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## PROPERTIES OF FERTILIZER MATERIALS

### Metal Potassium Phosphates

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Because very little information is available on the properties of the metal potassium phosphates, data are presented on their composition, K (K<sub>2</sub>O) and P (P<sub>2</sub>O<sub>5</sub>) availabilities, solubilities, thermal stabilities, and x-ray diffraction spectra. The solubilities of MgKPO<sub>4</sub>·H<sub>2</sub>O and MgKPO<sub>4</sub>·6H<sub>2</sub>O in water, dilute HCl, and NaOH are slightly higher than the corresponding magnesium ammonium phosphates. Magnesium potassium phosphate dissolves incongruently. X-ray diffraction data indicate that the monohydrate, upon digestion in water at room temperature, is completely converted to the hexahydrate over a period of about 100 hours and that Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·22H<sub>2</sub>O is present in the residue. Thermogravimetric analyses indicate complete dehydration of magnesium potassium phosphate monohydrate at 150° to 160° C. and of the hexahydrate at 60° to 70° C.

THE METAL potassium phosphates are a series of compounds having the general formula MeKPO<sub>4</sub>·xH<sub>2</sub>O, where Me is a divalent metal ion and x is 0, 1, or 6. Metals which form compounds of this type are magnesium, manganese, copper, zinc, cobalt, nickel, and cadmium (2).

The metal potassium phosphates are only slightly soluble in water. As with metal ammonium phosphates (3), this property suggested their use in non-burning and long-lasting fertilizers. A mixture of metal ammonium phosphates and metal potassium phosphates could supply essentially all the necessary plant nutrients in a nearly water-insoluble form.

Magnesium potassium phosphate is a very efficient source of both potash and phosphate (5). Good response was reported with tomatoes, ryegrass, and other crops. Response depended on granule

size making it possible to tailor potassium and phosphorus supply for a given crop or cropping period. The soluble salt level in soils was reduced by using MgKPO<sub>4</sub>·H<sub>2</sub>O rather than the usual potash sources. The compounds seemed well suited to supply nutrients close to the plant in direct seeded crops (5).

The other metal potassium phosphates are potential sources of trace elements. These materials can be mixed with other fertilizers to supply the necessary trace elements. The quantities added would depend on factors such as crop requirements and soil deficiencies; however, the trace element usage would probably not exceed more than about 1 to 2% of the fertilizer.

The compounds are similar both chemically and physically to the metal ammonium phosphates (3). This is to be expected because the ammonium ion and potassium ion are approximately the same size—i.e., 1.42 Å. and 1.33 Å., respectively. There are many examples of isomorphism between ammonium and potassium compounds.

The metal potassium phosphates could be used as a research tool by agronomists to study the interactions of K and P with various trace metals in much the same way as metal ammonium phosphates can be used to study N-P-metal interactions. All of the compounds are similar chemically except for the variation in the metal in combination with either ammonia or potassium. Having several plant nutrients together in a single compound might be different agronomically than mixtures of compounds containing the same nutrients.

The rate of release of nutrients from magnesium ammonium phosphate and magnesium potassium phosphate is different from particles of the same size. This is probably due to the fact that the rate of release of nitrogen from magnesium ammonium phosphate is affected by nitrifying bacteria, whereas the potassium salt does not have this type of breakdown. Presumably the nutrients are released from magnesium potassium phosphate only by solubility. Therefore, the rates of release of nutrients

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from metal potassium phosphates should be considerably less than from metal ammonium phosphates. This opens an interesting area of agronomic investigation.

### Composition of Metal Potassium Phosphates

The metal potassium phosphates investigated during this study are listed in Table I. Included in the table are the colors, molecular weights, and theoretical compositions of the compounds. Like the metal ammonium phosphates (3), the monohydrate is the most common hydrated state. Although all the hydrated compounds may be dried until anhydrous, only the zinc and cobalt compounds are precipitated as anhydrous compounds. Magnesium forms three separate compounds containing 0, 1, and 6 moles of water of crystallization.

Apparently, a relationship exists between the ionic radius of the divalent metal ion and the stability of the metal ammonium phosphates. Metals whose divalent ions are smaller than that of calcium (0.99 Å) form stable metal ammonium phosphates; those whose divalent ions are larger do not. Calcium is a borderline case. The  $\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$  is stable in an ammonia atmosphere but upon exposure to air decomposes with the loss of ammonia and water to form dicalcium phosphate. Although the monohydrate is stable in air (4), it disproportionates in water to form hydroxyapatite (or other tricalcium phosphates) and ammonium phosphate.

