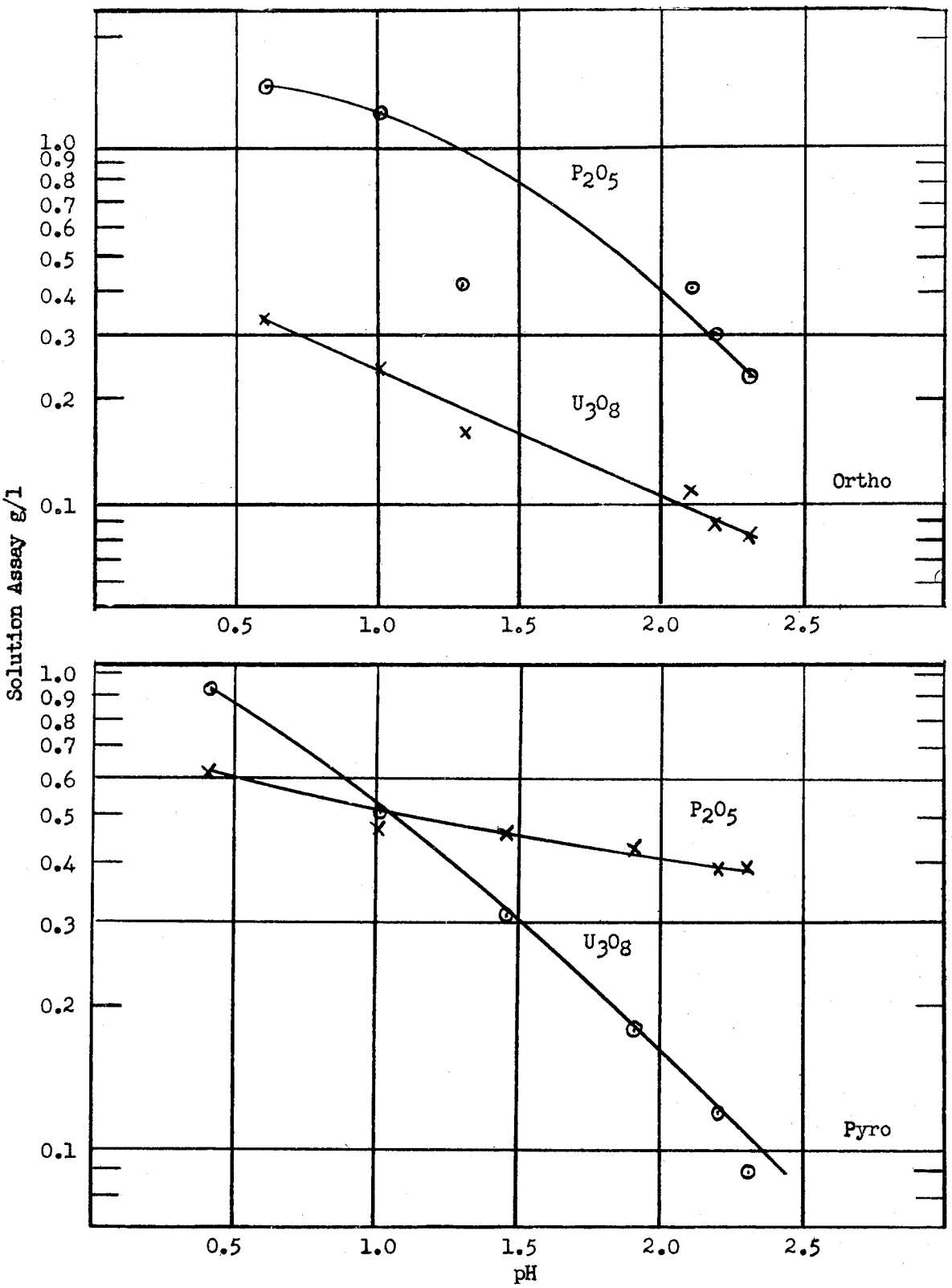


Figure 2. Solubilities of Uranous Phosphates in HNO_3

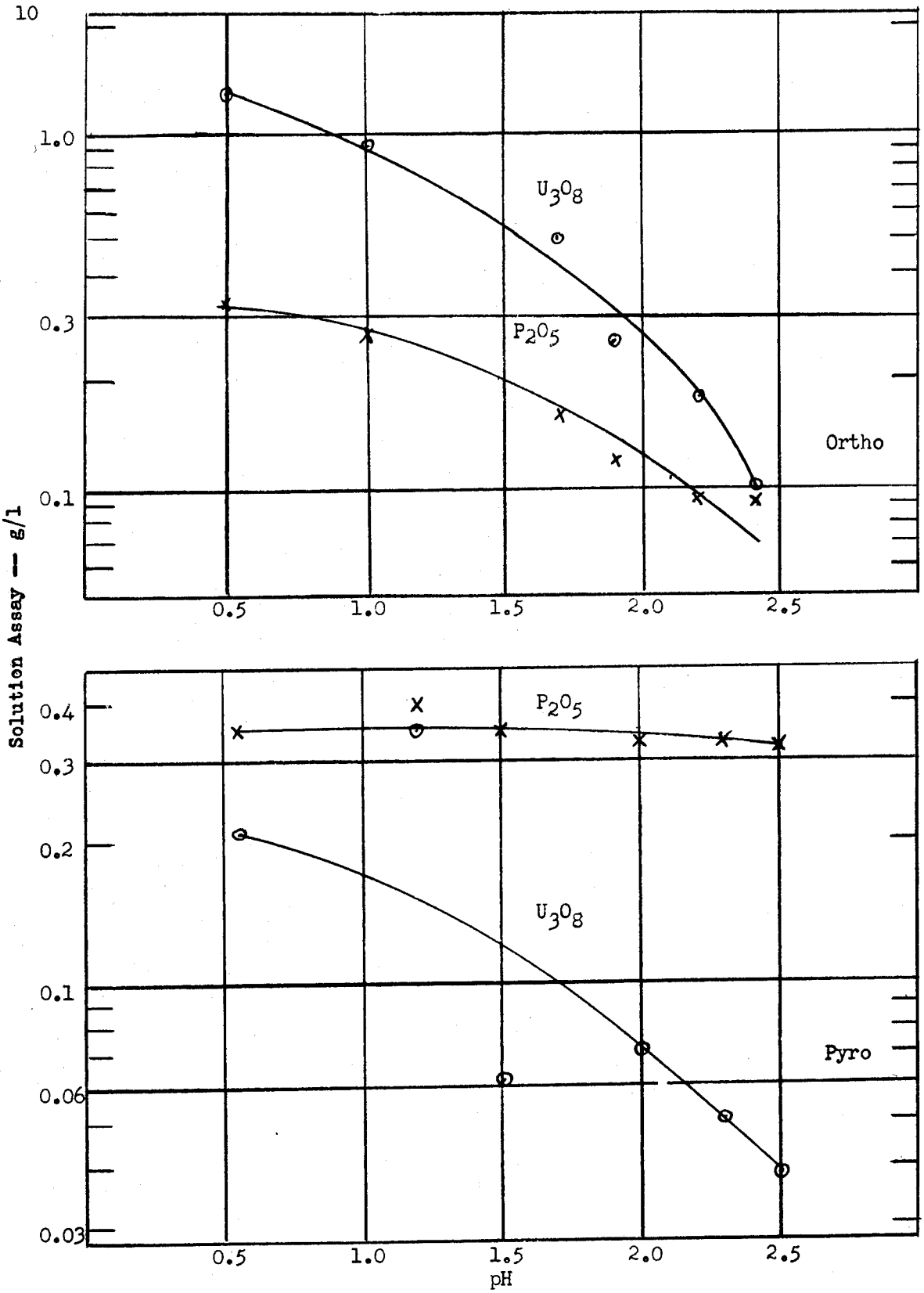


Figure 3. Solubilities of Uranous Phosphates in HCl

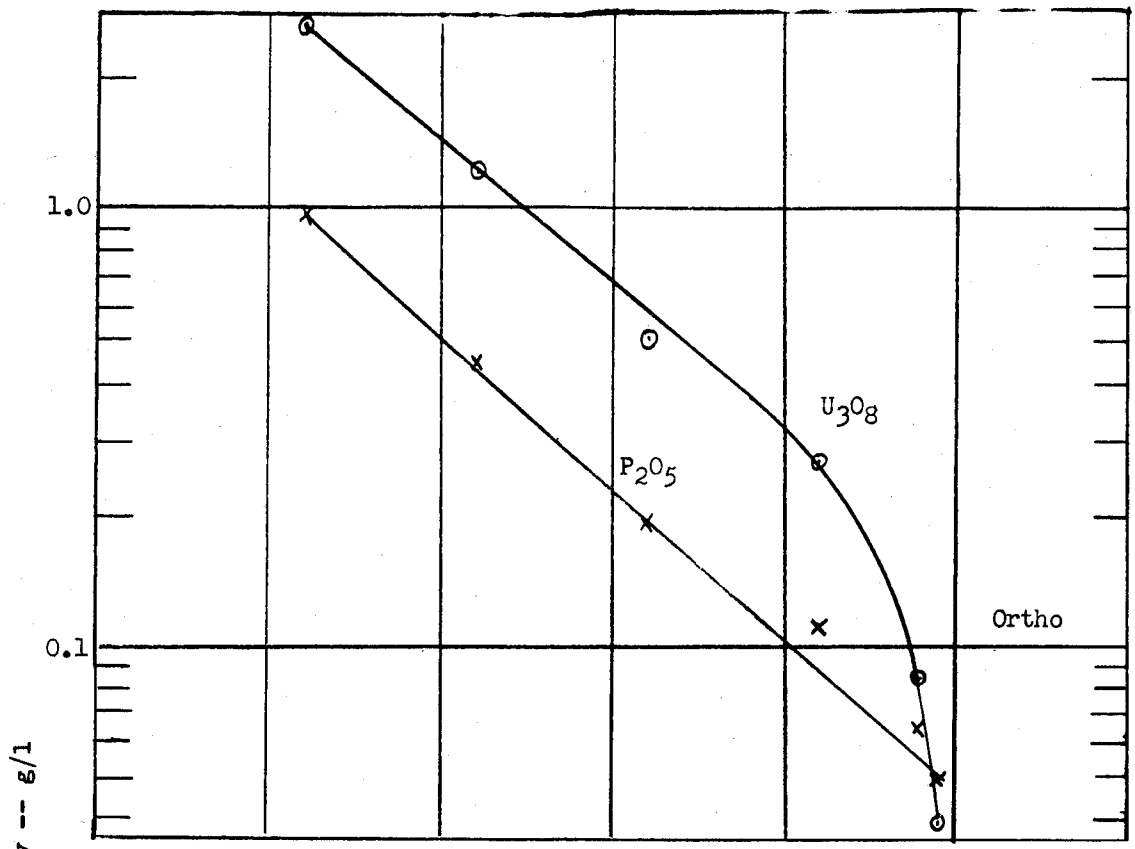
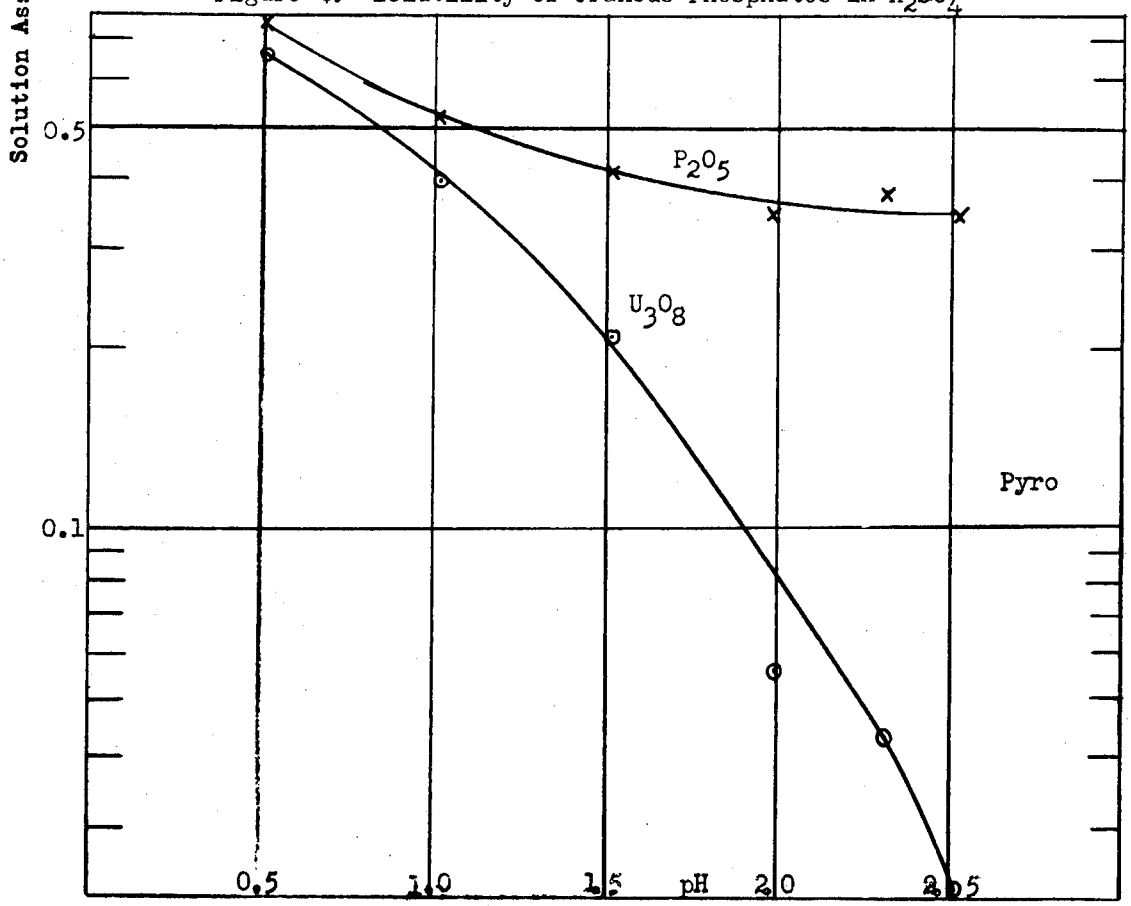


