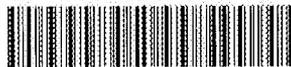


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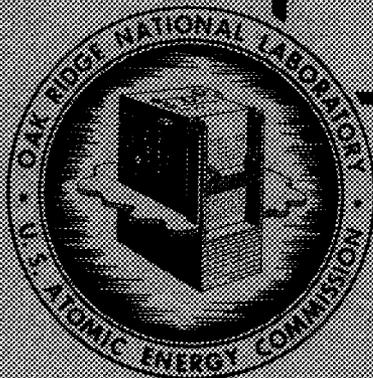
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THE CHEMISTRY OF URANIUM(IV) ORTHOPHOSPHATE
SOLUTIONS: PART I, THE SOLUBILITY OF
URANIUM(IV) ORTHOPHOSPHATES IN
PHOSPHORIC ACID SOLUTIONS

J. M. Schreyer



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THE CHEMISTRY OF URANIUM(IV) ORTHOPHOSPHATE SOLUTIONS:
PART I, THE SOLUBILITY OF URANIUM(IV) ORTHOPHOSPHATES
IN PHOSPHORIC ACID SOLUTIONS

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INTRODUCTION AND SUMMARY

This is the first in a series of reports describing investigations of the chemistry of the uranium(IV) orthophosphate system which are being carried out in this laboratory. Solubility, spectrophotometric, and potentiometric techniques are being used in these studies, which may eventually lead to the identification of the ionic species that exist in uranium(IV) phosphate solutions. The work thus far has been primarily concerned with phase studies in the pure uranium(IV) phosphate system as a prelude to further studies in more complex systems such as $\text{UO}_2\text{-P}_2\text{O}_5\text{-Cl}_2\text{O}_7\text{-H}_2\text{O}$, $\text{UO}_2\text{-P}_2\text{O}_5\text{-CaO-H}_2\text{O}$, $\text{UO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{F}_2\text{-H}_2\text{O}$, and $\text{UO}_2\text{-P}_2\text{O}_5\text{-CaO-H}_2\text{F}_2\text{-H}_2\text{O}$. The results of the $\text{UO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ solubility investigation obtained to date are included in this report.

Investigations in the uranium(IV) orthophosphate system reported prior to the present work are incomplete with regard to solubilities as well as to the composition of the solid phases in equilibrium with the phosphate solutions. Some early investigators, C. F. Rammelsberg, R. Arendt and W. Knop, P. Chastaing, J. Aloy,⁽¹⁾ and Schaap, Andrews and Gates,⁽²⁾ reported the preparation of $\text{U}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ by various precipitation methods. J. Aloy⁽¹⁾ also reported the preparation of $\text{U}(\text{HPO}_4)_2 \cdot 5\text{H}_2\text{O}$.

As a result of an investigation aimed at characterizing phosphates of tetravalent uranium, Pannell and Rubino⁽³⁾ reported that these compounds, when formed by precipitation, are gelatinous substances of somewhat variable composition. Some solubility measurements of uranium(IV) phosphates in aqueous solutions of nitric, hydrochloric, sulfuric, phosphoric, perchloric, and acetic acid in the pH range of 0.5 to 2.5 were also made. Unfortunately, the samples were shaken mechanically for only 4.5 hours which the investigators recognized as an insufficient time to attain equilibrium. In addition, no mention was made of temperature control during the solubility runs. G. L. Milward⁽⁴⁾ described the titration of a uranium(IV) sulfate solution with 0.1M Na_2HPO_4 , and reported that an inflection point on the titration curve indicated the formation of $\text{U}_3(\text{PO}_4)_4$ under these conditions.

The present solubility measurements in the $\text{UO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ system were made at $25^\circ \pm 0.1^\circ\text{C}$ by precipitation and dissolution

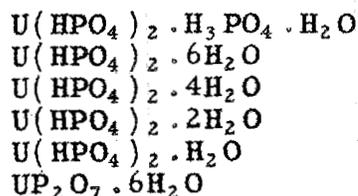
techniques in the range from 1.5 to 15M total dissolved phosphate. The stable solid phase below 9.8M total phosphate was found to be $U(HPO_4)_2 \cdot 6H_2O$ and above 9.8M, $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$.

The solubility of $U(HPO_4)_2 \cdot 6H_2O$ was found to increase with increasing phosphate concentration from $2 \times 10^{-4}M$ uranium at 1.5M phosphate to 0.62M uranium at 9.8M phosphate. In the metastable region above 9.8M phosphate the solubility of the hexahydrate rose to 1.25M uranium at 11.3M phosphate. From 1.5 to 11.3M phosphate the solubility of the hexahydrate can be represented by the empirical equation

$$[U^{+4}] = 2.55 \times 10^{-5} [PO_4^{-3}]^{4.41}$$

The solubility of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ increased less rapidly with increasing phosphate concentration, from 0.62M uranium at the transition point to 1.3M uranium at 15M phosphate.

During the investigation the following solids were identified:



The first two of these were separated from saturated solutions by filtering and were identified by Schreinemakers' wet-residue method. Attempts to further separate and purify them were unsuccessful due to chemical alteration to other orthophosphate solids. Acetone washing converted the hexahydrate and the H_3PO_4 addition compound to the tetrahydrate and monohydrate, respectively. The latter compounds were identified by chemical analysis.

The monohydrate was also produced by perchloric acid dehydration of the tetrahydrate. Thermal dehydration of the tetrahydrate gave the dihydrate, but this reverted to the tetrahydrate when exposed to the atmosphere. The tetrahydrate, which was stable under ordinary atmospheric conditions, was used as the starting material for solubility determinations.

The uranium(IV) pyrophosphate hexahydrate was prepared for the purpose of establishing an X-ray diffraction pattern. Its solubility was not determined. X-ray diffraction patterns were obtained for all of the orthophosphate solids except the dihydrate.

STABILITY OF URANIUM(IV) ORTHOPHOSPHATE SOLUTIONS

To obtain information on the stability of uranium(IV) toward air oxidation in phosphoric acid solutions, two solutions containing different concentrations of phosphate and uranium(IV) (prepared by dissolving $U(HPO_4)_2 \cdot 4H_2O$ in the appropriate phosphoric acid solution) were vigorously aerated at 25°C. Aliquots were removed at various time intervals and analyzed for uranium(IV). The data in Table 1 show no significant change in concentration of uranium(IV) during these periods of aeration.

Table 1

STABILITY OF URANIUM(IV) PHOSPHATE

SOLUTIONS AT 25°C

<u>$[PO_4^{-3}]$</u> gram ions/l	<u>Time of</u> <u>Aeration</u> <u>Minutes</u>	<u>$[U^{+4}]$</u> gram ions/l
8.50	0	0.02009
	30	0.02010
	120	0.02012
	240	0.02010
	360	0.02010
3.18	0	0.003300
	90	0.003298
	210	0.003308
	420	0.003298

The stability toward air oxidation of uranium(IV) in phosphoric acid solutions is greater than has been reported by Nichols⁽⁵⁾ for uranium(IV) chloride solutions and by Sill and Peterson⁽⁶⁾ for uranium(IV) sulfate solutions, indicating a comparatively stronger complex formation between uranium(IV) and phosphate in acid solutions. As a result, it was unnecessary to remove oxygen from the solubility mixtures above 3.18M total phosphate prior to shaking, and also the filtration of the equilibrium mixtures could be performed without protecting the

mother liquor from air. Studies below 3.18M total phosphate were not made because below this concentration the uranium(IV) phosphate solubility was found to be too low for detection of small changes in uranium(IV) by the available analytical methods. Operations in the solubility determination in this region were carried out in a nitrogen atmosphere.

PREPARATION AND PURIFICATION OF $U(HPO_4)_2 \cdot 4H_2O$

Uranium(IV) orthophosphate is a light green hydrogel when freshly precipitated from aqueous solution. Except for the color, it resembles freshly precipitated hydrous aluminum oxide. On the basis of this similarity, the method of Willstätter⁽⁷⁾ for dehydrating hydrous oxides with acetone was employed. It was found that this method not only removed the entrained water from the uranium(IV) orthophosphate gel, but also removed perchlorate impurities and some of the water of hydration. The last traces of acetone were difficult to remove by evacuation, but could be washed out with carbon tetrachloride which was then removed by vacuum drying.

The detailed procedure for preparing samples of $U(HPO_4)_2 \cdot 4H_2O$ for use in the solubility studies is given below.

About 500 ml of a uranium(VI) phosphate solution containing approximately 0.25M UO_2^{++} , 3M H_3PO_4 , and 3.5 to 4.5M H_2SO_4 was reduced in a Jones reductor. In a previous report⁽⁸⁾ it was shown that under these conditions uranium(VI) is reduced quantitatively to uranium(IV). Uranium(IV) phosphate was precipitated from this reduced solution by slowly diluting with water until the concentration of sulfuric acid was approximately 1M. Vigorous stirring was required during the dilution and for several hours afterwards to produce a uniform product. The gelatinous precipitate was separated by filtering with suction through a coarse fritted glass filter.

The solid was washed twice with 2-liter portions of 1M $HClO_4$ and five times with 1500 ml portions of acetone. Each wash was performed with vigorous stirring for two hours followed by filtration. The solid was mixed on the filter with two 100-ml portions of CCl_4 , then placed in a vacuum desiccator with continuous suction for 3 hours. The resulting solid was a grayish green dusty powder. A yield of from 70 to 80 grams was obtained.