Calcium potassium phosphate is stable, and strontium (1.13 Å) and barium (1.35 Å) also form metal potassium phosphates (10). Apparently the smaller potassium ion can be compensated by larger divalent metal ions in the crystal lattice without disrupting the structure that is possible with the ammonium compounds. On the other hand, the very small divalent ions—e.g., beryllium (0.31 Å)—do not appear to form stable metal potassium phosphates, although they do form stable ammonium homologs. Even magnesium (0.65 Å) forms compounds which show a considerable difference in stability, the ammonium compound being very stable whereas the potassium compound is considerably less stable. For example, magnesium potassium phosphate slowly disproportionates in water to trimagnesium phosphate and potassium phosphate. In contrast, magnesium ammonium phosphate seems to dissolve congruently (6).

Based on size relationships a stable ferrous potassium phosphate ( $\text{FeKPO}_4$ ) should exist. However, no indication was found in the published literature that the compound had ever been prepared. All attempts to prepare the compound in the laboratory were unsuccessful due to oxidation of the iron at the pH (>8) required for the formation

Table I. Theoretical Composition of Metal Potassium Phosphates

Compound	Color	Mol. Wt.	% K	% $\text{K}_2\text{O}$	% P	% $\text{P}_2\text{O}_5$	% Metal
$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$	White	266.491	14.67	17.67	11.64	26.64	9.13 <sup>a</sup>
$\text{MgKPO}_4 \cdot 3\text{H}_2\text{O}$	White	176.411	22.17	26.70	17.59	40.23	13.79 <sup>b</sup>
$\text{MgKPO}_4$	White	158.395	24.69	29.74	19.59	44.81	15.35 <sup>c</sup>
$\text{ZnKPO}_4$	White	199.455	19.60	23.61	15.56	35.59	32.29
$\text{CuKPO}_4 \cdot \text{H}_2\text{O}$	Blue	215.631	18.13	21.84	14.39	32.92	29.47
$\text{MnKPO}_4 \cdot \text{H}_2\text{O}$	Light Pink	207.031	18.89	22.75	14.98	34.28	26.54
$\text{CoKPO}_4 \cdot \text{H}_2\text{O}$	Purple	211.031	18.53	22.32	14.70	33.63	27.93
$\text{CoKPO}_4$	Dark Blue	193.015	20.26	24.40	16.07	36.77	30.54

<sup>a</sup> 15.13%  $\text{MgO}$ . <sup>b</sup> 22.86%  $\text{MgO}$ . <sup>c</sup> 25.46%  $\text{MgO}$ .

Table II. Compositions of Magnesium Potassium Phosphate Hydrates

Composition	$\text{MgKPO}_4 \cdot \text{H}_2\text{O}$			$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$		
	% Calcd.	% Found	Atomic ratio	% Calcd.	% Found	Atomic ratio
$\text{K}_2\text{O}$ (Total)	26.70	25.68	...	17.67	16.96	...
(A.O.A.C.)	...	24.54	...	...	16.96	...
(Water sol.)	...	0.63	...	...	2.80	...
K (Total)	22.17	21.32	0.99	14.67	14.08	0.94
(A.O.A.C.)	...	20.37	...	...	14.08	...
(Water sol.)	...	0.52	...	...	2.32	...
$\text{P}_2\text{O}_5$ (Total)	40.23	39.00	...	26.64	27.10	...
(Avail.)	...	38.96	...	...	27.06	...
P (Total)	17.58	17.05	1.00	11.64	11.85	1.00
(Avail.)	...	17.03	...	...	11.83	...
MgO	22.86	22.98	...	15.13	15.49	...
Mg	13.79	13.86	1.04	9.13	9.34	1.00

of the metal potassium phosphates. Oxidation is a problem even in the preparation of ferrous ammonium phosphate but can be controlled at the lower pH (~7) at which the ammonium compounds are formed.

### Preparation of Metal Potassium Phosphates

The metal potassium phosphates used in this investigation were prepared by the methods of Bassett and Bedwell (2). A solution of the metal chloride was added to one of dipotassium phosphate. A large excess of dipotassium phosphate was used to buffer the solution at the pH required for the formation of metal potassium phosphates. After digestion until it became crystalline, the precipitate was filtered, washed, and dried.

**Magnesium Potassium Phosphate.** Precipitation at room temperature results in the formation of the hexahydrate ( $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ ), whereas precipitation at 60° to 70° C. yields the monohydrate ( $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ ). The anhydrous compound ( $\text{MgKPO}_4$ ) is prepared by drying either of the hydrated compounds at temperatures in excess of 200° C.

