Preparation and Properties of Mono-, Di-, and Tricalcium Phosphates

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THE three common phosphates of calcium—namely, the mono-, di-, and tricalcium phosphates—are of great importance because of their usage as fertilizers, their presence in soils, and their use in numerous commercial products. Monocalcium phosphate is the essential constituent of superphosphate fertilizer, which is manufactured to the extent of about 15,000,000 tons annually, and valued at several hundred million dollars. Di- and tricalcium phosphates find a restricted use as fertilizers at present, but this use may increase. Notwithstanding the great importance of these phosphates, information regarding their preparation and properties in pure crystalline form leaves much to be desired. Because samples of pure crystalline material were often not at hand, the results of these determinations of their properties are in many cases open to question. It was for the purpose of preparing these phosphates in pure crystalline form and determining some of the more important properties of these pure forms that this investigation was undertaken.

General Laboratory Methods

Phosphorus was determined by both the colorimetric and gravimetric methods. The colorimetric method followed is that described by Truog and Meyer (*28*). The gravimetric method followed is essentially that given by Treadwell and Hall (*26*), except that a smaller sample (approximately 0.035 gram of P_2O_5) was used, 5 grams of ammonium nitrate were added to each solution previous to precipitation, and the ammonium molybdate solution used was prepared according to official methods (*1*). The colorimetric method was used whenever the amount of phosphorus involved was so small that the gravimetric method could not be used conveniently.

Calcium was determined by precipitation as the oxalate and titration with potassium permanganate.

The loss of water by the salts at different temperatures was determined by heating 1-gram samples in an electric oven for the temperature range of 40° to 185° C., in an electric furnace equipped with a pyrometer for the temperature range of 190° to 800° C., and over Bunsen and Méker burners for temperatures above 850° C.

The carbon dioxide-free water used in solubility studies was prepared by drawing carbon dioxide-free air through distilled water for approximately 48 hours. Throughout this paper, water so treated will be designated as "water." The carbon dioxide-saturated water was prepared by passing carbon dioxide through distilled water until it attained a pH of 3.8.

The solubility studies, unless stated otherwise, were conducted by shaking the suspensions for the designated period, after which they were allowed to stand with intermittent shaking for 24 hours in a water bath maintained at 25° C.

The pH of water solutions of the three phosphates was determined with the hydrogen electrode.

Monocalcium Phosphate Monohydrate

PREPARATION. A review of the literature pertaining to the preparation of pure crystalline monocalcium phosphate monohydrate shows that the ratio of P_2O_5 to CaO (*2, 24*), temperature at which crystallization takes places (*2*), and kind of washing liquids used (*24, 25*) are factors to be considered.

Clark (*10*) attempted to prepare the pure salt by dissolving the commercial product in water and evaporating until crystallization had proceeded for some time. Then the mixture was cooled to 50° C. and centrifuged. The ratio of P_2O_5 to CaO of his product was slightly higher than the theoretical, due to the presence of free acid.

In some preliminary trials, the writer was unable to obtain pure crystalline products from solutions evaporated at 40° C. when the ratios of P_2O_5 to CaO were 3 to 1 and 4 to 1. With a ratio of 5 to 1, a pure crystalline product was finally obtained when prepared in the following manner:

To 3 liters of water containing 332 grams of P_2O_5 as phosphoric acid, calcium hydroxide equivalent to 66.4 grams of CaO was added. The filtered solution was evaporated at 35° to 40° C., using an air current to hasten evaporation. The solution was stirred several times a day, and any salt crystallizing on the side of the beaker was pushed down into the solution to dissolve. Crystallization began when the volume had been reduced from 3 liters to approximately 850 cc. The temperature was then lowered to 30° to 33° C. When the volume had been reduced to 500 cc., the supernatant liquid was decanted, the crystalline mass crushed somewhat to liberate occluded phosphoric acid, and the excess liquid removed by suction, using a Büchner funnel. The crystalline mass was washed once by decantation with 800 cc. of absolute alcohol, then transferred to a Büchner funnel with absolute alcohol, and washed six times with 125-cc. portions of absolute alcohol. The suction was stopped before each addition until the alcohol had become well distributed. The crystals were finally washed, similarly, three times with absolute ether, spread onto a sheet of paper, and maintained at a temperature of approximately 25° C. until the ether had evaporated. The salt was ground to pass a 20-mesh sieve, the yield being about 66 per cent of the theoretical. The salt did not take on a tarry odor during a period of one year, which Clark (*10*) found to be the case when he used alcohol and ether for washing his product.