Figure 4. Solubility of Uranous Phosphates in H_2SO_4



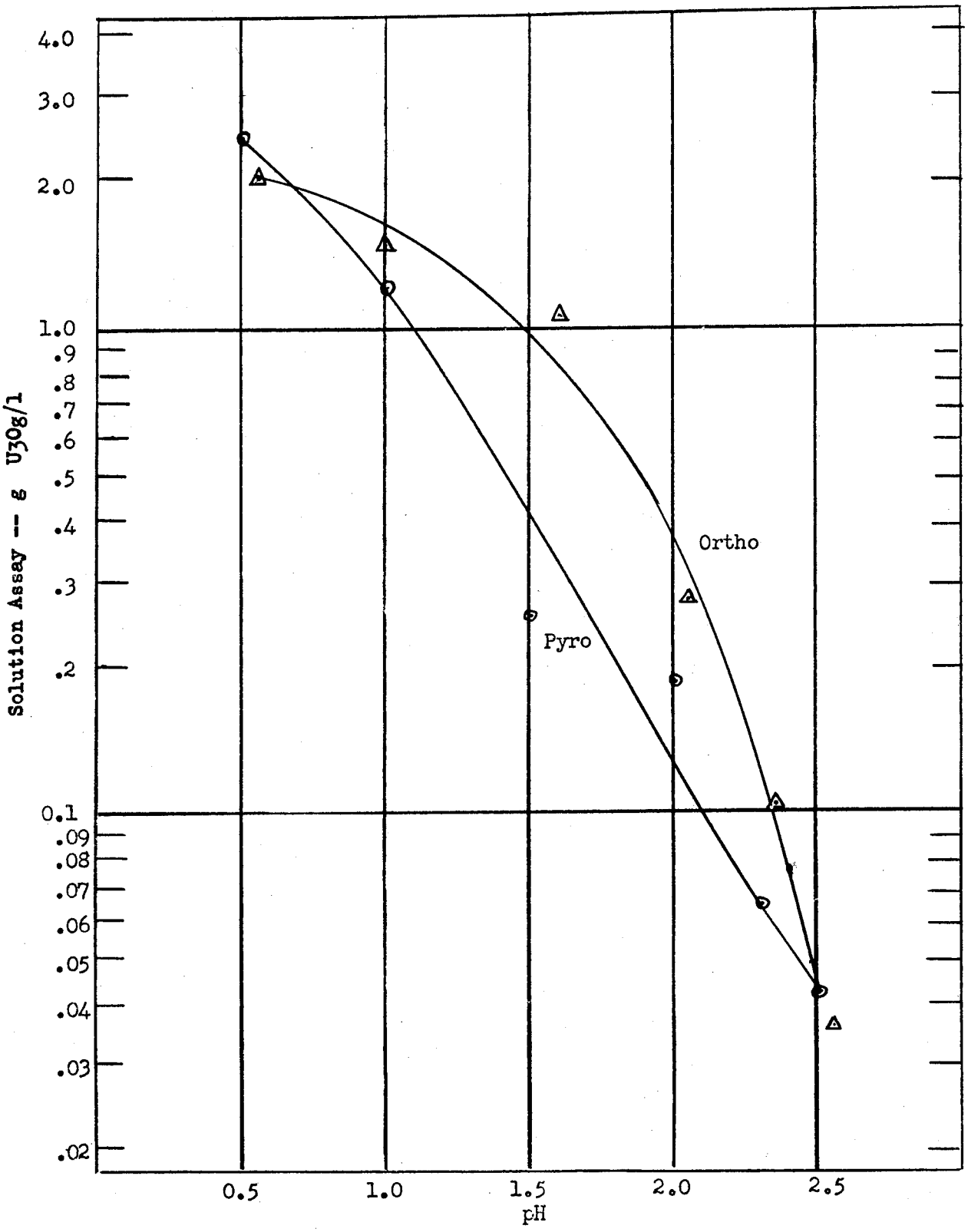


Figure 5. Solubility of Uranous Phosphates in H_3PO_4

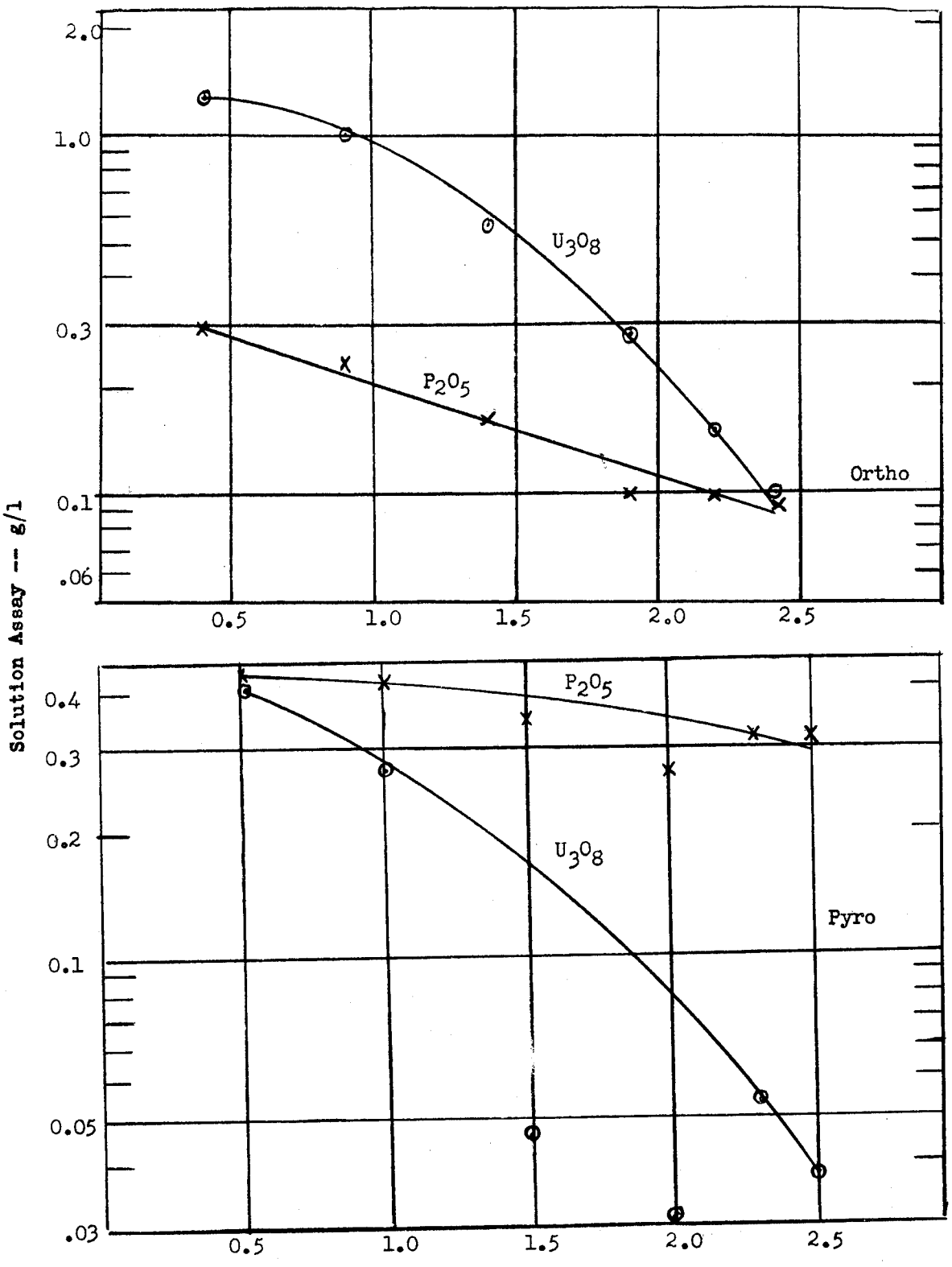


Figure 6. Solubilities of Uranous Phosphates in $HClO_4$

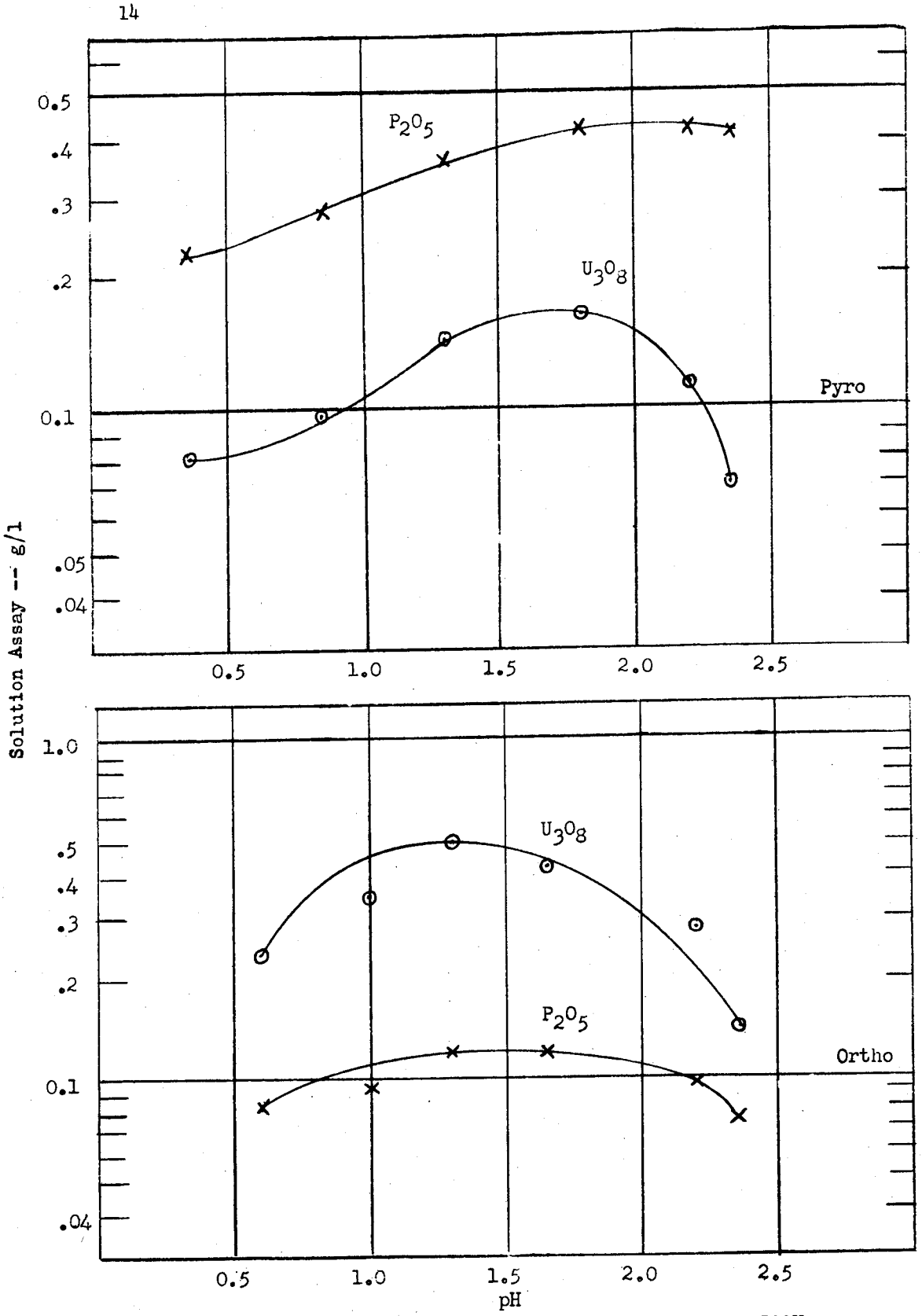


Figure 7, Solubility of Uranous Phosphates in CH_3COOH

portionately high P_2O_5 content. Therefore, while the orthophosphate may have dissolved without change, the pyrophosphate either may have reacted with the solvent or itself may have contained a soluble phase with high phosphate content. Neither possibility is likely; the anions present all form soluble salts with U(IV), at least up to pH 1.4; the highest phosphate : uranium ratio theoretically possible for $U(H_3P_2O_7)_4$ is some 1 : 0.85 while ratios as high as 1 : 0.1 were encountered. It is probably significant that the phosphate : uranium ratio decreases with pH in all acids but acetic, suggesting that more than one mechanism for dissolution was at play.

In terms of uranium the data do not show clearly whether the pyro or the orthophosphate is the more soluble; it appears that large differences may exist between different lots of the same compound. This immediately raises the question, of what significance are these figures for solubilities of uranous phosphates. It can be stated that the actual values mean very little; confirmation of this fact was obtained in several ways. An investigation of the time required to attain saturation indicated there was no equilibrium even after continuous shaking for several days, but the quantity of phosphate dissolved continued to increase. The experiment was run in an atmosphere of prepurified (99.9 per cent) nitrogen and samples of the solution were removed by use of the same gas. After a short period of shaking, part of the material became dispersed in a gelatinous or finely-divided condition and the proportion of the solid so dispersed increased with longer periods of shaking. For that reason the samples removed were difficult to filter even with the aid of paper pulp and a tight filter paper. The curves in Figures 8 and 9 show the results which are interpreted to mean that the solid phase was being broken down and finally transformed into a solution. It can be seen that solubility was increasing steeply at the 4-1/2 hour mark.

Truer and more useful values for solubilities were found by analysis of filtrates from precipitation with near stoichiometric quantities of reagents. The results of these assays are plotted in the form of grams U_3O_8 per liter vs grams P_2O_5 per liter in Figure 10 and show a median at about 0.04 gram U_3O_8 per liter, but fall in areas whose long axes show a direct rather than an inverse, relation between P_2O_5 and U_3O_8. This may be regarded as an illustration of the fact that excess phosphate tends to increase the solubility in contradiction to the general solubility product law. In order to obtain further information on such complexing, experiments were run in which various amounts of phosphate in excess of stoichiometric were added to aliquots of a solution containing 0.5 gram uranium per liter. The filtrates were analyzed fluorimetrically and the results plotted to show the per cent uranium removed from the solutions at the three pH levels of 1.0, 1.5, and 2.0. Complexing by large excess of pyrophosphate is readily apparent in the curves of Figures 11, 12, and 13, while the effect of orthophosphate in similar excess is negligible. The degree of complexing appeared to increase with increasing pH, suggesting a relationship to ionized pyrophosphate activity. Repetitions of this test with even greater excess of H_3PO_4 indicated that the leveling off at 60 per cent precipitated in Figures 11 and