The compositions of the monohydrate and hexahydrate are shown in Table II. Per cent K ( $\text{K}_2\text{O}$ ) (A.O.A.C.) is the percentage of potassium in the sample which is soluble in ammonium oxalate solution according to a prescribed analysis of the Association of Official Agricultural Chemists (8). By law this is the percentage of potassium in the sample which can be sold as fertilizer. For both samples, most of the potassium

is soluble in the ammonium oxalate solution, yet the percentages of truly water-soluble potassium are very low. The P ( $\text{P}_2\text{O}_5$ ) for both samples has a high availability. The atomic ratio K:P:metal (magnesium in this case) is theoretically 1:1:1 for metal potassium phosphates.

**Zinc Potassium Phosphate.** A solution of 140 grams of  $\text{K}_2\text{HPO}_4$  (or 184 grams of  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ) in 400 ml. of water was heated to 70° C. Then a solution of 7 grams of  $\text{ZnCl}_2$  in 200 ml. of water was added slowly with stirring. The mixture was digested several days at 65° C. Because the precipitate did not develop filterable crystals, it was centrifuged. The resulting cake was washed and then dried overnight at room temperature.

The dried solid was white with a bluish cast and weighed 10 grams. The calculated weight of  $\text{ZnKPO}_4$  based on the amount of  $\text{ZnCl}_2$  used was 10.22 grams; therefore, a yield of 98% was obtained. The chemical analysis of the zinc potassium phosphate is shown in Table III. The atomic ratio indicates that the sample is essentially  $\text{ZnKPO}_4$  contaminated with a small amount of excess P ( $\text{P}_2\text{O}_5$ ). Therefore, the sample contains less K ( $\text{K}_2\text{O}$ ) and Zn than calculated for  $\text{ZnKPO}_4$  but more P ( $\text{P}_2\text{O}_5$ ).

**Copper Potassium Phosphate.** A solution was prepared containing 400 grams of  $\text{K}_2\text{HPO}_4$  dissolved in 600 ml. of water. Then a solution of 8 grams of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml. of water was added slowly with stirring. After the mixture was digested for 4 days at 60° to

**Table III. Composition of Anhydrous Zinc Potassium Phosphate**

Composition	% Calcd. for $ZnKPO_4$	% Found	Atomic Ratio
$K_2O$ (Total) (A.O.A.C.)	23.61	20.48	...
K (Total) (A.O.A.C.)	19.60	17.00	0.85
$P_2O_5$ (Total) (Avail.)	35.59	36.20	...
P (Total) (Avail.)	15.56	15.82	1.00
Zn	32.29	31.29	0.94

**Table IV. Composition of Copper Potassium Phosphate Monohydrate**

Composition	% Calcd. for $CuKPO_4 \cdot H_2O$	% Found	Atomic Ratio
$K_2O$ (Total) (A.O.A.C.)	21.84	21.56	...
K (Total) (A.O.A.C.)	18.13	17.90	0.97
$P_2O_5$ (Total) (Avail.)	32.92	33.40	...
P (Total) (Avail.)	14.39	14.60	1.00
Cu	29.47	29.16	0.98

70° C., the precipitate was filtered, washed, and dried overnight at room temperature.

The dried solid was blue and weighed 10 grams. The calculated weight of  $CuKPO_4 \cdot H_2O$  based on the amount of  $CuCl_2 \cdot 2H_2O$  was 10.11 grams. Therefore, a yield of 99% was obtained. The chemical analysis of the copper potassium phosphate is shown in Table IV. The data indicate that the sample is  $CuKPO_4 \cdot H_2O$  containing a very slight excess of P ( $P_2O_5$ ) and that all of the potassium in the copper potassium phosphate could be sold as fertilizer according to the A.O.A.C. test.

**Manganese Potassium Phosphate.** Ten grams of  $MnCl_2 \cdot 4H_2O$  were dissolved in 100 ml. of water and added

slowly with stirring to a solution of 200 grams of  $K_2HPO_4$  (or 262 grams of  $K_2HPO_4 \cdot 3H_2O$ ) in 500 ml. of water. Then 2 grams of hydroxylamine hydrochloride were added to prevent oxidation of the manganese and the mixture was digested for 1 day at 60° to 70° C. The precipitate was filtered, washed, and dried overnight at room temperature.