As indicated in Table 2, 5 acetone washes will remove the major portion of the sorbed perchlorate. In addition, the acetone dehydrates the solid from the hexahydrate, the equilibrium solid phase below 9.8M total phosphate, at least to the tetrahydrate.*

Table 2
REMOVAL OF PERCHLORATE FROM $U(HPO_4)_2 \cdot 4H_2O$
WITH ACETONE
(500 ml per 25 gram samples)

<u>Sample Number</u>	<u>No. of Acetone Washes</u>	<u>Percentage (ClO_4^-)</u>
M-220	1	5.7
	2	0.42
	3	0.24
*M-204	1	31.4
	2	3.04
M-325	5	0.02**

*This sample was washed with 3M $HClO_4$ instead of 1M $HClO_4$.

**Limit of detectibility of analytical method.

*Ethanol and water were also tested as washing agents. In one determination the perchlorate concentration was reduced to less than 0.03% by two ethanol washes, giving a product with a $U^{+4}/PO_4^{-3}/H_2O$ mole ratio of 1/2.01/3.91. However, because the ethanol slurry of the solid filtered very slowly, acetone was chosen as the washing agent.

Pannell and Rubino⁽³⁾ used water as a washing agent to remove impurities from their uranium(IV) phosphate preparations. In this investigation, water was found to be inadequate for removal of these impurities due to the hydrophilic nature of the product.

Analyses of the $U(HPO_4)_2 \cdot 4H_2O$ preparations used in this study are shown in Table 3. The percentages of water, as determined by difference, did not show a uniform state of hydration, although the ratios of U^{+4}/PO_4^{-3} were in good agreement with the formula $U(HPO_4)_2 \cdot xH_2O$. It was observed that the preparations whose state of hydration was less than 4 very slowly increased in weight when exposed to the atmosphere.

Table 3

ANALYSIS OF $U(HPO_4)_2 \cdot 4H_2O$ PREPARATIONS

Theory:

$U(HPO_4)_2 \cdot 6H_2O$; U^{+4} (44.23%), PO_4^{-3} (35.29%), H_2O (20.06%)
 $U(HPO_4)_2 \cdot 4H_2O$; U^{+4} (47.4%), PO_4^{-3} (37.8%), H_2O (14.4%)
 $U(HPO_4)_2 \cdot 3H_2O$; U^{+4} (49.2%), PO_4^{-3} (39.2%), H_2O (11.2%)

Sample Code	Percentage U^{+4}	Percentage PO_4^{-3}	Percentage Water By Difference	Mole Ratio $U^{+4}/PO_4^{-3}/H_2O$
M-83	47.3	38.2	14.1	1/2.02/3.94
M-134	48.1	37.2	14.3	1/1.93/3.93
M-174	47.2	37.4	15.0	1/1.99/4.19
M-183	48.1	38.6	12.9	1/2.01/3.55
M-233	49.4	36.2	14.0	1/1.84/3.74
M-234	48.7	38.8	12.1	1/2.00/3.28
M-242	48.8	38.9	11.9	1/2.00/3.22
M-290	47.2	37.6	14.8	1/1.99/4.14

Table 4 contains data on the change of hydration of an acetone dried uranium(IV) phosphate preparation when continuously exposed to the atmosphere. These data demonstrate that acetone can dehydrate the $U(HPO_4)_2 \cdot 6H_2O$ below the tetrahydrate but that the product is hygroscopic and approaches the tetrahydrate. It will also be shown later that the lower

hydrate, $U(HPO_4)_2 \cdot 2H_2O$, is hygroscopic and returns to the tetrahydrate.

Table 4
CHANGE OF HYDRATION OF AN ACETONE DRIED
URANIUM(IV) ORTHOPHOSPHATE PREPARATION

Days Exposed to Atmosphere	Mole Ratio		
	<u>U+4</u>	<u>PO₄⁻³</u>	<u>H₂O</u>
0	1	1.97	2.73
10	1	1.99	3.13
17	1	2.02	3.18
28	1	2.01	3.33
42	1	2.01	3.36
64	1	1.97	3.72
98	1	1.98	3.84
113	1	1.95	3.80

No crystals were observed by microscopic examination of the $U(HPO_4)_2 \cdot 4H_2O$ preparations. The compound was stable to the atmosphere, only slightly soluble in dilute acid but slowly dissolved in cold concentrated acids. Rapid dissolution could be obtained in concentrated nitric acid through the oxidation of the uranium(IV) to uranium(VI).

All of the samples of $U(HPO_4)_2 \cdot 4H_2O$ gave the same X-ray pattern as is shown in Photograph 20742 in Figure 1. Pannell and Rubino⁽³⁾ detected no diffraction patterns in any of their unroasted uranium(IV) orthophosphate preparations.

SOLUBILITY OF URANIUM(IV) ORTHOPHOSPHATES
IN PHOSPHORIC ACID SOLUTIONS

1. EXPERIMENTAL

The solubility measurements were carried out by adding $U(HPO_4)_2 \cdot 4H_2O$ to a solution of known composition, placing the

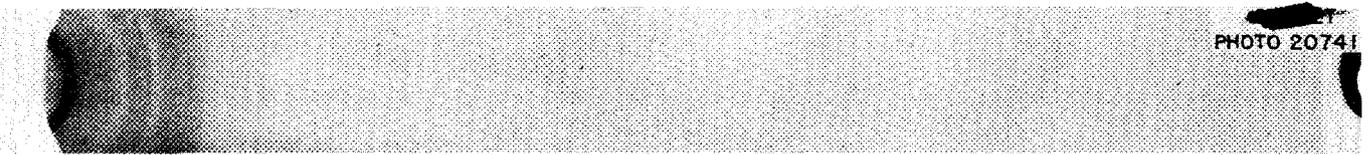


PHOTO 20741

PATTERN OF $U(HPO_4)_2 \cdot 6H_2O$

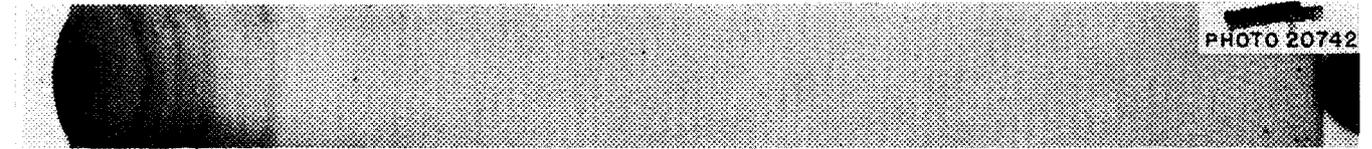


PHOTO 20742

PATTERN OF $U(HPO_4)_2 \cdot 4H_2O$

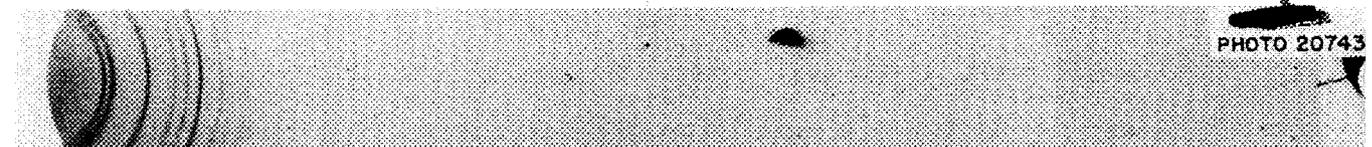


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PATTERN OF $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$

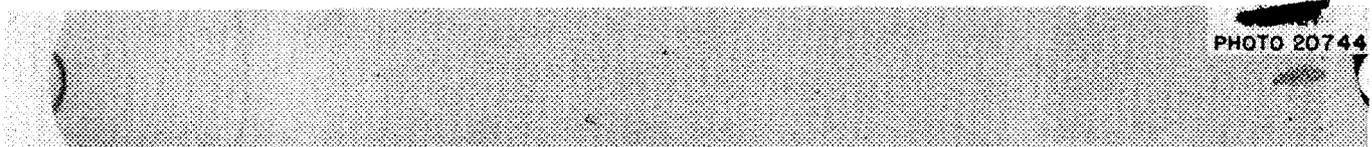


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PATTERN OF $U(HPO_4)_2 \cdot H_2O$ (PERCHLORIC ACID DEHYDRATION)

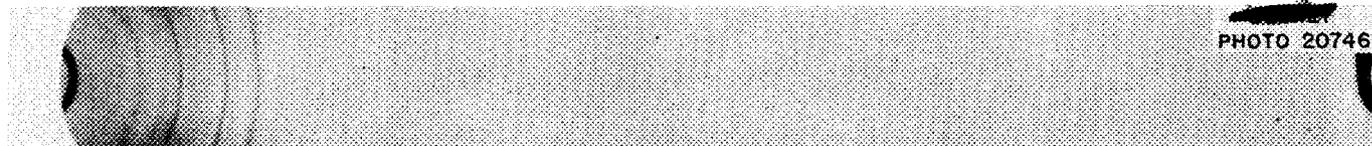


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PATTERN OF $U(HPO_4)_2 \cdot H_2O$ (ACETONE WASHED $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$)

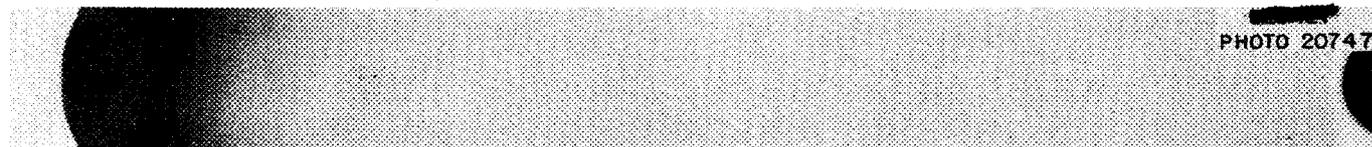


PHOTO 20747

PATTERN OF $UP_2O_7 \cdot 6H_2O$

FIGURE I

X-RAY DIFFRACTION PATTERNS

PATTERNS PREPARED BY H.W. DUNN, ISOTOPE ANALYSIS METHODS LABORATORY
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mixture in a round bottom Pyrex flask and shaking in a water bath at $25^{\circ} \pm 0.1^{\circ}\text{C}$ for a period which was sufficient to attain equilibrium conditions. In each experiment, the tetrahydrate was converted to the hexahydrate. In high concentrations of phosphoric acid the hexahydrate, in turn, was changed to $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$. Since neither of the latter two equilibrium compounds could be obtained as pure solids for direct dissolution experiments, the solubility measurements were made by the indirect route, starting with the tetrahydrate. In addition, a few precipitation runs were made by diluting saturated mother liquors with water.