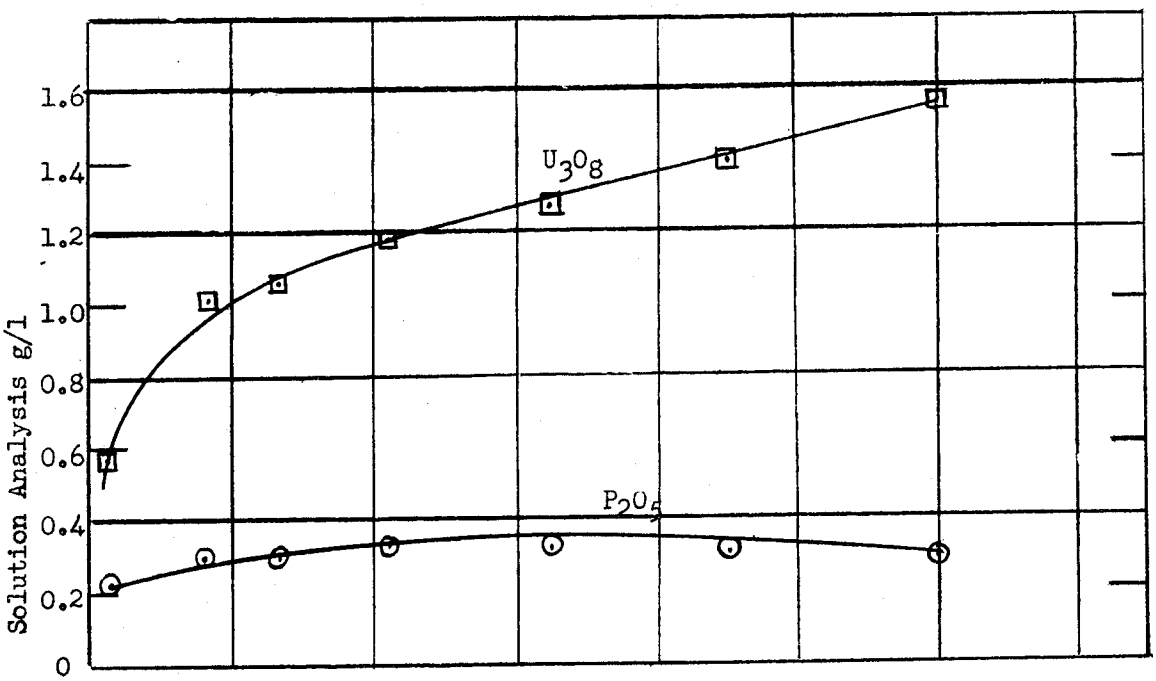


Figure 8. Effect of Time on Solubility of $U_3(PO_4)_4$ in H_2SO_4 at pH 1.5

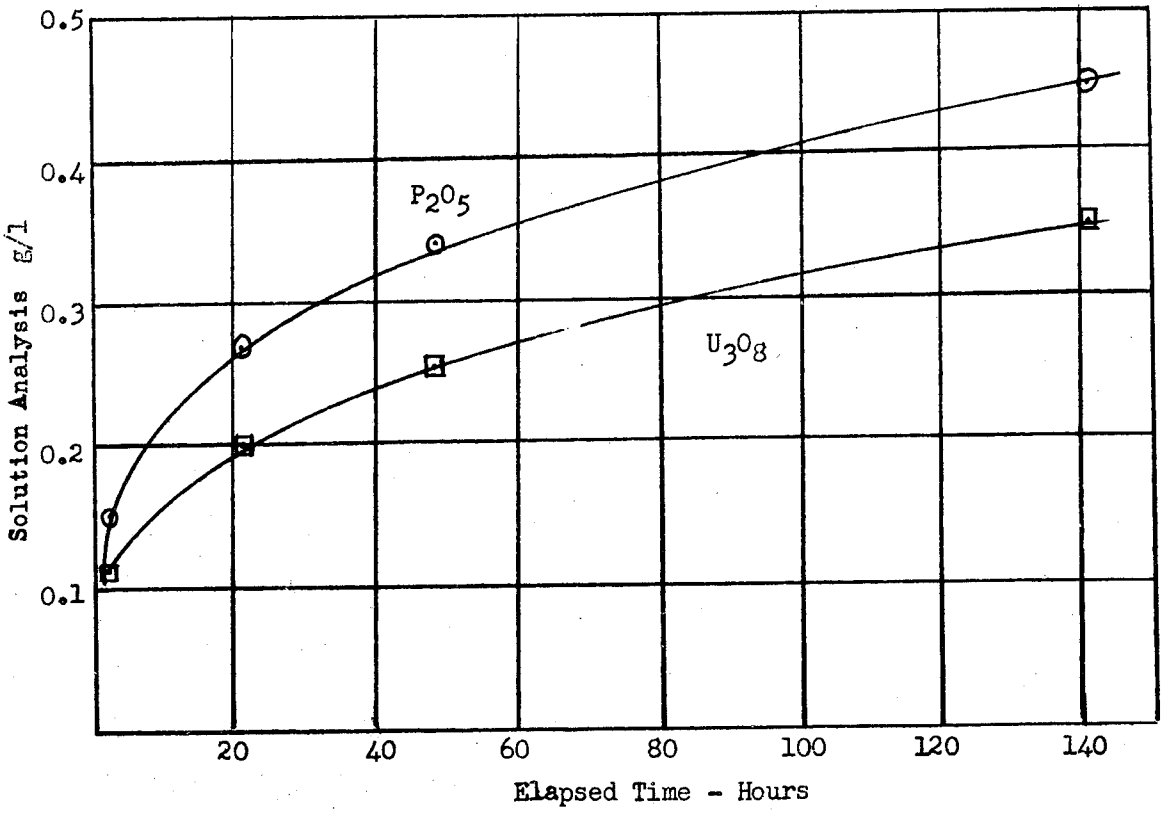


Figure 9. Effect of Time on Solubility of UP_2O_7 in H_2SO_4 at pH 1.5

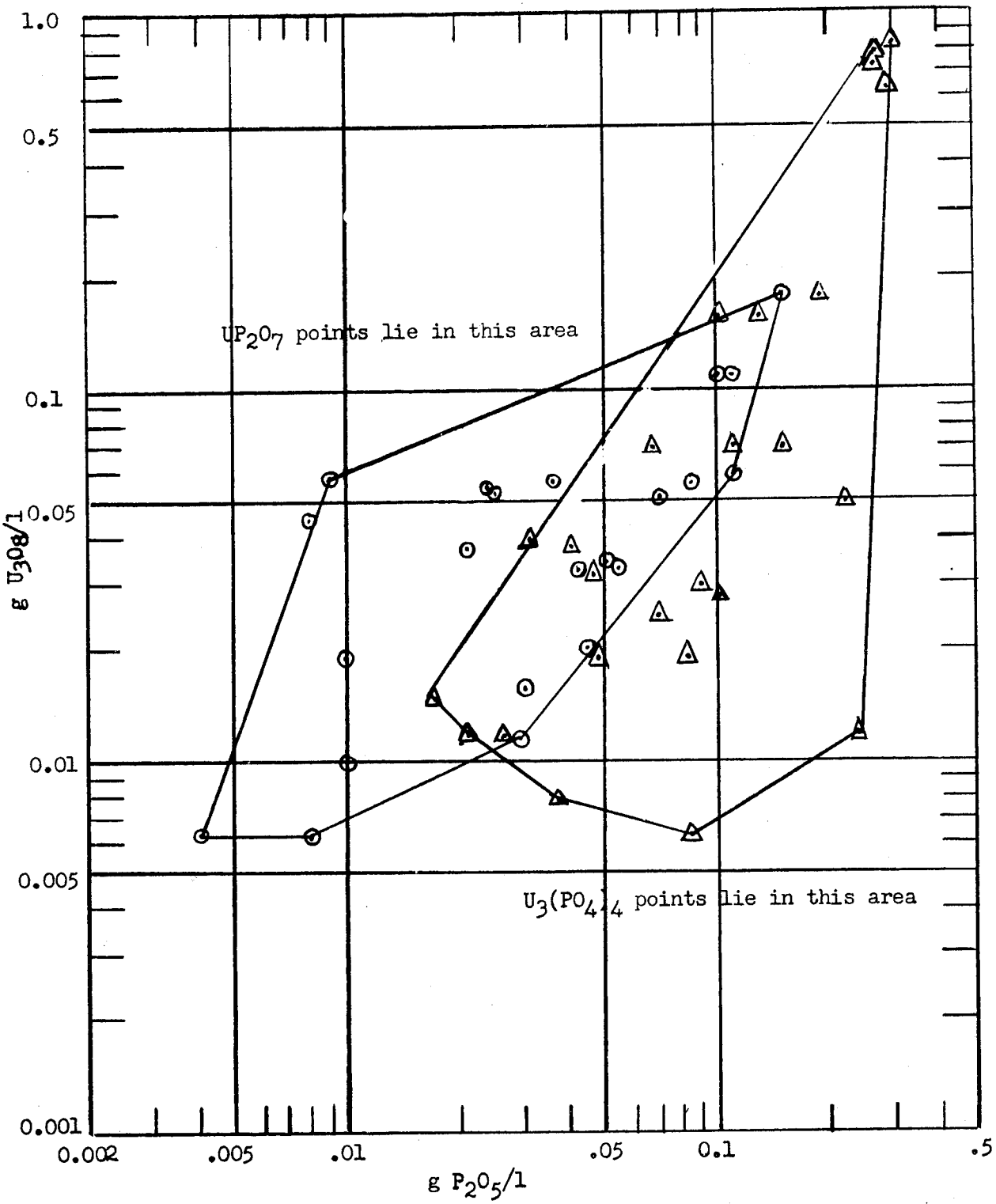


Figure 10. Analyses of Filtrates from Precipitation of Uranium (IV) with Near Stoichiometric Amounts of Phosphate