The dried product was faintly pink. It weighed 10.2 grams compared to a calculated weight for  $MnKPO_4 \cdot H_2O$  (based on the amount of  $MnCl_2 \cdot 4H_2O$ ) of 10.47 grams. Therefore, a yield of 98% was obtained. The chemical analysis is shown in Table V, and the data indicate that the sample is  $MnKPO_4 \cdot H_2O$ . As has been the case with the other metal potassium phosphates

**Table V. Composition of Manganese Potassium Phosphate Monohydrate**

Composition	% Calcd. for $MnKPO_4 \cdot H_2O$	% Found	Atomic Ratio
$K_2O$ (Total) (A.O.A.C.)	22.75	21.72	...
K (Total) (A.O.A.C.)	19.25	18.03	0.95
$P_2O_5$ (Total) (Avail.)	34.28	34.60	...
P (Total) (Avail.)	14.98	15.12	1.00
Mn	26.54	25.60	0.96

**Table VI. Composition of Anhydrous Cobalt Potassium Phosphate**

Composition	% Calcd. for $CoKPO_4$	% Found	Atomic Ratio
$K_2O$ (Total) (A.O.A.C.)	24.40	24.32	...
K (Total) (A.O.A.C.)	20.26	20.19	0.98
$P_2O_5$ (Total)	36.77	37.30	...
P (Total)	16.07	16.30	1.00
Co	30.54	30.43	0.98

prepared by the method of Bassett and Bedwell (2), the sample contained a very small excess of P ( $P_2O_5$ ).

**Cobalt Potassium Phosphate. ANHYDROUS COMPOUND.** A solution containing 140 grams of  $K_2HPO_4$  (or 184 grams of  $K_2HPO_4 \cdot 3H_2O$ ) in 400 ml. of water was heated to 70° C. Then, a solution of 13 grams of  $CoCl_2 \cdot 6H_2O$  in 200 ml. of water was added slowly with stirring. The mixture was digested for 1 to 2 hours at 70° C. after which the resulting dense crystalline precipitate was filtered, washed, and dried overnight at room temperature.

The dried product, which was a deep royal blue, weighed 10.5 grams. The calculated weight of  $CoKPO_4$  based on

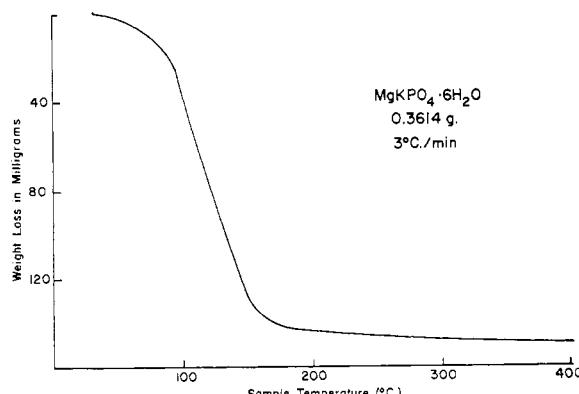


Figure 1. Thermogram of magnesium potassium phosphate hexahydrate

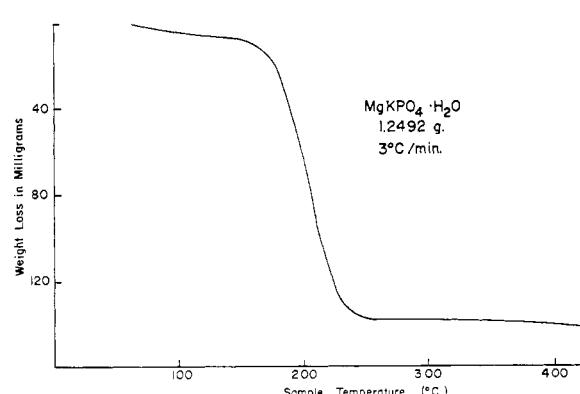


Figure 2. Thermogram of magnesium potassium phosphate monohydrate

Table VII. Composition of Cobalt Potassium Phosphate Monohydrate

Composition	% Calcd. for CoKPO <sub>4</sub> ·H <sub>2</sub> O	% Found	Atomic Ratio
K <sub>2</sub> O (Total) (A.O.A.C.)	22.32	21.50	...
	...	16.50	...
K (Total) (A.O.A.C.)	18.53	17.85	0.95
	...	13.70	...
P <sub>2</sub> O <sub>5</sub> (Total) (Avail.)	33.63	34.10	...
	...	34.06	...
P (Total) (Avail.)	14.70	14.91	1.00
	...	14.89	...
Co	27.93	28.57	1.01