The attainment of solubility equilibrium in the various samples was demonstrated by studies of the rates of dissolution and by a comparison of solubilities obtained from both dissolution and precipitation runs. In the rate studies, $\text{U}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ was added to phosphoric acid solutions and aliquots were removed for analysis periodically. In 8.5M and 5.9M total phosphate, equilibrium was attained in 12 and 18 days, respectively. These results suggested that a shaking time of two to three weeks would be sufficient to assure solubility equilibrium. It was found that in the region below 9.8M total phosphate, this shaking time gave solubility results which were consistent with those obtained from the precipitation runs.

In the region above 9.8M total phosphate, where $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ was found to be the stable solid phase, shaking times longer than three weeks were found to be necessary. In this region, $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ was always found as a metastable intermediate solid phase in the conversion of $\text{U}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ to $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, which probably explains the slower attainment of equilibrium. In an experiment with 11.8M total phosphate, complete conversion and equilibration were not attained until 23 days. In a rate study in 10.9M total phosphate, $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ was identified even after 21 days of shaking. The conversion of the hexahydrate to $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ between 9.8 and 11.76M total phosphate was so slow that solubility values for $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ in this region were not obtained.

The rapid addition of water to any of the saturated uranium(IV) phosphate solutions precipitated $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$. Even upon slow addition of water, the precipitation of $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ was difficult. In the only run (X-22) listed as a precipitation run above 9.8M total phosphate, water was added dropwise with vigorous stirring in an attempt to minimize the local precipitation of $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$. In addition, this sample was shaken for 34 days in an attempt to insure conversion of any $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ that might have been formed.

In both the dissolution and precipitation studies, filtration was carried out by using a pressure filter

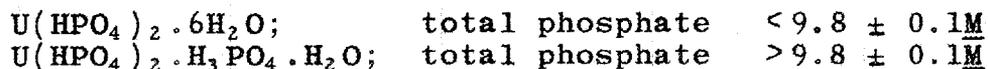
apparatus⁽⁹⁾ immersed in a water bath at $25^{\circ} \pm 0.1^{\circ}\text{C}$. The mother liquors were sampled by means of calibrated pipets or calibrated pycnometers, depending on the viscosity of the solution. After the determination of the densities of the mother liquors, they were analyzed for uranium(IV) and phosphate as described in the section on analysis.

The precipitation runs were much more difficult to filter than were the dissolution runs. This difficulty was probably due to the more gelatinous nature of the precipitated $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$.

In the determinations in concentrated phosphoric acid, the solutions were so viscous that filtration was very slow. This was not serious since filtration was carried out with the assembly completely immersed under water at 25°C . However, it was found necessary in these cases to fit the receiving flask with an anhydrous magnesium perchlorate drying tube in order to prevent water absorption by the concentrated phosphoric acid in the mother liquor.

2. DISCUSSION OF RESULTS

The solubility behavior of uranium(IV) orthophosphate in phosphoric acid solutions was studied over the range of 1.50 to 15.24M total phosphate. The solubility curve was found to be composed of two branches, each of which corresponds to a different equilibrium solid phase. The solid phases and their regions of stability are as follows:



The highest total phosphate concentration obtained from the solubility determinations in concentrated phosphoric acid was 14.97M. The solubility curve was extended to 15.24M total phosphate by dissolving P_2O_5 in 85% phosphoric acid and using this viscous liquid as the solvent. Although this solution may have contained some pyrophosphate, $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ was found as the equilibrium solid phase.

The assembled solubility data are shown in Table 5 and a log-log plot of these data is shown in Figure 2. The coordinates of each point in this figure represent the total formal concentration of uranium(IV) and of phosphate in the corresponding saturated solutions as determined by analysis. The concentrations of uranium(IV) and phosphate in the mother liquor at the transition point were determined to be $0.62 \pm 0.02\text{M}$ and $9.8 \pm 0.1\text{M}$, respectively, from an enlargement of

Table 5

THE SOLUBILITY OF URANIUM(IV) ORTHOPHOSPHATE

IN PHOSPHORIC ACID SOLUTIONS

Code Number	Solid Added	Mother Liquor Density g/ml	Composition of Mother Liquor		Equilibrium Solid Phase X-ray Diffraction of Slurries
			Analytical [U ⁺⁴] g ions/l	Analytical [PO ₄ ⁻³] g ions/l	
X-27	U(HPO ₄) ₂ .4H ₂ O	1.0757	0.0002	1.495	- - - - -
X-25	"	1.0951	0.000525	1.863	U(HPO ₄) ₂ .6H ₂ O
X-11	"	1.0972	0.000624	1.937	- - - - -
X-9	"	- - -	0.00110	2.358	- - - - -
X-10	"	- - -	0.00389	3.240	- - - - -
X-13	Precipitation Run	- - -	0.00427	3.150	- - - - -
X-5	U(HPO ₄) ₂ .4H ₂ O	- - -	0.00684	3.630	- - - - -
X-5-2	"	1.1913	0.00690	3.794	- - - - -
X-6	"	- - -	0.01652	4.243	- - - - -
X-14	Precipitation Run	1.2694	0.0317	5.190	- - - - -
X-7	U(HPO ₄) ₂ .4H ₂ O	- - -	0.0436	5.94	- - - - -
X-16	Precipitation Run	1.3384	0.0999	6.306	- - - - -
X-2	U(HPO ₄) ₂ .4H ₂ O	1.4187	0.1907	7.356	- - - - -
X-2-1	"	1.4170	0.1734	7.463	- - - - -
X-2-2	"	1.4215	0.1933	7.567	- - - - -
X-1	"	1.5118	0.3739	8.972	- - - - -
X-1-1	"	1.5062	0.3541	8.556	- - - - -
X-19	Precipitation Run	1.5623	0.5078	9.133	- - - - -
X-18	U(HPO ₄) ₂ .4H ₂ O	1.5850	0.5203	9.382	- - - - -
**X-3-2	"	1.7597	0.9256	10.91	U(HPO ₄) ₂ .6H ₂ O
**X-8	"	1.8882	1.2340	11.48	- - - - -
**X-8-1	"	1.8877	1.2535	11.32	- - - - -

Table 5 (Cont'd.)

THE SOLUBILITY OF URANIUM(IV) ORTHOPHOSPHATE
IN PHOSPHORIC ACID SOLUTIONS

Code Number	Solid Added	Mother Liquor Density g/ml	Composition of Mother Liquor		Equilibrium Solid Phase X-ray Diffraction of Slurries
			Analytical [U ⁺⁴] g ions/l	Analytical [PO ₄ ⁻³] g ions/l	
- - -	*Transition Values	1.63	0.62	9.8	- - - - -
X-8-3	U(HPO ₄) ₂ ·4H ₂ O	1.7848	0.7800	11.76	U(HPO ₄) ₂ ·H ₃ PO ₄ ·H ₂ O
X-8-2	"	1.7613	0.7868	11.79	- - - - -
X-17	"	1.8082	0.8156	12.16	- - - - -
X-20	"	1.8226	0.8597	12.42	- - - - -
X-22	Precipitation Run	1.8128	0.8552	12.42	U(HPO ₄) ₂ ·H ₃ PO ₄ ·H ₂ O
X-12-3	U(HPO ₄) ₂ ·4H ₂ O	1.9455	1.0417	14.19	- - - - -
X-12-2	"	1.9566	1.1366	14.30	- - - - -
X-12-1	"	2.0219	1.3199	14.97	U(HPO ₄) ₂ ·H ₃ PO ₄ ·H ₂ O
X-21	"	2.0382	1.2743	15.24	U(HPO ₄) ₂ ·H ₃ PO ₄ ·H ₂ O

*These values were estimated from Figures 2 and 6.