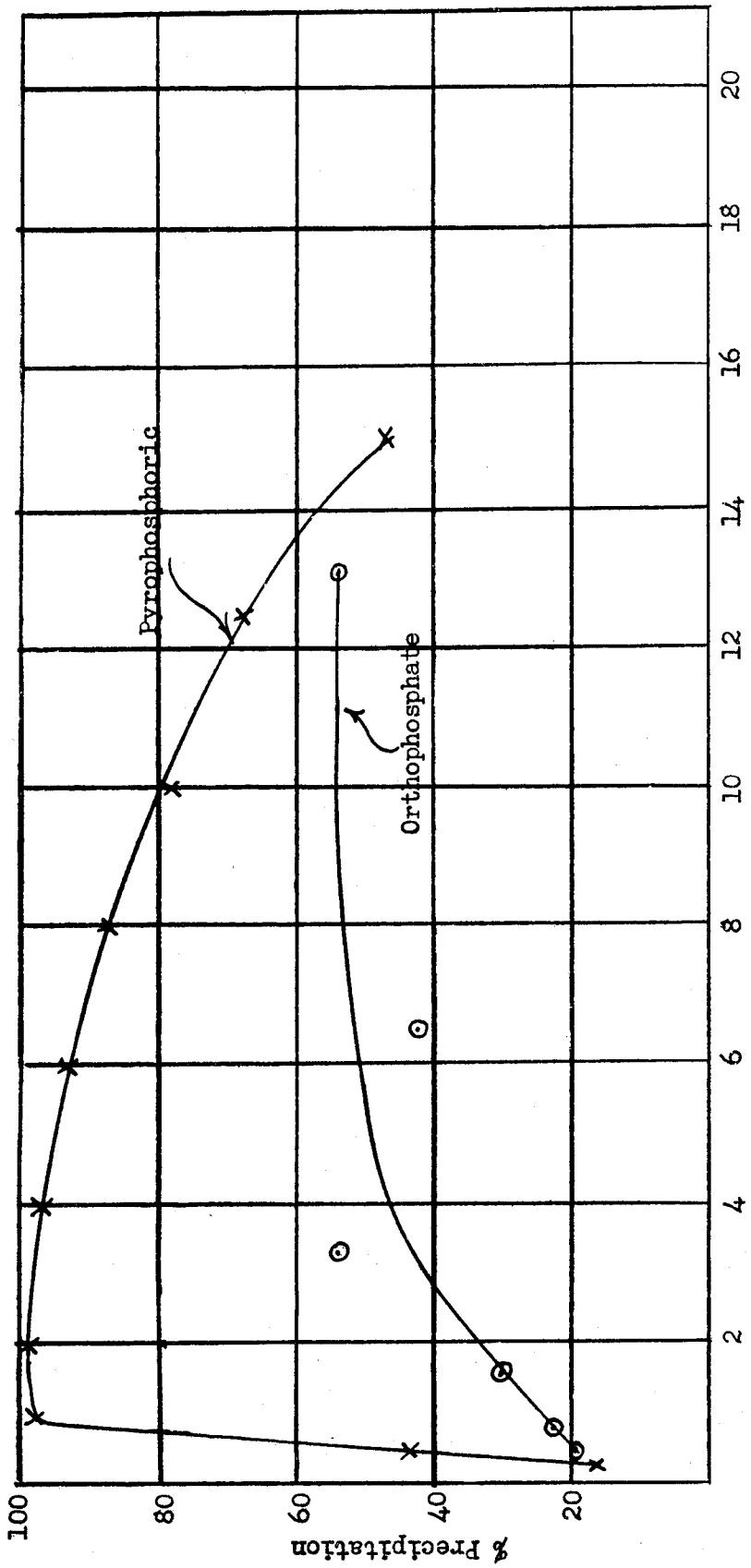


Figure 11. Precipitation of Uranium(IV) From a Pure Solution With Excessive Amounts of H_3PO_4 and $H_4P_2O_7$ at pH 1.0

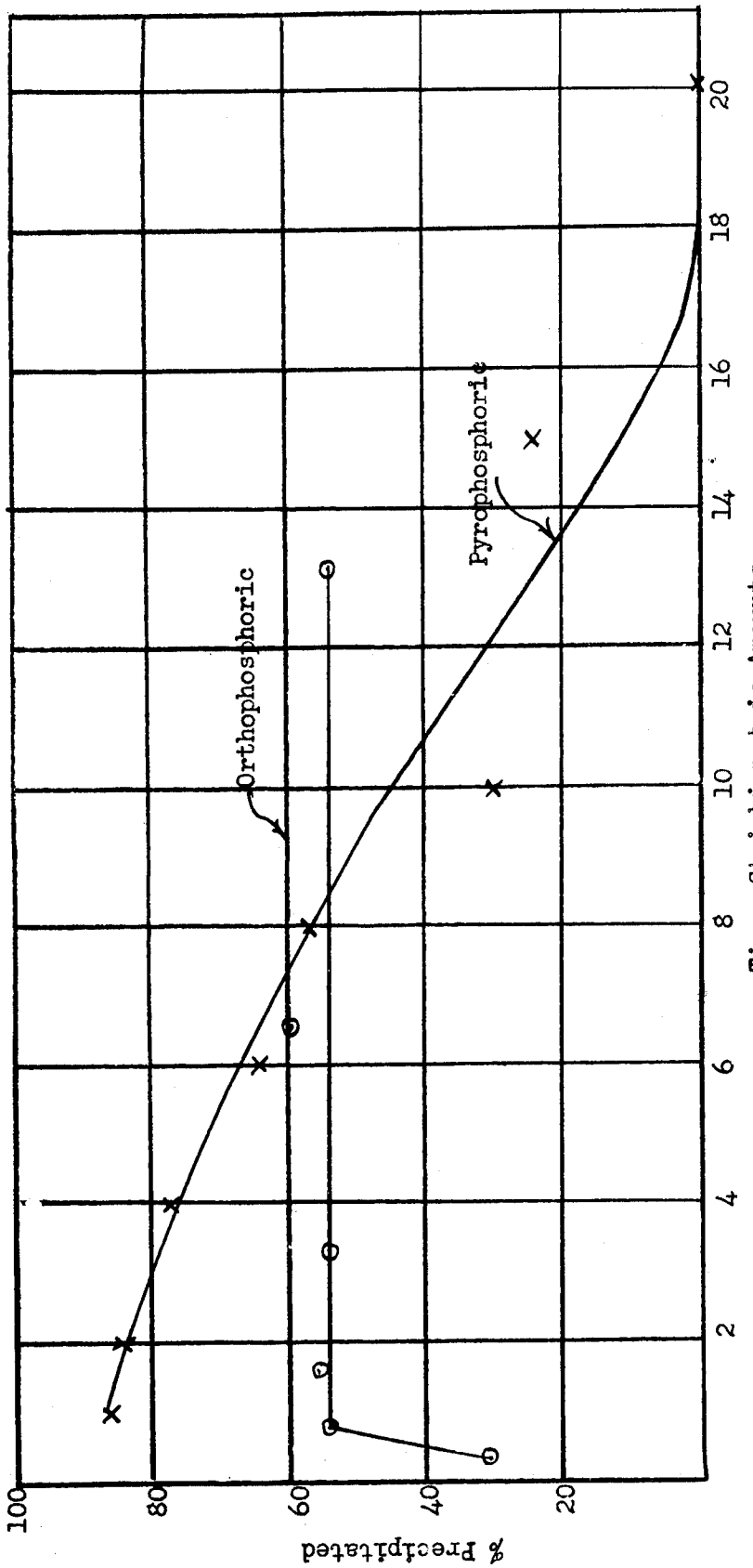


Figure 12. Precipitation of Uranium(IV) From a Pure Solution With Excessive Amounts of H_3PO_4 and $H_4P_2O_7$ at pH 1.5