Table VIII. Thermal Data for Metal Potassium Phosphates

Compound	Decom- position Temp. (°C.)	Sample Wt. (Grams)	Wt. Loss (Mg.)	Moles of H <sub>2</sub> O <sup>a</sup>	
MgKPO <sub>4</sub> ·6H <sub>2</sub> O	70°	0.3614	144	5.9	
MgKPO <sub>4</sub> ·H <sub>2</sub> O	150°	1.2492	143	1.1	
MnKPO <sub>4</sub> ·H <sub>2</sub> O	190°	0.4626	41	1.0	
CoKPO <sub>4</sub> ·H <sub>2</sub> O	170°	0.9389	83	1.0	

<sup>a</sup> Moles of H<sub>2</sub>O lost per mole of compound ignited.

the amount of CoCl<sub>2</sub>·6H<sub>2</sub>O was 10.53 grams, indicating a yield of 99.7%. The chemical analysis of the anhydrous cobalt potassium phosphate is shown in Table VI. The data indicate that the sample is CoKPO<sub>4</sub> of fairly high purity.

**MONOHYDRATE.** An attempt was made to prepare the cobalt compound without the large excess of K<sub>2</sub>HPO<sub>4</sub> prescribed by Bassett and Bedwell (2). A solution containing 205 grams of K<sub>2</sub>HPO<sub>4</sub> in 1500 ml. of water was heated to 90° C. Then, two solutions were prepared, one containing 330 grams of CoSO<sub>4</sub>·7H<sub>2</sub>O in 600 ml. of water, and a second containing 66 grams of KOH in 100 ml. of water. The two solutions were added slowly and simultaneously with stirring to the hot K<sub>2</sub>HPO<sub>4</sub> solution at such a rate that a pH of 8 and a temperature of 90° C. were maintained.

The mixture was digested for 2 hours at 90° C. The precipitate was filtered, washed, and dried overnight at 100° C.

The dried product was light purple or fuchsia and weighed 240 grams. The calculated weight of CoKPO<sub>4</sub>·H<sub>2</sub>O based on CoSO<sub>4</sub>·7H<sub>2</sub>O was 248 grams, which indicated a yield of 97%. The chemical analysis, shown in Table VII, indicates that the sample is primarily CoKPO<sub>4</sub>·H<sub>2</sub>O but is probably contaminated with a small amount of the anhydrous compound.

#### Phosphate and Potassium Availabilities

The phosphate availabilities of the metal potassium phosphates closely parallel those of the metal ammonium phosphates (3) as determined by the standard A.O.A.C. ammonium citrate method (8). The magnesium, copper,

and cobalt compounds have very high phosphate availabilities, whereas only 50 to 60% of the phosphate in the zinc and manganese compounds is soluble in ammonium citrate solution under the conditions of the standard test.

Although the potassium in the metal potassium phosphates is insoluble in water, solubilities are high in ammonium oxalate solution under the conditions of standard A.O.A.C. method for determining K (K<sub>2</sub>O) availability (8). The principal exception was the zinc compound, for which only 78% of the potassium was soluble.

#### Thermal Stabilities of Metal Potassium Phosphates

The metal potassium phosphates are thermally stable in the anhydrous form. The hydrated compounds lose water when heated to form the anhydrous compounds. Thermograms of MgKPO<sub>4</sub>·6H<sub>2</sub>O, MgKPO<sub>4</sub>·H<sub>2</sub>O, MnKPO<sub>4</sub>·H<sub>2</sub>O, and CoKPO<sub>4</sub>·H<sub>2</sub>O are shown in Figures 1 through 4, respectively.

The experiments were conducted in air at atmospheric pressure with an Aminco (American Instrument Co.) thermobalance at heating rates of 3° or 6° C. per minute. Those experiments conducted at a heating rate of 3° C. per minute are over the sample temperature range of 0° to 500° C., while those at a rate of 6° C. per minute are over the furnace temperature range of 0° to 1000° C. There was a small lag in the decomposition temperatures for the 0° to 1000° C. runs as a result of the faster heating rate. Sample sizes were chosen, when a sufficient amount of sample was available, so that the maximum weight loss would be in the order of 120 to 160 mg. A small initial loss of weight was frequently observed because of evaporation of surface moisture from the samples.