**Solubilities of metastable U(HPO₄)₂·6H₂O.

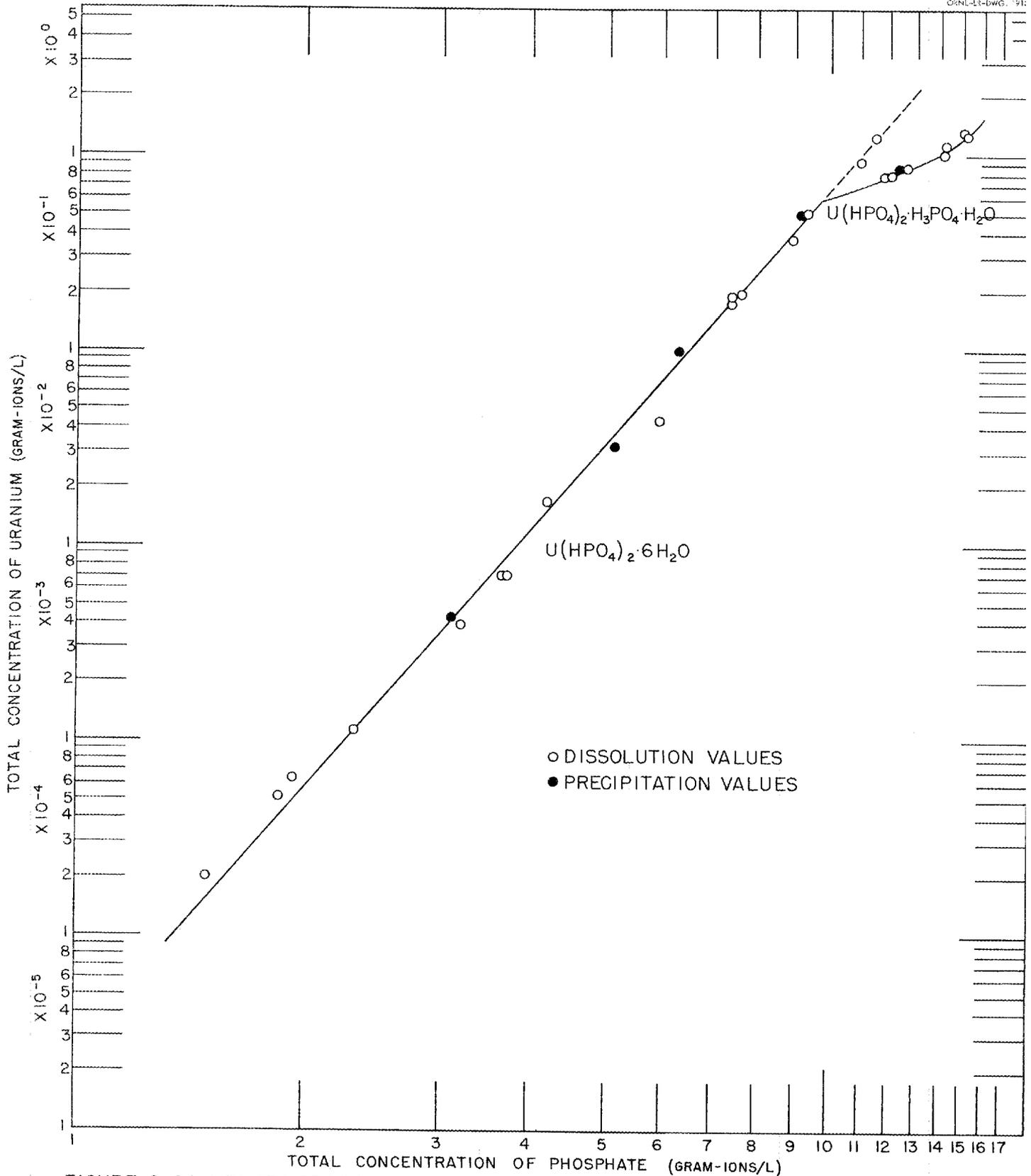


FIGURE 2. SOLUBILITY OF URANIUM IV ORTHOPHOSPHATE IN PHOSPHORIC ACID SOLUTIONS

this figure. The straight line representing the solubility curve of $U(HPO_4)_2 \cdot 6H_2O$ was drawn from the equation

$$[U^{+4}] = 2.55 \times 10^{-5} [PO_4^{-3}]^{4.41}$$

which was determined by the method of least squares, assuming the uranium values to be more reliable than the phosphate.

IDENTIFICATION OF EQUILIBRIUM SOLID PHASES

1. EXPERIMENTAL

A thorough study was made of the equilibrium solid phases over the entire range of solubility studies. It was observed that when dry $U(HPO_4)_2 \cdot 4H_2O$ was added to phosphoric acid solutions, the solid phase became a hydrogel. In concentrated phosphoric acid, after long periods of shaking, the solid phase became crystalline.

Filtration of the equilibrium solubility mixtures was continued only to incipient dryness in order to minimize evaporation of the mother liquor in the wet residue. The wet residues were weighed and analyzed for uranium and phosphate as described in the section on analysis. Wet residues from solutions above 9M total phosphate were transferred to a weighing bottle in a dry box because of their hygroscopicity.

The weights of the wet residues were corrected for silicious material* which did not dissolve during the course of analysis. The quantity of this material in the wet residues increased rapidly with phosphate concentrations in solutions above 12M. Table 7, column 4, and Figure 3 show the magnitude of this correction as a function of the phosphate concentration.

*Spectrographic analysis performed by Isotope Analysis Methods Laboratory, Oak Ridge National Laboratory, Y-12, showed these solids to contain appreciable quantities of aluminum, boron, sodium, potassium and a much larger quantity of silicon. These impurities came from the action of concentrated phosphoric acid on the glass shaking flask during the formation of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$. K. Hüttner⁽¹⁰⁾ reported that glass surfaces left in contact with concentrated phosphoric acid at ordinary temperatures for long periods showed considerable corrosion.

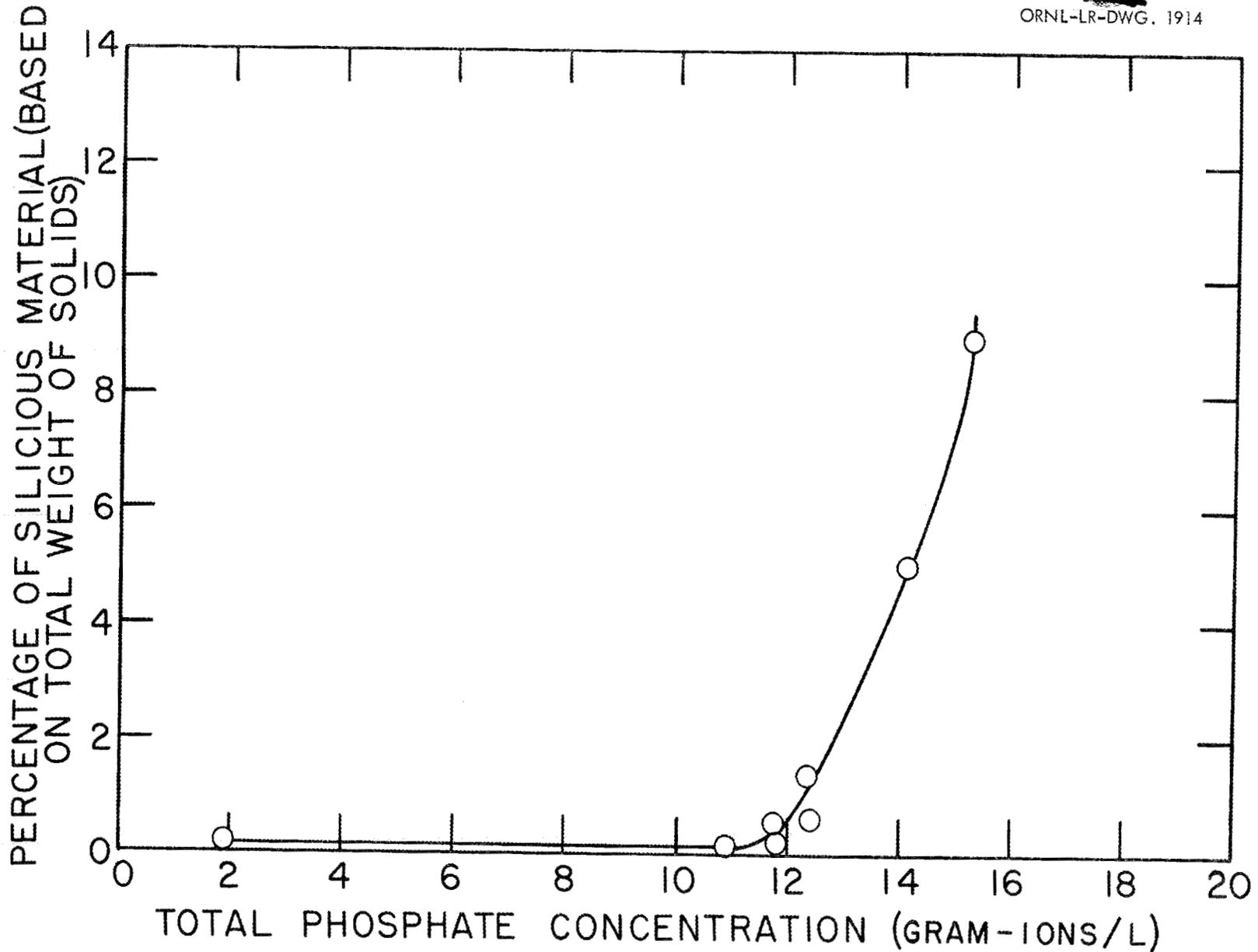


FIGURE 3. SILICIOUS MATERIAL PRODUCED BY ACTION OF PHOSPHORIC ACID ON GLASS AT 25°C DURING SOLUBILITY DETERMINATIONS

After removal of the silicious materials, numerous mother liquors were evaporated to dryness with perchloric acid with the detection of only traces of silica.

X-ray diffraction patterns were obtained for solids in slurries with their mother liquors. *The slurries were drawn into small glass capillary tubes by means of a syringe. After completely filling, the capillary tubes were sealed on both ends with Apiezon Compound Q. Each of the capillary tubes was then mounted in a camera and an X-ray pattern obtained. The capillaries used for the slurries above 9M total phosphate were filled in a dry box because of the hygroscopic nature of the concentrated phosphoric acid solutions.

2. DISCUSSION OF RESULTS

The system $\text{UO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25°C is graphically represented in Figure 4 by reference to the two sides of a right isosceles triangle. This type of diagram, which was first suggested by Roozeboom,⁽¹¹⁾ was found to best present the data collected. The concentrations of the three components are expressed in terms of grams per 100 grams of the total mixture. The percentage of water corresponding to any point is represented by its distance from the hypotenuse of the triangle. The results of analyses of mother liquors and their corresponding slurries are shown in Tables 6 and 7.