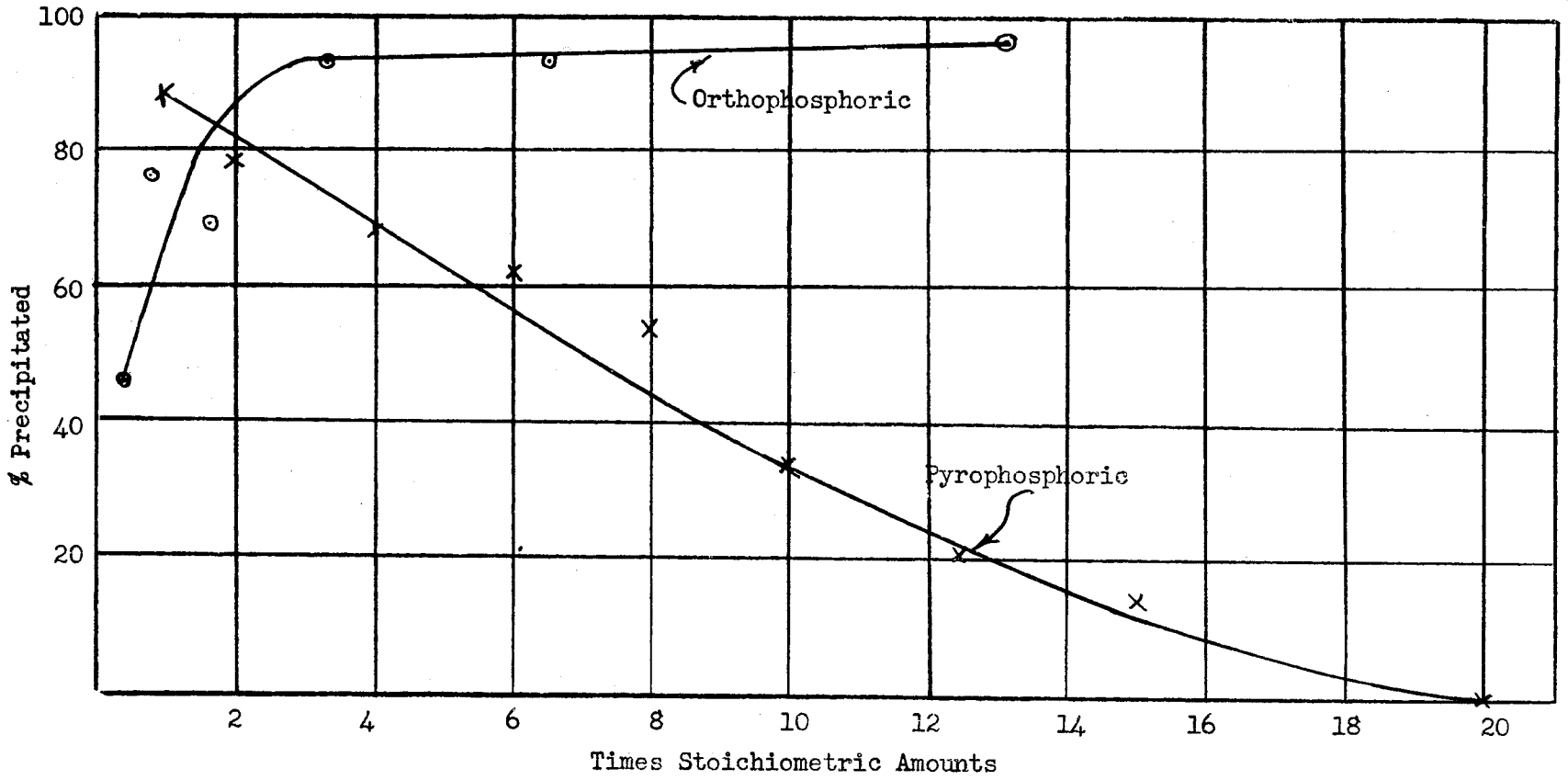


Figure 13. Precipitation of Uranium(IV) From a Pure Solution With Excessive Amounts of H_3PO_4 and $H_4P_2O_7$ at pH 2.0

12 is indicative of inadvertent oxidation of 40 per cent of the uranium. Thus, the significant feature of the curves is their shape and not their positions.

Correlative information on the relative solubilities of the ortho and pyrophosphates was derived from tests reported in MITG-A99, Appendix D, using pyrophosphate tagged with P^{32}. The results showed that in a mixture of ortho and pyrophosphoric acids uranium preferentially precipitated the pyro acid even in the presence of excess ortho acid. Hence, it is likely that the pyrophosphate is the less soluble.

To summarize measurements of "solubilities" it can be said that the data obtained show:

(a) a nonequilibrium system,
(b) an inverse dependence on pH,
(c) the formation of a soluble complex with excess pyrophosphate,
(d) the likelihood that UP_2O_7 is less soluble than $U_3(PO_4)_4$ in absence of large excess precipitant.

Thermal Decomposition of Uranous Phosphates

Besides their use in elucidating the composition and structure of the uranous phosphates, roasting experiments were expected to yield some information to explain the increased solubility in sodium carbonate of roasted ammonia precipitate from commercial phosphoric acid over the solubility of the dried material (MITG-229, -238). No information was available to indicate whether oxidation or an intramolecular change could be induced by ignition.

Most of the ignitions were carried out in muffle or tube furnaces with air present but no measurable differences were noted whether air was present or was replaced by nitrogen. By flowing nitrogen through a tube furnace and then through an alkaline solution, it was shown that no P_2O_5 was liberated. The most noticeable effect of roasting was to cause a shrinkage in bulk and weight. Most of the loss in weight occurred at temperatures below 400°C. Thereafter ensued a slight progressive diminution in weight with a second inflection at about 600°C. The uranyl phosphates are bright yellow in color while the roasted uranous phosphates were generally a slate-gray--not markedly different from the dried material. Therefore, oxidation was probably not a major effect. In order to obtain data on the progressive changes occurring at increasing temperatures, samples of ortho and pyrophosphate containing relatively large amounts of sulfate were selected for ignitions at temperatures up to 600°C and 900°C. They were held at each temperature in air four hours. The results of this experiment are plotted in Figures 14 and 15, whereby the following conclusions are apparent:

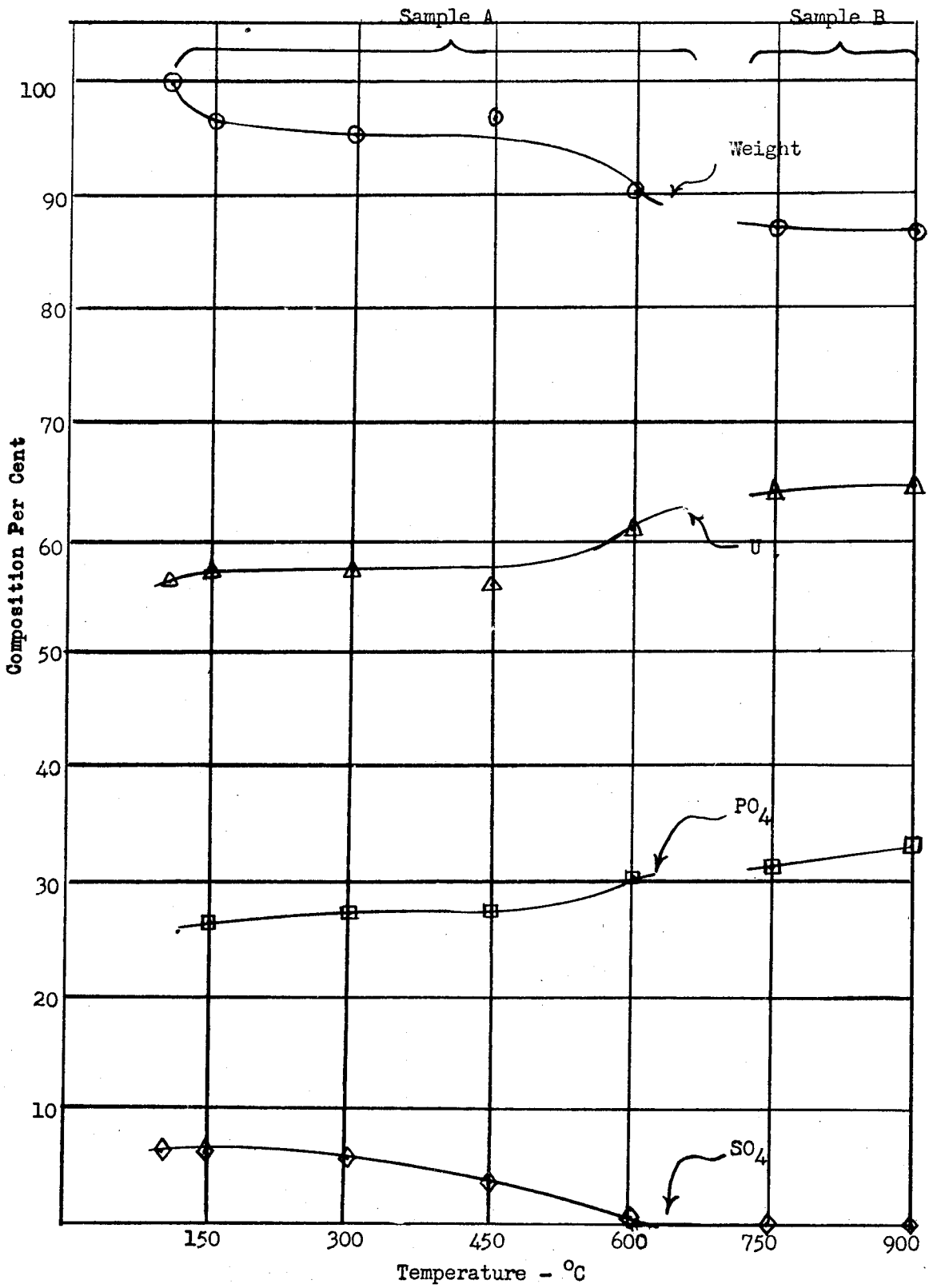


Figure 14. Effect of Heat Treatment on Composition of Uranous Orthophosphate

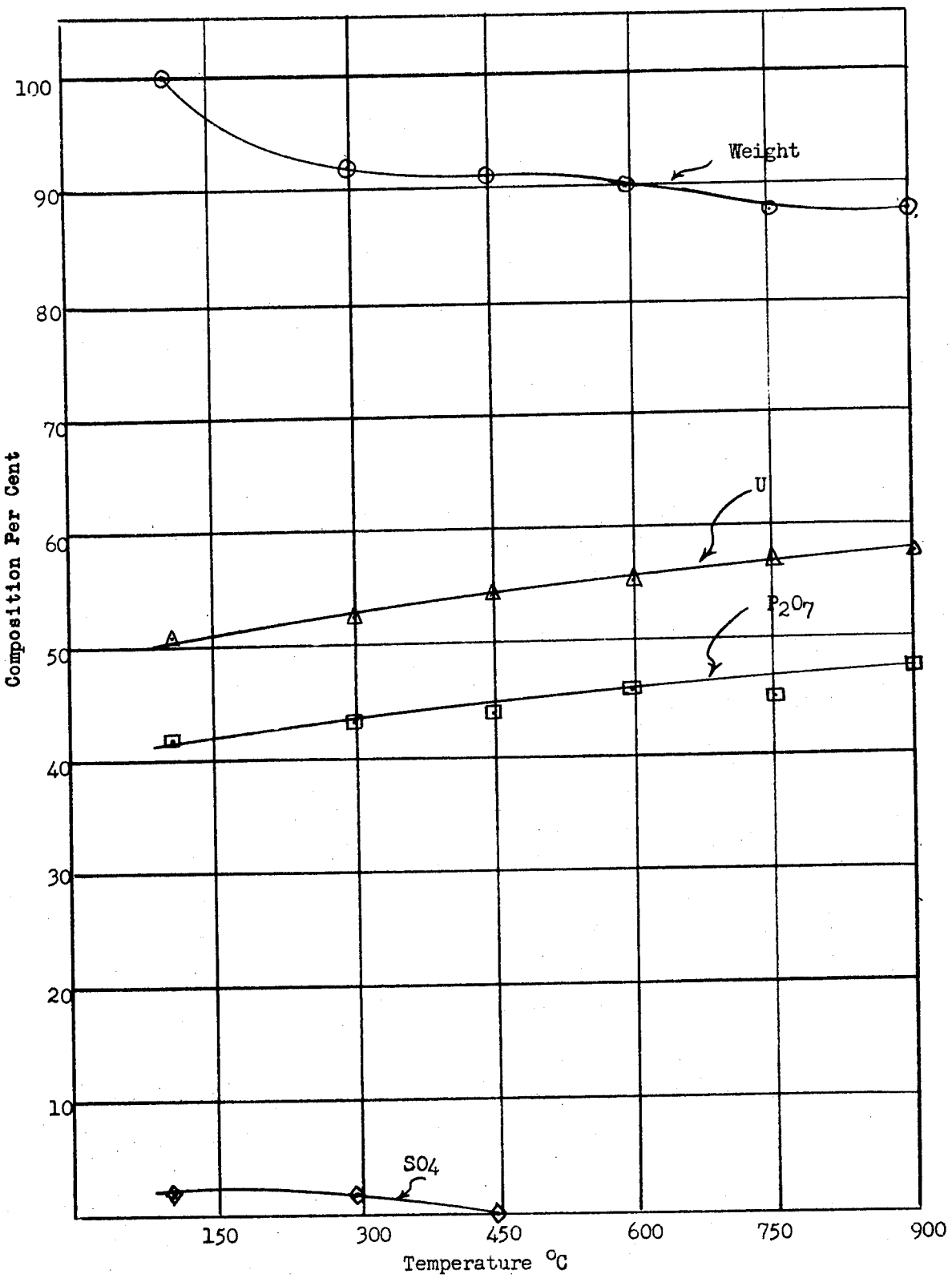


Figure 15. Effect of Heat Treatment on Composition of Uranous Pyrophosphate

1. The uranium : phosphate ratios remained approximately unchanged.

2. The sulfate persisted at temperatures above the boiling point of H_2SO_4 but was removed at 450-600°C and hence was probably present as uranous sulfate.