The thermal data taken from the curves are summarized in Table VIII. The manganese compound appears to be the most stable. All compounds are dehydrated directly to the anhydrous form. In every case, the loss of weight is closely equivalent to the moles of water of crystallization. The MgKPO<sub>4</sub>·6H<sub>2</sub>O

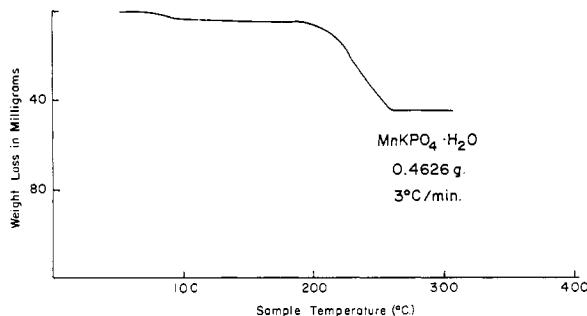


Figure 3. Thermogram of manganese potassium phosphate monohydrate

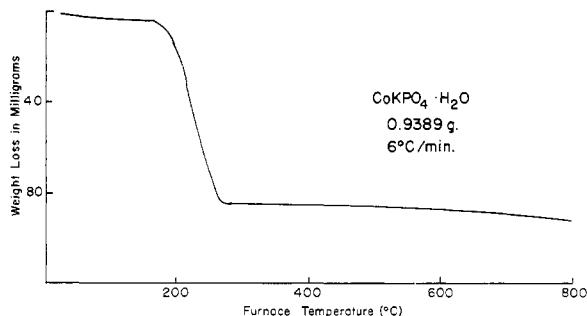


Figure 4. Thermogram of cobalt potassium phosphate monohydrate

**Table IX. X-Ray Diffraction Data for Magnesium Potassium Phosphates**

$MgKPO_4 \cdot H_2O$	$MgKPO_4 \cdot 6H_2O$		$MgKPO_4^a$ (Low Temperature)		$MgKPO_4^b$ (Low Temperature)		$MgKPO_4^c$ (High Temperature)	
	$d$ (A.)	$I/I_1$	$d$ (A.)	$I/I_1$	$d$ (A.)	$I/I_1$	$d$ (A.)	$I/I_1$
8.34	46	8.04	60	11.19	95	No diffraction	6.46	34
4.61	55	5.88	60	4.64	80	peaks	6.28	32
4.15	70	5.60	70	4.43	80	observed.	4.51	32
3.32	35	5.43	70	4.18	85		4.29	45
2.79	75	4.62	60	2.78	100		4.21	45
2.73	100	4.27	100	2.73	90		4.11	45
2.64	25	3.56	55	2.41	85		3.87	30
2.46	19	3.46	60				3.24	75
2.39	45	3.27	70				3.20	80
2.31	30	3.18	55				3.12	100
2.19	20	3.09	55				3.08	80
2.08	35	2.98	65				2.94	34
1.81	20	2.91	80				2.71	32
1.80	20	2.82	55				2.69	40
1.71	17	2.78	65				2.55	45
1.65	20	2.75	55				2.47	25
1.59	25	2.70	85				2.42	30
		2.65	70				2.14	30
		2.52	60				2.10	25
		2.37	55					
		2.33	60					
		2.25	60					

<sup>a</sup> From ignition of  $MgKPO_4 \cdot H_2O$  at 220° C. for 4 hours. <sup>b</sup> From ignition of  $MgKPO_4 \cdot 6H_2O$  at 140° C. for 4 hours. <sup>c</sup> From ignition of either  $MgKPO_4 \cdot H_2O$  or  $MgKPO_4 \cdot 6H_2O$  at 750° C. for 1 hour.

shows no tendency during its thermal decomposition to form the monohydrate or any other lower hydrate but yields the anhydrous compound at a considerably lower temperature than is possible by ignition of  $MgKPO_4 \cdot H_2O$ .

#### X-Ray Data for Metal Potassium Phosphates

X-ray diffraction data were obtained for  $MgKPO_4 \cdot 6H_2O$ ,  $MgKPO_4 \cdot H_2O$ , and their ignition products—i.e., anhydrous forms. The interplanar spacings  $d$  (A.) and relative intensities  $I/I_1$  of the diffraction lines of the compounds are given in Table IX.

Upon heating  $MgKPO_4 \cdot H_2O$  beyond its dehydration temperature, a crystalline anhydrous phase was produced while the same procedure for  $MgKPO_4 \cdot 6H_2O$  produced an amorphous anhydrous phase. Identical crystalline anhydrous phases were produced, however, by heating both compounds to 750° C. Therefore,  $MgKPO_4$  has at least two crystalline modifications—a low temperature form and a high temperature form.