The existence of $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ as the equilibrium solid phases is demonstrated in Figure 4 by use of the wet residue method of Schreinemakers.⁽¹²⁾ In this method lines drawn from points on a solubility curve through points representing the corresponding wet residues converge toward the point representing the composition of an equilibrium solid.

It was found by this method that $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ was the stable equilibrium solid phase from 1.5M to 9.8M total phosphate and was metastable from 9.8M to 11.3M total phosphate. In the stable region, the data from determinations X-5-2, X-18, and X-2-2 are considered the most reliable in the identification of $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ because in these dissolution runs it was possible to remove more mother liquor from the hydrogel than was possible in the precipitation runs, X-14, X-16, and X-19. In the low phosphate runs (X-11, X-25, X-27, and X-29), the proximity of the tie-lines to the hydration line of $\text{U}(\text{HPO}_4)_2$ makes these data of little value in the identification of a particular hydrate.

*Procedure carried out by H. W. Dunn, Isotope Analysis Methods Laboratory, Oak Ridge National Laboratory, Carbide and Carbon Chemicals Company, Y-12 Plant.

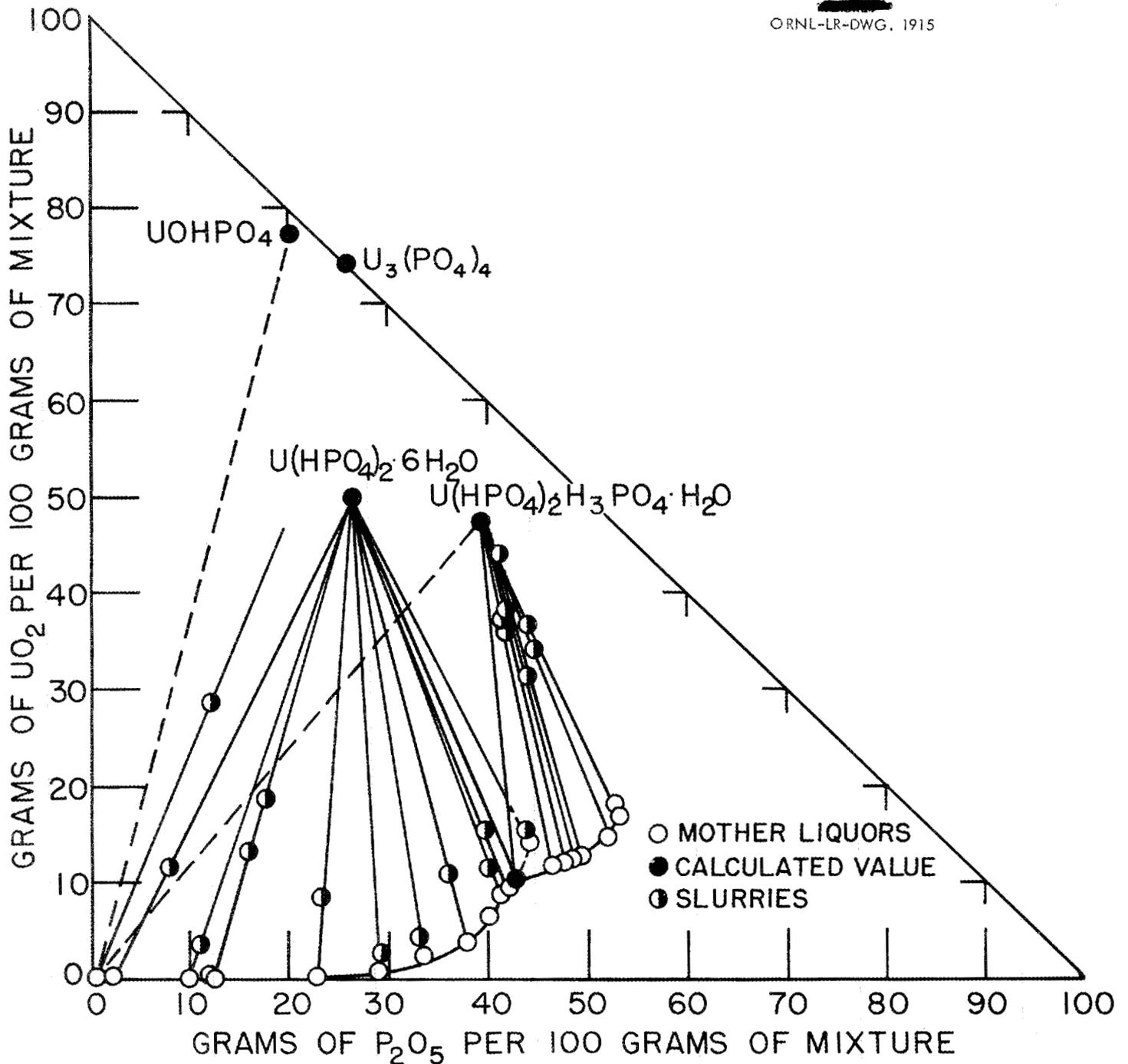


FIGURE 4. THE SYSTEM UO_2 - P_2O_5 - H_2O AT 25°C .

Table 6

ANALYSES OF MOTHER LIQUORS FROM SOLUBILITY DETERMINATIONS
IN WHICH WET RESIDUES WERE OBTAINED

<u>Code No.</u>	<u>P₂O₅</u> <u>grams/ml</u>	<u>UO₂</u> <u>grams/ml</u>	<u>Density of</u> <u>Mother Liquor</u> <u>grams/ml</u>	<u>Weight</u> <u>Percent</u> <u>P₂O₅</u>	<u>Weight</u> <u>Percent</u> <u>UO₂</u>
X-24	0.00047	-----	0.9977	0.047	-----
X-29	0.01987	-----	1.0121	1.96	-----
X-27	0.1061	-----	1.0757	9.86	-----
X-25	0.1322	0.00016	1.0951	12.07	-----
X-11	0.1375	0.00017	1.0972	12.53	0.015
X-5-2	0.2693	0.0019	1.1913	22.60	0.156
X-14	0.3677	0.00856	1.2694	28.97	0.67
X-16	0.4476	0.0270	1.3384	33.44	2.02
X-2-2	0.5371	0.0522	1.4215	37.78	3.67
X-1	0.6073	0.09604	1.5062	40.32	6.38
X-19	0.6480	0.1371	1.5623	41.48	8.77
X-18	0.6659	0.1405	1.5850	42.01	8.86
X-3-2	0.7744	0.2499	1.7597	44.00	14.20
*Calculated	0.696	0.167	1.63	42.6	10.3
X-8-3	0.8347	0.2106	1.7848	46.74	11.79
X-8-2	0.8371	0.2124	1.7613	47.53	12.06
X-20	0.8816	0.2321	1.8226	48.37	12.73
X-22	0.8816	0.2309	1.8128	48.63	12.73
X-12-3	1.0076	0.2825	1.9455	51.79	14.52
X-12-1	1.0626	0.3579	2.0219	52.55	17.70
X-21	1.0817	0.3441	2.0382	53.07	16.88

*The concentration of phosphate and uranium as well as the density was estimated from Figures 2 and 6.

Table 7

ANALYSIS OF WET RESIDUES FROM SOLUBILITY DETERMINATIONS

<u>Code Number</u>	<u>Weight of P₂O₅ (grams)</u>	<u>Weight of UO₂ (grams)</u>	<u>Percent Silicious Material</u>	<u>*Corrected Weight of Slurry (grams)</u>	<u>Weight-Percent P₂O₅</u>	<u>Weight-Percent UO₂</u>
X-24	0.3437	0.8000	0.14	2.8105	12.23	28.46
X-29	0.3168	0.4706	0.14	4.0806	7.76	11.53
X-27	0.2159	0.0669	0.24	1.9622	11.00	3.40
X-25	3.3779	2.7432	0.082	21.1309	15.98	12.98
X-11	0.6591	0.6800	-----	3.6648	17.98	18.55
X-5-2	0.8141	0.2924	-----	3.5003	23.26	8.35
X-14	4.3638	0.3299	-----	14.8641	29.36	2.22
X-16	3.4446	0.4401	-----	10.3503	33.28	4.25
X-2-2	1.4870	0.4482	-----	4.1330	35.97	10.84
X-19	1.905	0.5411	-----	4.7718	39.92	11.34
X-18	2.1223	0.8159	-----	5.3567	39.62	15.23
X-3-2**	2.0698	0.7109	0.055	4.7357	43.71	15.01
X-8-3	1.9243	1.6737	0.42	4.6355	41.51	36.10
X-8-2	2.3572	2.1376	0.094	5.6693	41.58	37.70
X-20	4.0203	3.564	0.60	9.6542	41.64	36.91
X-22	1.0384	0.7430	1.29	2.3645	43.92	31.42
X-12-3	2.1819	1.6942	5.00	4.8756	44.75	34.75
X-12-1	2.46996	2.6866	-----	6.0961	40.51	44.07
X-21	1.4345	1.1907	8.96	3.2604	44.00	36.52

*The weights of slurries were corrected for the insoluble silicious materials contaminating the samples.

**This wet residue probably contained some $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$.

The compound, $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$, was identified by the wet residue method as the stable equilibrium solid phase from 9.8M to 15.24M total phosphate. The crystalline nature of this compound made possible a more complete removal of mother liquor, resulting in a shorter extrapolation of tie lines and a more conclusive identification of the solid.

Although a pure $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ preparation could not be made, it was possible to obtain a photomicrograph of the crystals while still in contact with mother liquor (see Figure 5).

Additional information to substantiate the existence of the above mentioned equilibrium solid phases was obtained from X-ray diffraction patterns. In addition to those reported in Table 5, X-ray diffraction patterns were made of slurries from 2.95M, 6.73M and 7.52M total phosphate. All of the patterns obtained with slurries from 1.85M to 10.9M total phosphate were identical, indicating the same solid phase over this range, but were different from the reference pattern for $U(HPO_4)_2 \cdot 4H_2O$. A representative X-ray diffraction pattern of $U(HPO_4)_2 \cdot 6H_2O$ is shown in Photograph 20741 in Figure 1.