3. Assays of P_2O_7 and uranium on pyrophosphate continued to increase with ignition temperature even after totaling 100 per cent. At 900°C they total 106 per cent.

Identification by X-ray Patterns

The obvious application of x-ray diffraction to the problem of differentiating among uranous phosphates was found to be of limited value because these substances were not sufficiently crystalline to give any lines. Through the courtesy of Professor John T. Norton of MIT, a persistent search for patterns was made and they were found for phosphates ignited to or above 600°C. The pattern improved as the temperature of ignition was raised but could not be found for low temperatue ignitions even when these were of several days' duration.

Patterns obtained for UP_2O_7 were duplicated but augmented in those obtained for $U_3(PO_4)_4$. Moreover, many lines in the UP_2O_7 pattern coincided with those obtained by Peyronel* in a classic study of pyrophosphates. It is reasonable to assume, for that reason and because of the known properties of pyro compounds, that the UP_2O_7 is stable to ignition, which results, therefore, primarily in dehydration. Hence, it must be accepted that some UP_2O_7 is formed when $U_3(PO_4)_4$ is heated to 600°C as in the reaction

$$U_3(PO_4)_4 \longrightarrow 2UP_2O_7 + UO_2$$

Oxidation of UO_2 by air at the roasting temperatures would produce U_3O_8 so that the lines in the orthophosphate pattern which are not attributable to UP_2O_7 should be those of UO_2 or U_3O_8. Patterns were therefore obtained on UO_2, prepared by the decomposition of $UO_2SO_4 \cdot 3H_2O$ at 800°C in a stream of H_2, and on a National Bureau of Standards sample of U_3O_8. No reasonably accurate correlation of the unknown phase with either oxide was obtained although the oxide patterns were subsequently authenticated by reference to published data**. Comparison of the d-spacings, presented in Appendix A, suggests that the unknown phase might consist of a distorted U_3O_8 lattice but expert advice on this point is lacking.

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* Peyronel, O., Zeitschi, F. Kristallographic 92, 311 (1936)

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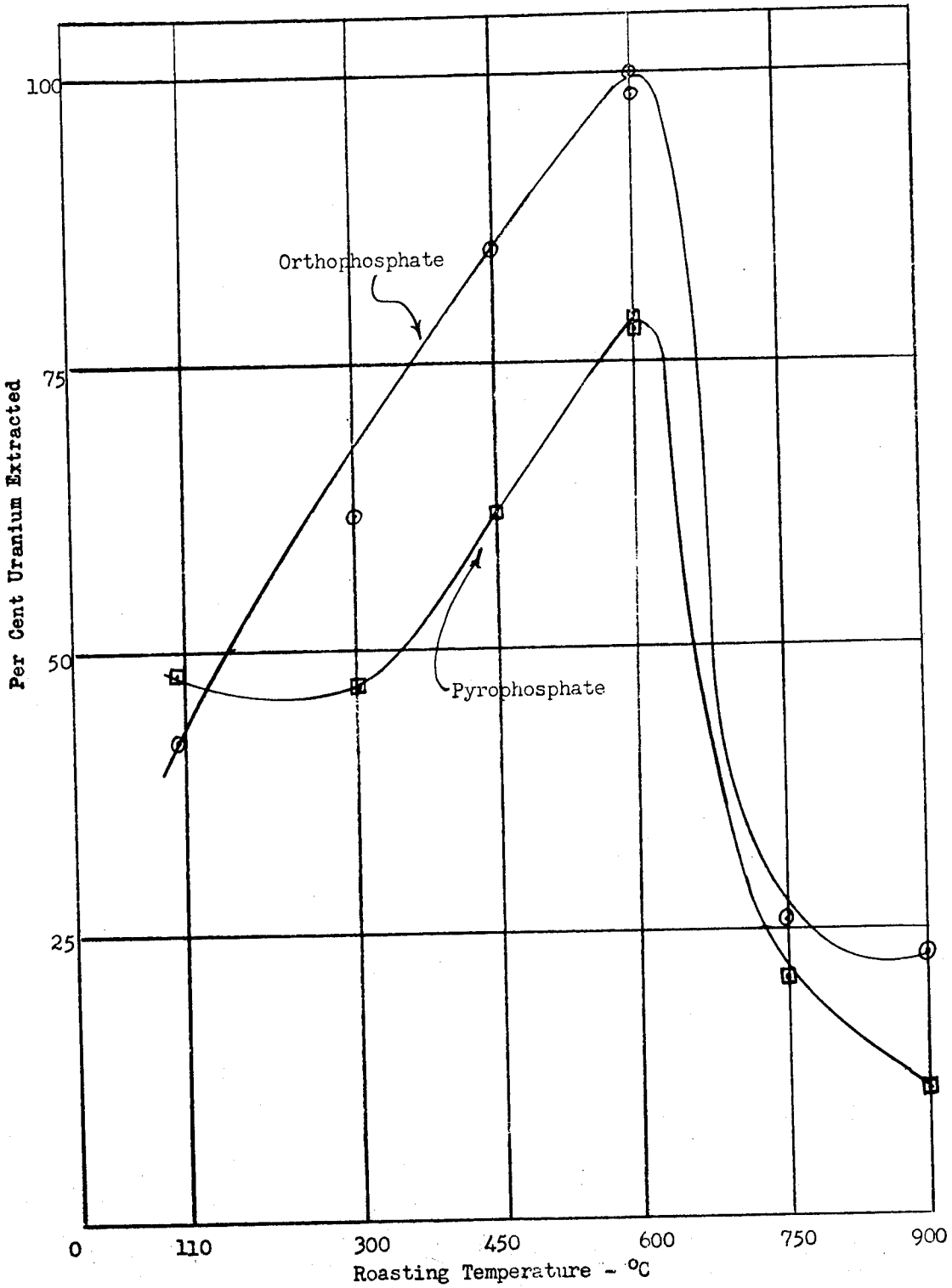

Figure 16. Effect of Roasting Temperature on Solubility of Uranous Phosphates in 4 Per Cent Na_2CO_3 Solution

Leaching Roasted Phosphates

Further information on the changes induced by roasting was obtained by sodium carbonate leaching of the roasted material. This experiment was pertinent to the method adopted for upgrading uranium extracted from commercial phosphoric acid and was carried out as follows: weighed amounts of dried phosphate were heated for 4 hours to 110°, 300°, 450°, 600°, 750°, and 900°C, reweighed, crushed, and dumped into 500 ml of a solution containing 40 grams Na_2CO_3 per liter. The solutions were stirred automatically for 16 hours at room temperature, then filtered, the residues washed and the filtrates made up to 1 liter. The per cent uranium extracted in these tests is shown in Figure 16 whence it is seen that the solubility of the uranium was at a maximum for those phosphates ignited at about 600°C but fell off sharply at lower and higher temperatures. This is true of both ortho and pyrophosphates, although the pyro appeared to be somewhat less soluble. The similarity between this result and that obtained by Clevenger on a low-grade (MITG-229) uranium precipitate from commercial phosphoric acid is probably merely coincidental as the behavior of uranium in those materials appears to depend on the presence of vanadium (MITG-241).

Precipitation of Uranium from a Simulated Leach Liquor

As already stated, tests were made to determine the effect of excess phosphate on the degree to which uranium could be precipitated from a solution devoid of interfering cations. An extension of this investigation into a more complex system, containing the principal cations found in leach liquors, served to demonstrate the impossibility of applying data obtained on one system to another. The simulated leach solution was made by dissolving sulfates of the following metals in sulfuric acid at pH 1.0 to give the concentration noted:

Fe(III)	2.0	g/l
Fe(II)	4.0	g/l
Al(III)	1.8	g/l
Mn(II)	3.0	g/l
U(VI)	0.3	g/l

Reduction was effected with a Jones reductor and the effluent was adjusted to the desired pH by addition of NH_4OH before division into a number of aliquots. To each an amount of precipitant, which was at the same pH, was added up to 140 times stoichiometric for the uranium; this figure giving stoichiometric amounts for all cations present. The precipitate was allowed to stand at room temperature for a minimum of 3 hours before filtration. Analyses of the filtrates for U_3O_8 gave the figures used in preparing the graphs in Figures 17, 18, and 19. Better precipitation was obtained with pyro than with orthophosphoric acid under all conditions except at pH 1.0 with 40 times stoichiometric or more, when complexing was apparent.

At first glance one might suspect that incomplete reduction was partly responsible for the ineffectiveness of precipitation with H_3PO_4 as seen in Figures 18 and 19, although this is unlikely because the tests at pH 2.0 with ortho and pyro were both made on aliquots of the same solution. However, in order to check this point a quadruple-strength leach solution was made up and reduced at a pH below 0.5 before dilution and neutralization. The results obtained by precipitating the uranium with H_3PO_4 were substantially in agreement with those obtained previously.

Some clue to a correct interpretation of these results was looked for in the precipitates which were washed, ignited at 500°C, and weighed. By precipitation with orthophosphate, residues weighing between 15 and 60 mg were obtained, the weights showing little relation to amounts of uranium precipitated. The average precipitate should have contained about 20 mg of uranous phosphate. With pyrophosphate, on the other hand, copious precipitates were obtained at the higher pH levels. At pH 1.0 they weighed between 36 and 46 mg but at pH 2.0 weighed between 8 and 376 mg, the weights following roughly the same curve as the amount of uranium precipitated. It seemed clear that at pH 1.5 or 2.0 other cations competed for the pyrophosphate. Spectrographic analyses showed the precipitate to contain besides uranium over 10 per cent Al_2O_3 and 1 to 10 per cent Fe_2O_3. As the pyrophosphate curves level off at the 30-fold excess point, corresponding to 0.585 gram P_2O_7, one may assume that the interference was saturated at that point and determine if it corresponds to some function of the amounts of other cations present. As the solutions contained 0.18 gram Al, the pyrophosphate tied up would not have sufficed to make more than a basic compound corresponding to the formula $(Al\ OH)_2\ P_2O_7$. Similarly, too much iron was present to form a simple compound with the pyrophosphate. Precipitation of the individual components was not successful with either ortho or pyrophosphate, and ferric, but not ferrous, ion, was the only one immediately precipitated below pH 2.0. As it was evident that the problem could not be solved rapidly, it was terminated and marked the end of excursions into a study of leach solutions. Although the need for further study is obvious, it is suggested that the explanation for the less effective precipitation in simulated, rather than an actual leach solution rests on the absence of silicate anion.