The interplanar spacings were calculated using a wavelength of 1.5418 Å. (copper K- $\alpha$ -average). The radiation was nickel-filtered. All line positions were measured to within  $\pm 0.1^\circ 2\theta$ . The strongest line was assigned an intensity of 100; all other lines are described with respect to the 100% intensity line.

X-ray diffraction data for several other metal potassium phosphates are given in Table X. Two crystalline forms of anhydrous  $CoKPO_4$  were observed—a low temperature form precipitated from a hot solution and a high tempera-

ture form resulting from ignition of the monohydrate,  $CoKPO_4 \cdot H_2O$ .

#### Solubility of Magnesium Potassium Phosphate

The solubilities of  $MgKPO_4 \cdot H_2O$  and  $MgKPO_4 \cdot 6H_2O$  in water, dilute hydrochloric acid, and dilute sodium hydroxide (0.01N and 0.001N) were determined. Two grams of each compound having a particle size of less than 53 microns were agitated with 100 ml. of solvent for 45 hours at 25° C. A portion of the liquid was filtered and analyzed for potassium by flame spectrophotometry and for magnesium and phosphorus by emission spectroscopy.

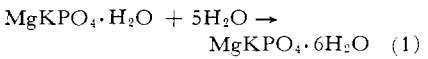
The emission spectrographic method utilized a rotating graphite electrode which dipped into the solution to be analyzed and carried the solution into an AC spark. Spectra were recorded on

Eastman Kodak SA3 emulsion. The analytical spectral lines, magnesium at 2852 Å, and phosphorus at 2535 Å, were referred to an internal standard line, yttrium at 3242 Å. The method was calibrated against a known sample of  $MgKPO_4 \cdot 6H_2O$ .

The analyses of the various solutions are given in Table XI. The solubilities are based on potassium analyses at equilibrium assuming that the compounds dissolve congruently. Little, if any, differences in the solubilities were observed for water, 0.001N HCl, and 0.001N NaOH. Small increases were observed in the more concentrated acid and base.

When  $MgKPO_4 \cdot H_2O$  is first mixed with water it has an apparent solubility of about 0.02 gram per 100 ml. based on potassium analysis. Hence, initially its solubility is about the same as  $MgNH_4PO_4 \cdot H_2O$  (3). After a few hours, the solubility of  $MgKPO_4 \cdot H_2O$  increases until equilibrium is obtained. This is shown in Figure 5. One-gram samples were agitated in 100 ml. of water at 25° C. for various lengths of time. At least 45 hours of digestion time were required for equilibrium. The equilibrium solubility based on potassium analysis was an order of magnitude higher than the initial apparent solubility.

The difficulty in attaining equilibrium results because magnesium potassium phosphate dissolves incongruently (9). It has been reported (7, 7) that  $MgK_4PO_4 \cdot H_2O$  and  $MgKPO_4 \cdot 6H_2O$  are partially hydrolyzed in water over a long period of time to  $K_3PO_4$  and  $Mg_3(PO_4)_2 \cdot 22H_2O$ . When  $MgKPO_4 \cdot H_2O$  is added to water it slowly hydrates to form the hexahydrate:



The rate of hydration is slow, taking several days for completion. The hexahydrate slowly disproportionates according to the following equation:

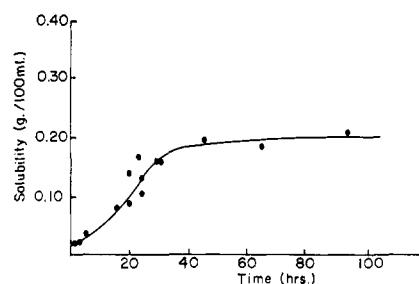
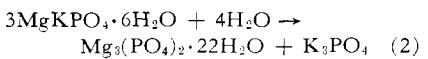


Figure 5. Effect of digestion time on the solubility of  $MgKPO_4 \cdot H_2O$  in water at 25° C.

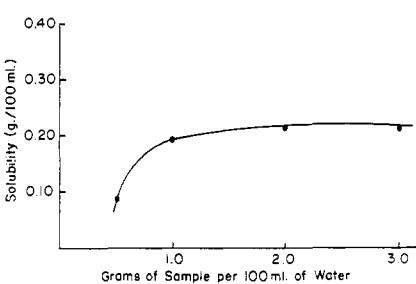


Figure 6. Effect of sample size on the solubility of  $MgKPO_4 \cdot H_2O$  in water at 25° C.