Identical X-ray patterns were obtained for slurries from 11.76M, 12.42M, 14.97M, and 15.24M total phosphate solutions, which are reported in Table 5. The pattern for $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ is shown in Photograph 20743 in Figure 1.

Since $U(HPO_4)_2 \cdot 6H_2O$ has been identified as the equilibrium solid phase below 9.8M total phosphate, it is evident that $U(HPO_4)_2 \cdot 6H_2O$, when treated with acetone and dried, is converted to $U(HPO_4)_2 \cdot 4H_2O$ and possibly to some $U(HPO_4)_2 \cdot 2H_2O$ during the uranium(IV) orthophosphate tetrahydrate preparation. The dihydrate, being hygroscopic, returns to the tetrahydrate.

The concentration of uranium(IV) and phosphate in the mother liquor at the transition point between $U(HPO_4)_2 \cdot 6H_2O$ and $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ have previously been shown to be 0.62 ± 0.02 and $9.8 \pm 0.1M$, respectively. The density of the transition mother liquor (1.63 ± 0.03 g/ml) was determined from the plot in Figure 6. Calculations with these data give 42.6% P_2O_5 and 10.3% UO_2 in the mother liquor at this transition point. These values were used to locate the point of intersection of the two solubility curves in Figure 4.

Figure 4 shows that $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ is incongruently soluble in water since a line joining the H_2O apex with the point representing the solid does not intersect the solubility curve of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$. Since this line passes through the area of stability of the $U(HPO_4)_2 \cdot 6H_2O$, the conversion of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ to $U(HPO_4)_2 \cdot 6H_2O$ by water was predicted. This was confirmed by X-ray diffraction analysis of the solid produced upon washing $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ with water.

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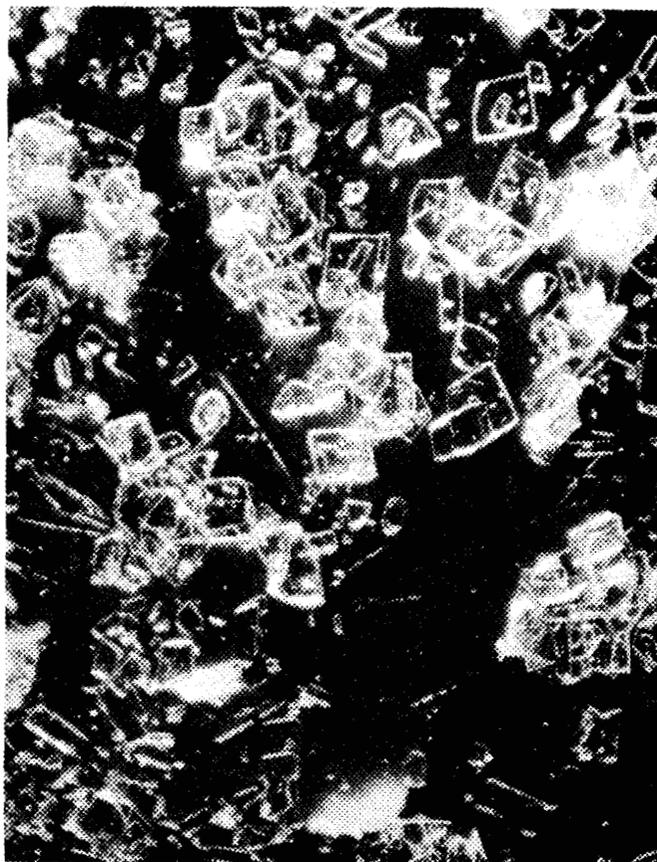


FIGURE 5

CRYSTALS OF $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$

PHOTOGRAPHED BY R.S. CROUSE AND E.R. BOYD
METALLURGY DIVISION, OAK RIDGE NATIONAL LABORATORY

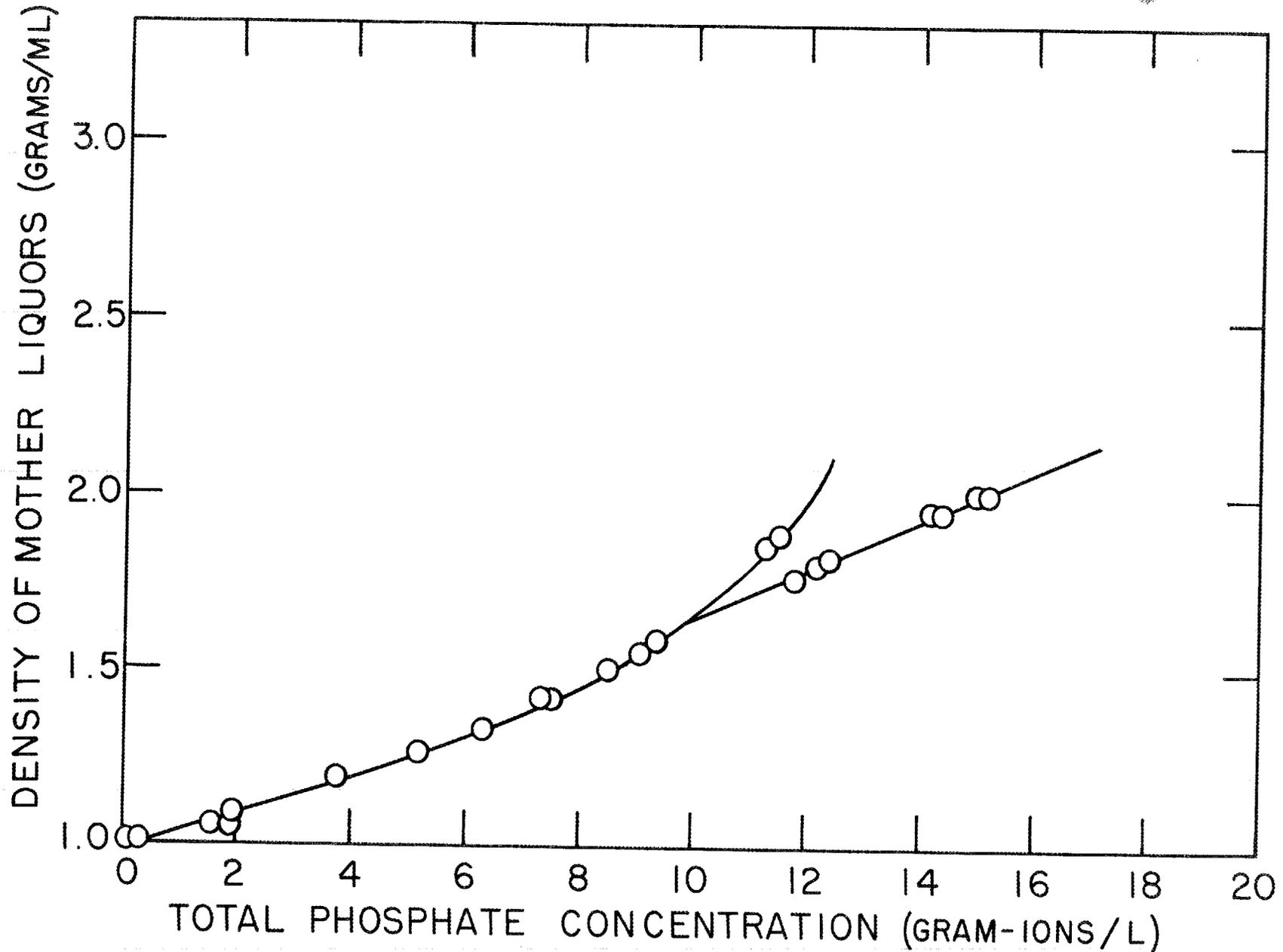


FIGURE 6. DENSITY OF MOTHER LIQUORS AS A FUNCTION OF THE TOTAL PHOSPHATE CONCENTRATION

A sample of $U(HPO_4)_2 \cdot 4H_2O$ which was shaken in water for 50 days at $25^\circ C$ gave a slurry X-ray pattern which indicated that the solid was not pure $U(HPO_4)_2 \cdot 6H_2O$ and that probably another compound was present. The compositions of the wet residue and mother liquor from this run are plotted in Figure 4. A line through these points does not intersect the composition of the hexahydrate. Analysis of the mother liquor showed the presence of a forty-five fold higher concentration of phosphate than uranium ($1.47 \times 10^{-4} M U^{+4}$ and $6.6 \times 10^{-3} M PO_4^{-3}$). It is suggested that hydrolysis occurred with the possible formation of a new product, such as $UOHPO_4$, or that the normal salt, $U_3(PO_4)_4$, was formed. At present no data are available on the rate of hydrolysis of solid $U(HPO_4)_2 \cdot 6H_2O$ in water, but the above experiment indicates that it is a slow reaction. Slow hydrolysis is not surprising in view of the low solubility of uranium(IV) orthophosphate solids in solutions of low acidity.

IDENTIFICATION OF OTHER URANIUM(IV) PHOSPHATE SOLIDS

1. IDENTIFICATION OF $UP_2O_7 \cdot 6H_2O$

A sample of $UP_2O_7 \cdot 6H_2O$ was prepared in order to establish an X-ray pattern for use in the identification of this compound as an impurity in the various uranium(IV) orthophosphate preparations.