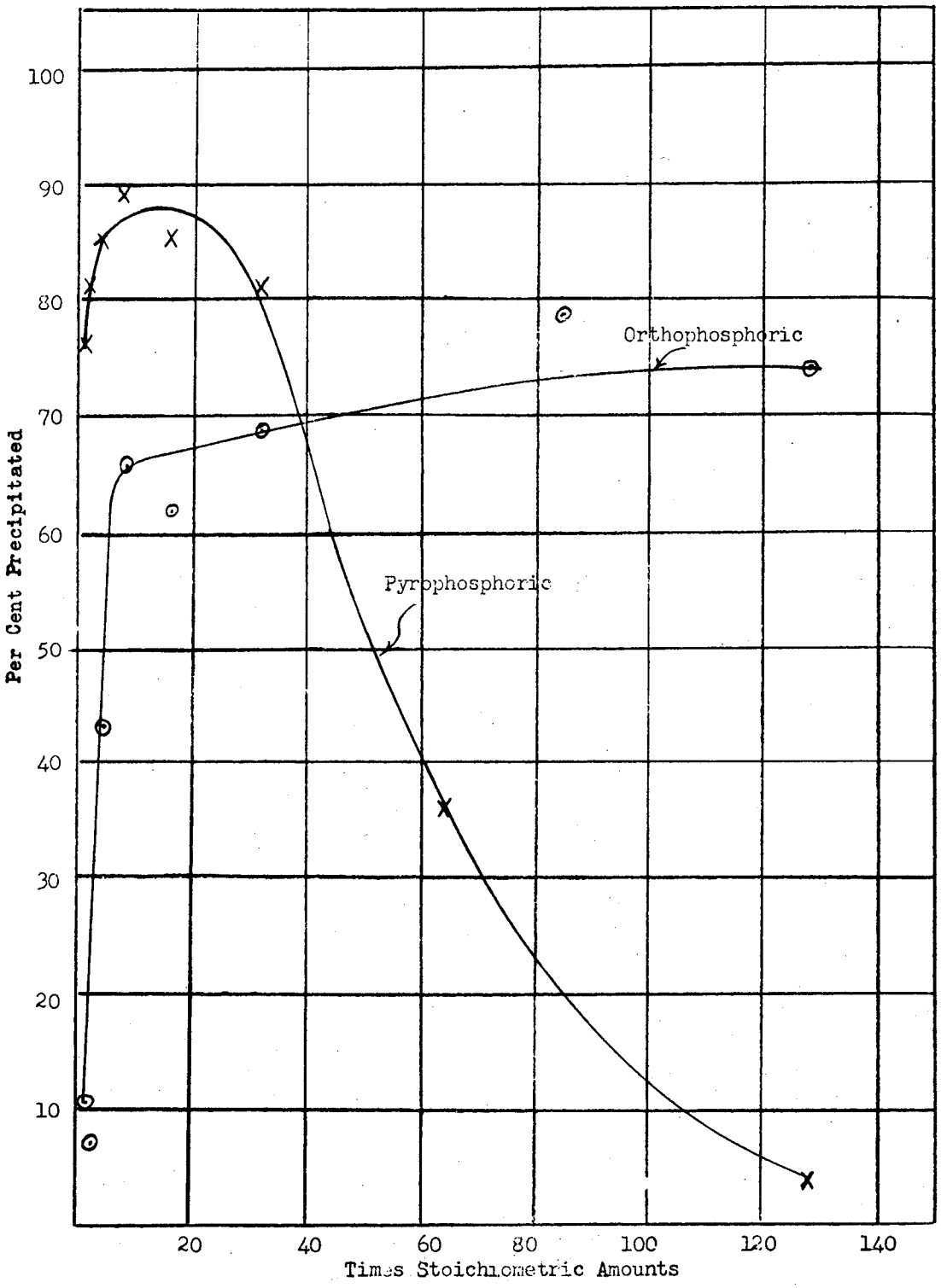

Figure 17. Precipitation of Uranium(IV) from a Pregnant Solution With H_3PO_4 and $H_4P_2O_7$ at pH 1.0

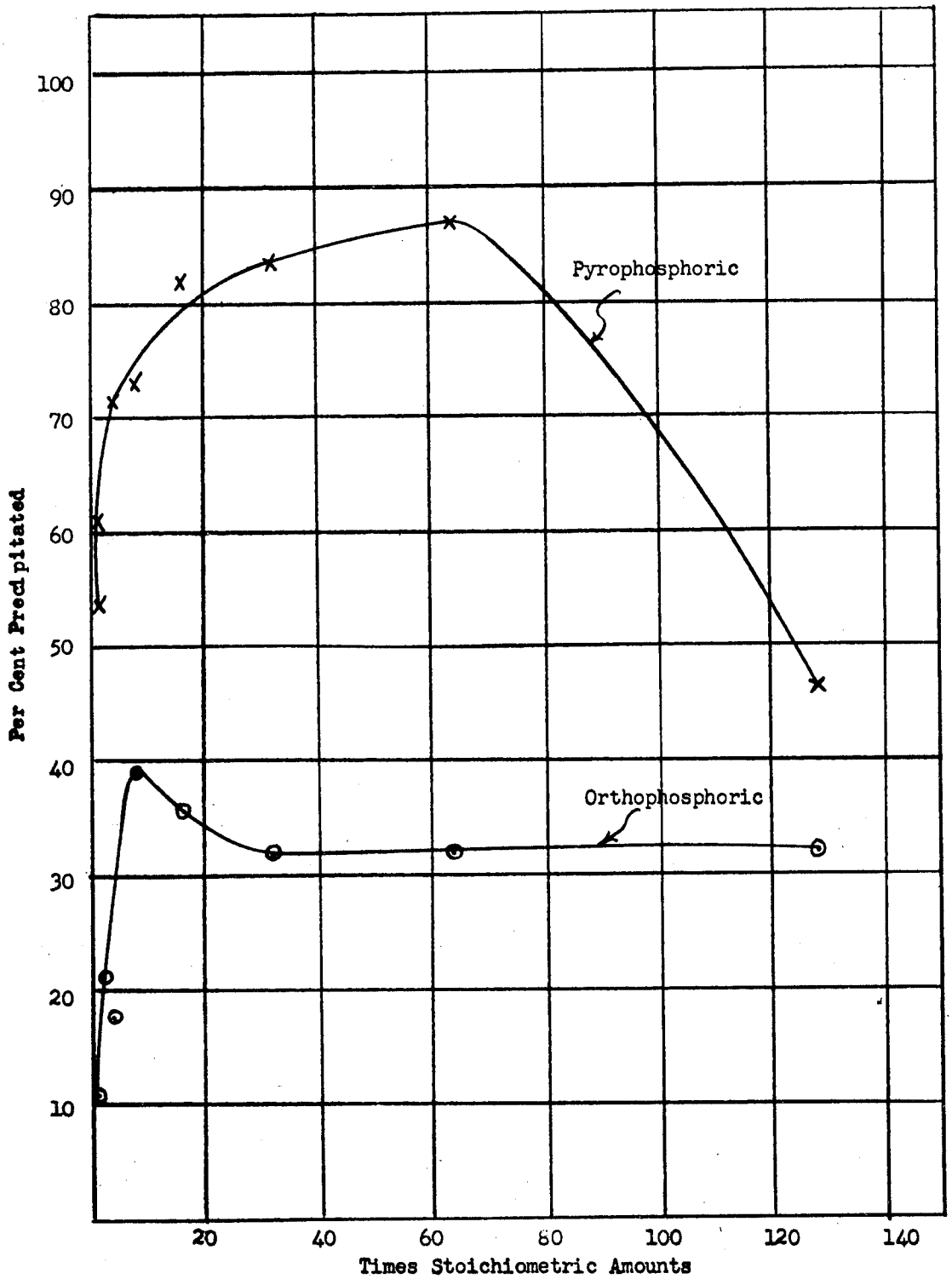

Figure 18. Precipitation of Uranium(IV) From a Simulated Pregnant Solution With H_3PO_4 and $H_4P_2O_7$ at pH 1.5

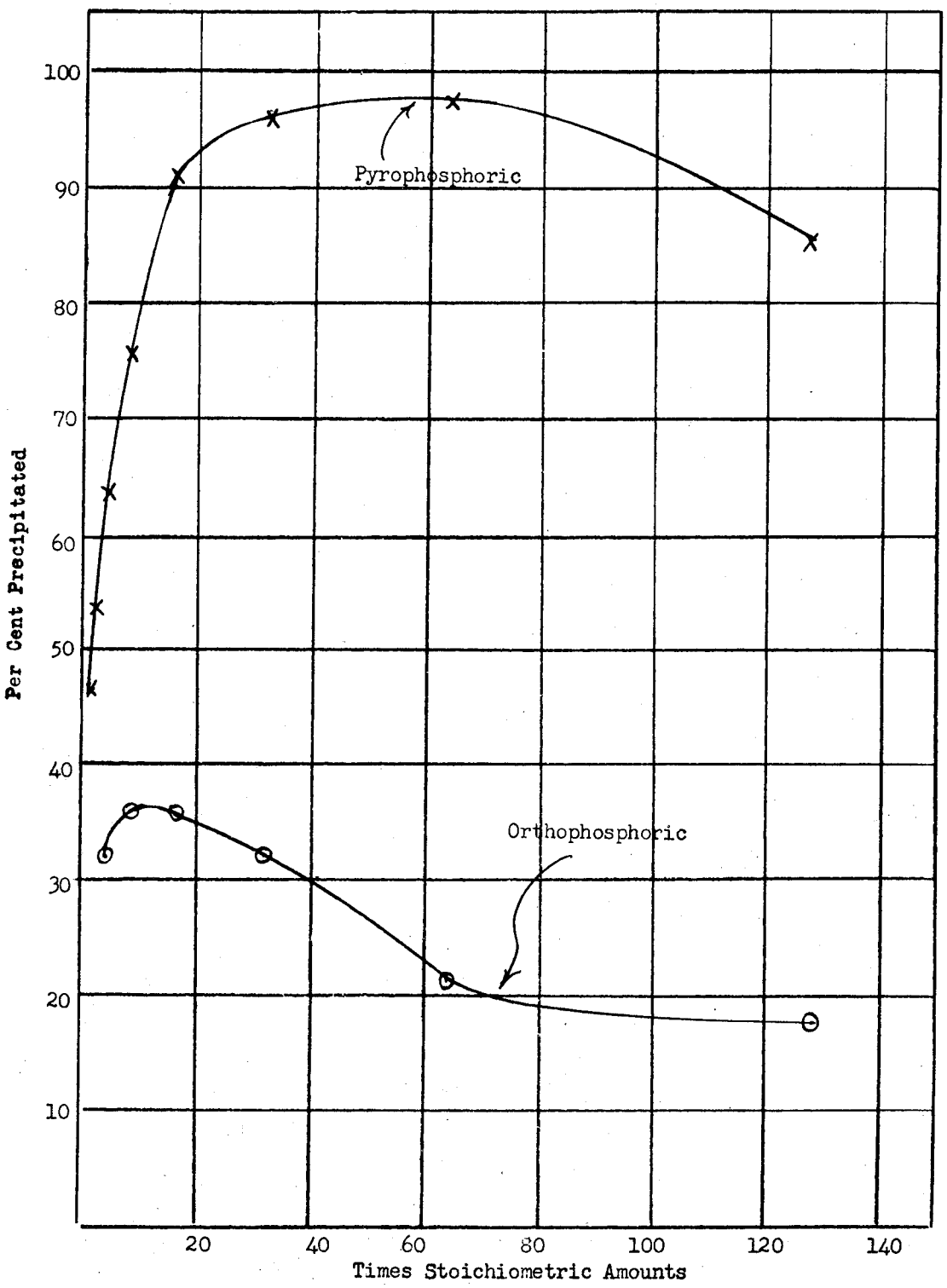

Figure 19. Precipitation of Uranium(IV) From a Simulated Pregnant Solution With H_3PO_4 and $H_4P_2O_7$ at pH 2.0

APPENDIX A

X-ray Diffraction Data

Plots of d-spacings, calculated from diffraction patterns obtained on a Norelco instrument at MIT, are presented in the following pages.