**Table X. X-Ray Diffraction Data for Metal Potassium Phosphates**

<i>ZnKPO<sub>4</sub></i>	<i>d</i> (A.)	<i>I/I<sub>1</sub></i>	<i>MnKPO<sub>4</sub>·H<sub>2</sub>O</i>	<i>d</i> (A.)	<i>I/I<sub>1</sub></i>	<i>CuKPO<sub>4</sub>·H<sub>2</sub>O</i>	<i>d</i> (A.)	<i>I/I<sub>1</sub></i>	<i>CoKPO<sub>4</sub>·H<sub>2</sub>O</i>	<i>d</i> (A.)	<i>I/I<sub>1</sub></i>	<i>CoKPO<sub>4</sub></i>	<i>d</i> (A.)	<i>I/I<sub>1</sub></i>
6.06	26	8.30	44	10.51	100	10.26	100	9.01	100	4.87	25			
4.54	15	4.69	17	5.24	3	4.11	24	3.32	16	4.52	25			
4.32	8	4.21	33	4.76	3	3.31	10	2.86	12	3.70	25			
4.24	32	3.70	14	4.39	2	2.78	7			3.49	25			
4.00	4	3.38	14	4.26	7	2.74	14			3.30	60			
3.83	4	2.82	42	3.50	7	2.72	33			3.27	100			
3.32	6	2.76	100	3.22	3	2.45	7			3.24	60			
3.10	100	2.44	14	3.13	3	2.37	14			3.20	40			
3.04	32	2.40	14	2.91	12	2.18	11			3.15	30			
3.02	30	2.34	14	2.89	11	2.06	10			2.79	50			
2.89	8	2.22	14	2.87	11					2.65	35			
2.66	53	2.11	14	2.84	18									
2.54	32	2.07	14	2.76	17									
2.45	11	1.80	14	2.59	2									
2.40	11			2.54	8									
2.19	11			2.45	3									
2.18	15			2.37	7									
2.13	8			2.33	5									
2.01	8			2.12	3									
1.93	11			2.07	3									
1.90	36			2.00	3									
1.65	17			1.82	3									
1.63	15			1.74	4									
1.59	15			1.70	3									
1.51	17													

**Table XI. Solubility of Magnesium Potassium Phosphate**

Solvent	Solubility (Grams per 100 ml.) <sup>a</sup>		<i>MgKPO<sub>4</sub>·H<sub>2</sub>O</i> (Mmoles per liter)			<i>MgKPO<sub>4</sub>·6H<sub>2</sub>O</i> (Mmoles per liter)		
	<i>MgKPO<sub>4</sub>·H<sub>2</sub>O</i>	<i>MgKPO<sub>4</sub>·6H<sub>2</sub>O</i>	K	Mg	P	K	Mg	P
Water	0.21	0.23	12.3	0.10	3.0	8.5	0.08	3.1
0.001N HCl	0.20	0.24	11.5	0.10	3.6	9.2	0.12	4.1
0.01N HCl	0.38	0.73	21.6	2.59	7.1	27.5	0.93	10.1
0.001N NaOH	0.20	0.20	11.1	0.23	7.1	7.7	<0.08	3.9
0.01N NaOH	0.23	0.26	13.3	0.13	7.5	9.8	<0.08	5.8

<sup>a</sup> Based on potassium analysis at equilibrium assuming that the compounds dissolve congruently.

This hypothesis was partially confirmed by x-ray analyses of the residues from the solubility experiments which indicated that  $Mg_3(PO_4)_2 \cdot 22H_2O$  was present. The monohydrate was partially converted to the hexahydrate after 45 hours of digestion and almost completely converted after 94 hours. In addition, analyses of the solutions by emission spectrometric methods for magnesium and phosphorus indicate a very low magnesium concentration and a high phosphorus concentration (Table XI) as would be expected from hydrolysis (Equation 2).

Figure 6 shows the effect of sample size on the solubility of  $MgKPO_4 \cdot H_2O$  (based on potassium analysis) in water at 25° C. Samples of different weights (0.5, 1.0, 2.0, and 3.0 grams) were agitated in 100 ml. of water for 45-hour periods. The filtrates were analyzed for

potassium. Figure 6 indicates a gradual increase in solubility with sample size up to about 2 grams. For this reason, 2-gram samples were taken for the solubility experiments reported in Table XI.

Although no solubility measurements have been made on the other metal potassium phosphates, all have low solubilities in water and appear to be more insoluble than magnesium potassium phosphate.

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