A 100 ml aliquot of a 0.1M uranyl sulfate solution was made 1M in perchloric acid and reduced in the Jones reductor. The reduced solution was diluted to 500 ml and aerated in order to oxidize the uranium(III) to uranium(IV). The light green solution was then made 1M in $HClO_4$. Solid $Na_4P_2O_7 \cdot 10H_2O$ was added slowly with stirring and a fine, light blue-green precipitate was obtained. After filtering, the solid was washed twice by shaking with 100 ml of 1M $HClO_4$ for 2 days. The solid was then washed with four 100 ml portions of acetone and vacuum dried.

Analysis of a preparation by this method gave 46.8% U^{+4} , 32.3% $P_2O_7^{-4}$ and 20.9% H_2O by difference, giving a $U^{+4}/P_2O_7^{-4}/H_2O$ ratio of 1/0.95/5.9. An X-ray pattern of this compound was obtained although the lines were very broad and diffuse and was of limited value in detecting this compound in other uranium(IV) phosphate preparations (see Photograph 20747, in Figure 1).

Chemical analysis alone would not distinguish between uranium(IV) orthophosphate and pyrophosphate, although combined

with other evidence it was apparent that the compound was a pyrophosphate. The hydration of pyrophosphoric acid to form orthophosphoric acid is known to be slow at ordinary temperatures. For example, T. Graham⁽¹³⁾ kept a dilute aqueous solution of pyrophosphoric acid for six months without change. Based on this fact, a negligible amount of orthophosphoric acid was present in the solution from which the pyrophosphate was precipitated. In addition, X-ray diffraction analysis did not detect the presence of uranium(IV) orthophosphate solids in the preparation.

2. IDENTIFICATION OF $U(HPO_4)_2 \cdot H_2O$

Uranium(IV) orthophosphate monohydrate was prepared by two methods. The first method was the dehydration of $U(HPO_4)_2 \cdot 4H_2O$ with perchloric acid,* while the second involved the extraction of H_3PO_4 from $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ with acetone. The procedure for the perchloric acid dehydration follows:

A sample of $U(HPO_4)_2 \cdot 4H_2O$ was washed with 1M perchloric acid solution, one portion of acetone, and two portions of carbon tetrachloride. The sample was dried on the filter by vacuum. This dry solid (containing from 3 to 5% $HClO_4$) was placed in an oven at 120-125°C for 24 hours. Copious fumes emanated from the sample during heating. The color changed from a light grayish green, characteristic of the tetrahydrate, to a blue green. The sample was washed 5 times with acetone (500 ml per 10 g solid) in order to wash out the perchloric acid and some oxidized uranium (UO_2^{++}), and then dried under continuous vacuum.

As indicated in Table 8 and Figure 7, 5 acetone washes were required to remove the major portion of the adsorbed or combined perchlorate. The X-ray diffraction pattern of this

*Hot concentrated perchloric acid is a powerful dehydrating agent. According to G. Frederick Smith,⁽¹⁴⁾ "The explanation of dehydrations using perchloric acid is associated with the formation momentarily in hot concentrated 72.4% perchloric acid of anhydrous perchloric acid. This anhydrous acid acts as a powerful dehydrator by taking up water to form the more stable hydrated forms of perchloric acid. These hydrates of perchloric acid boil off and the dehydration equilibrium is displaced in the direction of the removal of water."

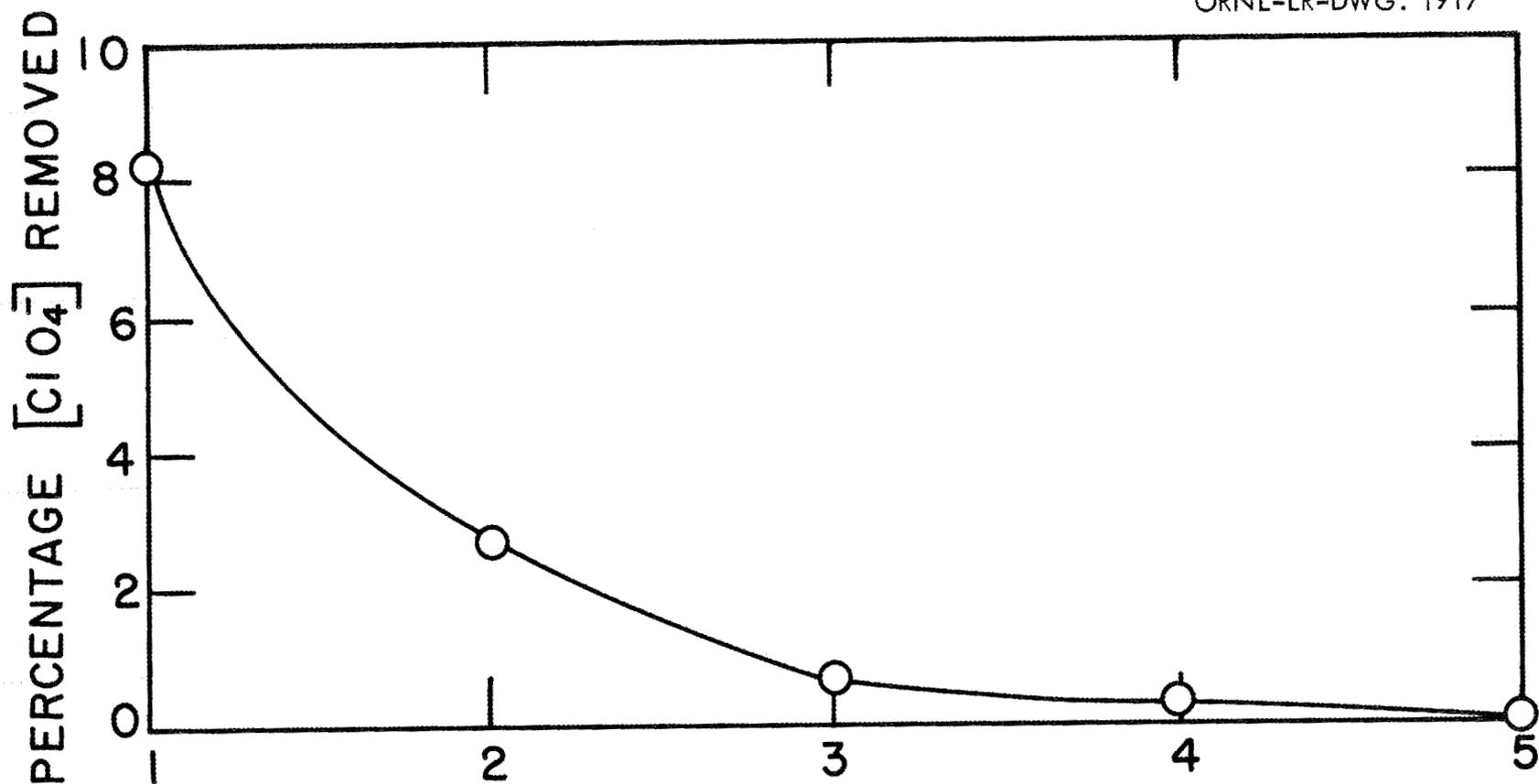
Table 8

ACETONE REMOVAL OF PERCHLORATE FROM $U(HPO_4)_2 \cdot H_2O$

Theory: $U(HPO_4)_2 \cdot H_2O$, U^{+4} (53.13%), PO_4^{-3} (42.39%), H_2O (4.02%)

<u>Number of Acetone Washes</u>	<u>Percentage U^{+4}</u>	<u>Percentage PO_4^{-3}</u>	<u>Percentage H_2O (By Difference)</u>	<u>Percentage ClO_4^{-}</u>	<u>Mole Ratio $U^{+4}/PO_4^{-3}/H_2O$</u>
1	49.1	40.7	1.55	8.2	1/2.08/0.42
2	52.4	39.9	4.55	2.70	1/1.91/1.14
3	53.8	40.8	4.31	0.64	1/1.90/1.06
4	53.6	41.2	4.50	0.25	1/1.93/1.10
5	53.5	42.0	4.05	*0.02	1/1.97/1.00

*Limit of detectibility of analytical method.



NUMBER OF WASHINGS WITH ACETONE
(500 ml. OF ACETONE PER 25g. DRY SOLID)

FIGURE 7. ACETONE REMOVAL OF PERCHLORATE
DURING THE PREPARATION OF $U(HPO_4)_2 \cdot H_2O$

sample (see Photograph 20744 in Figure 1) was different from that of the $U(HPO_4)_2 \cdot 4H_2O$. The pattern of the monohydrate has stronger lines than the tetrahydrate. Within the limit of detection (approx. 20%), the compound, $UP_2O_7 \cdot 6H_2O$ was not found by X-ray analysis.

Although one pure sample was prepared, this method did not give pure monohydrate each time. The amount of perchloric acid present and the length of time of heating had a marked effect on the composition of the preparations obtained from this method. In nearly every preparation of $U(HPO_4)_2 \cdot H_2O$ by this method an appreciable quantity of uranium(IV) was oxidized and the uranium(VI) was not completely washed out with acetone even though the first acetone wash was quite yellow, indicating the removal of UO_2^{++} . X-ray diffraction analysis indicated the possible presence of $UO_2(H_2PO_4)_2 \cdot 3H_2O^*$ in this preparation. The acetone wash removed only the UO_2^{++} in excess of the phosphate, i.e., as uranyl perchlorate, since the uranium(VI) phosphate salt is insoluble in acetone.

The solvent extraction procedure for the preparation of $U(HPO_4)_2 \cdot H_2O$ from $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ follows:

A sample from each of two filtered $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ preparations was shaken for about 5 days in a closed container with acetone (200 ml per 10 g of sample), this procedure being repeated 5 times. Both of these samples gave the characteristic X-ray pattern of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ before the acetone washes. Portions of these two wet residues, X-8-3 and X-21, also were used in the identification of $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ by Schreinemaker's method (see Tables 6 and 7).