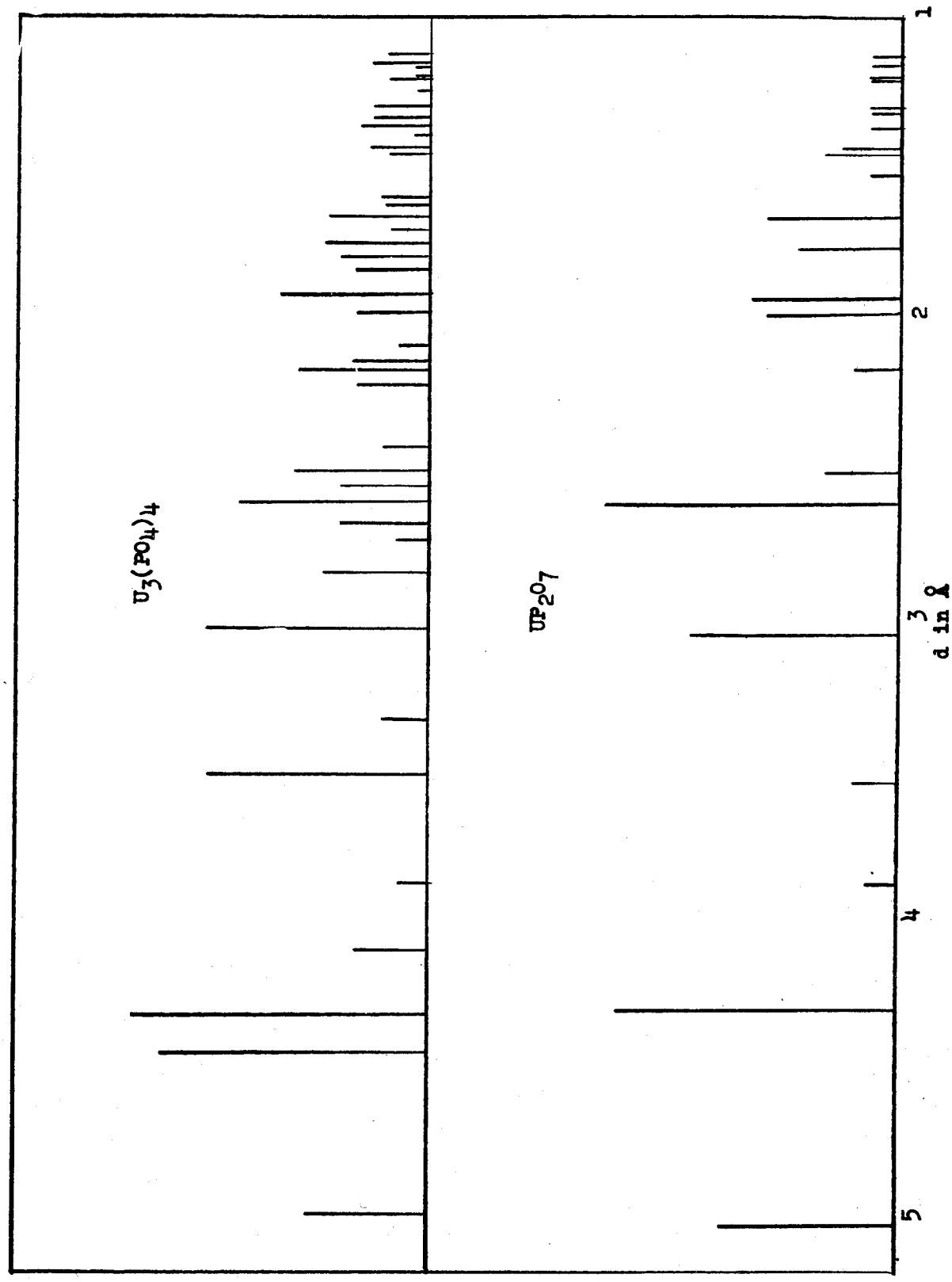

Figure A-1. d-Spacings in Uranous Phosphates Ignited to 750°C

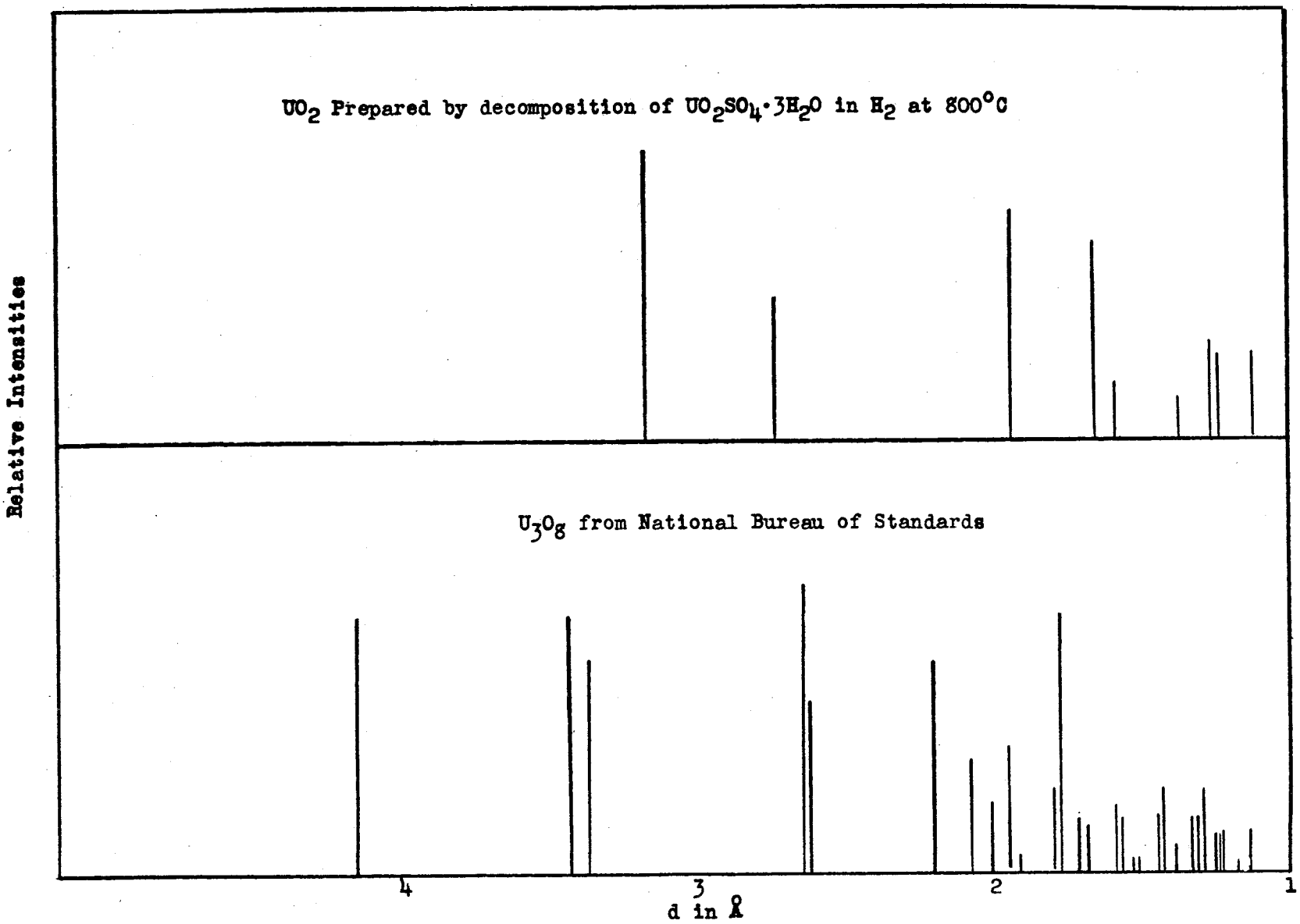

Figure A-2. d-Spacings in Uranium Oxides

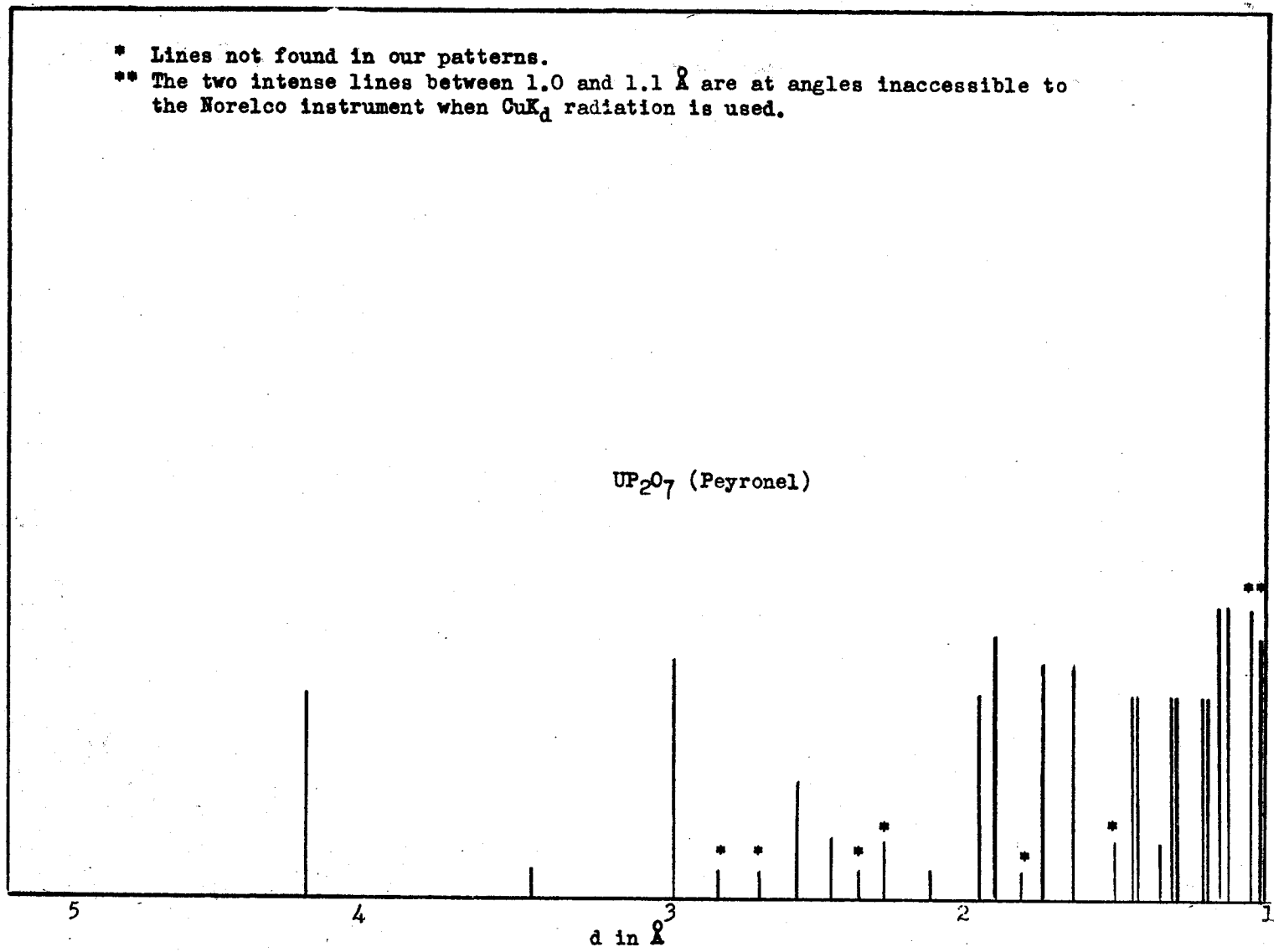

Figure A-3. d-Spacings Given by Peyronel for UP_2O_7 (Zeitschr, F Kristallographic, 92, 311, 1936)

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