Within a few days of shaking with acetone, the solid phase changed from a dark green to a light bluish green color, similar to that of the $U(HPO_4)_2 \cdot H_2O$ prepared from $U(HPO_4)_2 \cdot 4H_2O$ (cf. Table 8) by perchlorate dehydration. Table 9 contains analyses of the solids prepared by acetone treatment. The analyses in Table 9 were corrected for insoluble silicious material which contaminated the samples.

It is suggested from the data in Table 9 that acetone is removing H_3PO_4 from $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ to form $U(HPO_4)_2 \cdot H_2O$. These samples are not pure monohydrate for it is evident that the samples contain excess phosphate. The X-ray pattern of the acetone product from the X-8-3 preparation is shown in Photograph 20746 in Figure 1. This diffraction analysis

*A description of $UO_2(H_2PO_4)_2 \cdot 3H_2O$ was reported in ORNL-1578.(9)

indicates that the acetone washed product is the same as the $U(HPO_4)_2 \cdot H_2O$ prepared by perchloric acid dehydration of $U(HPO_4)_2 \cdot 4H_2O$.

Table 9

ANALYSES OF $U(HPO_4)_2 \cdot H_2O$ SAMPLES PREPARED

FROM $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$

Theory: $U(HPO_4)_2 \cdot H_2O$; U^{+4} (53.13%); PO_4^{-3} (42.39%); H_2O (4.02%),

<u>Sample Number</u>	<u>% U^{+4}</u>	<u>% PO_4^{-3}</u>	<u>% H_2O By Difference</u>	<u>Mole Ratio $U^{+4}/PO_4^{-3}/H_2O$</u>
X-8-3	52.56	43.12	3.87	1/2.05/0.97
X-21	51.80	43.23	4.52	1/2.09/1.15

3. IDENTIFICATION OF $U(HPO_4)_2 \cdot 2H_2O$

An attempt was made to prepare $U(HPO_4)_2 \cdot 2H_2O$ by heating $U(HPO_4)_2 \cdot 4H_2O$ in an oven at approximately 120°C, the temperature reported by Schaap, Andrews and Gates⁽²⁾ for the preparation of this compound.

A weighed sample (1.0734 g) of $U(HPO_4)_2 \cdot 4H_2O$ (sample M-290) was placed in an oven at 120-125°C. At 24-hour periods the sample was removed from the oven, placed in a desiccator to cool, and weighed rapidly. In each case, the sample was found to increase in weight rapidly during weighing. At the end of 144 hours of heating, the weighed sample was left exposed to the atmosphere until constant weight was attained. The final weight was found to be 1.0734 g, the same as the original sample.

X-ray diffraction analysis identified the final product as $U(HPO_4)_2 \cdot 4H_2O$. It is evident from Figure 8 that the loss in weight corresponded to the loss of $2H_2O$ to form $U(HPO_4)_2 \cdot 2H_2O$ but that the dihydrate is hygroscopic and returns to the tetrahydrate. No change in color was observed when $U(HPO_4)_2 \cdot 4H_2O$ was changed to $U(HPO_4)_2 \cdot 2H_2O$.

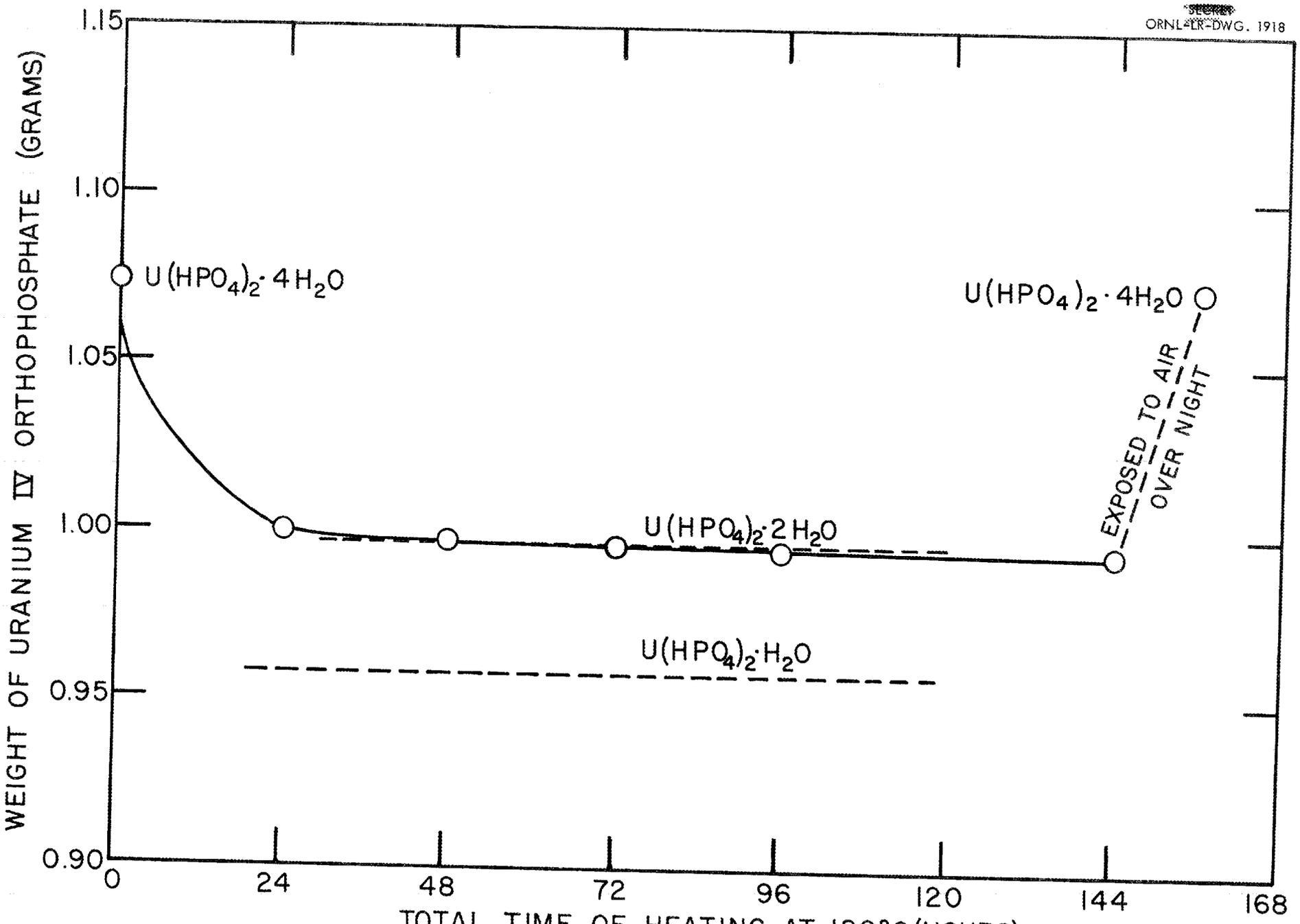


FIGURE 8. DEHYDRATION OF $U(HPO_4)_2 \cdot 4H_2O$ AT 120°C.

METHODS OF ANALYSIS

1. ANALYSIS FOR URANIUM(IV)

a. Analysis of Mother Liquors

Analysis for uranium(IV) in the various solutions was performed by the volumetric dichromate method⁽⁸⁾ except that the Jones reductor was not used since the uranium was already in the tetravalent state. Mother liquors containing uranium concentrations below $6 \times 10^{-4} M$ were analyzed by the fluorometric method.⁽¹⁵⁾

b. Analysis of Solids and Slurries

Difficulty was encountered in dissolving the uranium(IV) phosphate solids and slurries in sulfuric or perchloric acid. Nitric acid could not be used because of interference with the determination of uranium when a Jones reductor is used for reduction.

It was found that these uranium(IV) phosphate solids and slurries could be dissolved in sulfuric acid by the addition of a small amount of hydrogen peroxide. The excess hydrogen peroxide could not be removed from the resulting uranium(VI) solution by boiling. Analysis of these boiled solutions gave high results, probably because the hydrogen peroxide was not destroyed in the Jones reductor. This is in accord with the results of Sill and Peterson,⁽⁶⁾ who reported that hydrogen peroxide is formed in the Jones reductor in the presence of air.

This interference of hydrogen peroxide could be eliminated, however, in the following manner. The uranium(VI) solutions containing hydrogen peroxide were diluted to a desired volume and filtered to remove silicious materials. Aliquots were removed and titrated with a permanganate solution to a light pink end point in order to destroy the hydrogen peroxide. The solution was then heated to boiling to remove the dissolved oxygen. If the pink color disappeared, more permanganate was added until the color returned. This solution, containing a slight excess of permanganate, was cooled and analyzed for uranium by the dichromate method.^{(8)*}

*In order to determine whether the presence of permanganate or manganous ions in the uranium(VI) solutions will interfere in the analysis for uranium, a stock solution of uranium(VI) sulfate was prepared by dissolving UO_2 (purified by the peroxide method⁽⁹⁾) in concentrated sulfuric acid and diluting to give approximately $0.1M H_2SO_4$. This stock solution was analyzed by the dichromate method.⁽⁸⁾ In some of the analyses, permanganate was added before reduction. It was found that the presence of concentrations of permanganate or manganous ions as high as $0.001M$ in the uranium(VI) solutions does not interfere with the uranium determination.

2. ANALYSIS FOR PHOSPHATE

The uranium(IV) phosphate solutions to be analyzed for phosphate were oxidized with a minimum amount of hydrogen peroxide, while the solids were dissolved in sulfuric acid containing a small amount of hydrogen peroxide. Phosphate determinations were made on these oxidized solutions by a modified magnesium ammonium phosphate method described in ORNL-1578.(9)

3. ANALYSIS FOR PERCHLORATE

The analysis for perchlorate was made by the method of Loebich.(16)

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