COMPOSITION AND CRYSTAL PROPERTIES. The results of analyses for phosphorus and calcium of the prepared monocalcium phosphate monohydrate are given in Table I, as are also results of analyses of di- and tricalcium phosphates. These analyses show that the salt prepared was pure and a monohydrate. The crystals were white and rhomboidal in shape.

TABLE I. ACTUAL AND THEORETICAL COMPOSITION OF THREE PHOSPHATES PREPARED

	Composition					
	By analysis of those prepared			Theoretical		
Phosphate	P_2O_5	CaO	$\frac{P_2O_5}{CaO}$	P_2O_5	CaO	$\frac{P_2O_5}{CaO}$
	%	%		%	%	
$CaH_4(PO_4)_2 \cdot H_2O$	56.65	22.40	2.54	56.30	22.12	2.54
	56.60	22.25				
$Ca_2H_2(PO_4)_2 \cdot 4H_2O$	41.46	32.90	1.25	41.27	32.48	1.27
	41.14	33.20				
$Ca_3(PO_4)_2 \cdot H_2O$	42.40	51.20	0.83	43.30	51.10	0.84
	42.50	51.20				

Results of petrographic examination are given in Table II. The crystals are very finely twinned, but not of the same orientation, thus necessitating the choosing of single crystals for optical work. The x-ray diffraction pattern is represented in Figure 1, and differs markedly from those of di- and tricalcium phosphates, the lines being more prominent than those of the latter phosphate but less so than those of the former.

LOSS OF WATER AND TRANSFORMATION ON HEATING. Results of the effect of heating monocalcium phosphate monohydrate at different temperatures for short and long periods of time on loss of weight are given in Table III. Prolonged

TABLE II. CRYSTAL PROPERTIES OF MONOCALCIUM PHOSPHATE MONOHYDRATE AND DICALCIUM PHOSPHATE TETRAHYDRATE

Phosphate	Properties of Crystals: System	Sign	Value of 2*V*	Refractive indices using "D" light: *N_g*	*N_m*	*N_p*
Monocalcium phosphate monohydrate	Triclinic	Minus	70°	1.5292	1.5176	1.4932
Dicalcium phosphate tetrahydrate	Monoclinic	Minus	83°	1.5516	1.5457	1.5394

heating at 100° C. caused a loss in weight equivalent to 0.96 molecule of water (variation from 1 molecule is within limit of error), showing that the molecule of water is lost at a lower temperature than is reported by some investigators (*4*, *14*), and that the anhydrous salt is quite stable when heated for long periods of time at this temperature. It is also stable when heated for 5-hour periods over a temperature range of 103° to 153° C.

When the salt was heated at 200° to 205° C. for nearly 10 weeks, it gradually lost weight equivalent to 2.5 molecules of water. This loss can be accounted for by the formation of a mixture of calcium pyrophosphate and metaphosphoric acid in accordance with the equation given by Stoklasa (*24*):

$$2CaH_4(PO_4)_2.H_2O = Ca_2P_2O_7 + 2HPO_3 + 5H_2O\uparrow$$

The mixture thus obtained was dissolved in water acidified with sulfuric acid, and the presence of one or both compounds in solution was shown by the formation of a white precipitate when silver nitrate was added. Pyrophosphate was shown to be present in the mixture by the formation of a white precipitate when zinc sulfate was added in excess to the solution at approximately pH 5.4. A few drops of a water extract of the mixture caused coagulation of a solution of albumin, indicating the presence of metaphosphate.

In order to confirm further the presence of metaphosphate and pyrophosphate, the relative rate of hydrolysis to orthophosphate in boiling water of the mixture obtained by heating and of pure calcium pyrophosphate was investigated.

The relative rate of hydrolysis was studied by boiling 0.05-gram samples in 500 cc. of water for the given period. After cooling, aliquots were filtered and analyzed for orthophosphate by the colorimetric method. The remainder of the unfiltered aliquot was then boiled for the next desired period. The mixture at first hydrolyzed much more rapidly than did a sample of pyrophosphate. The velocity of hydrolysis of the mixture became much slower after an amount of phosphorus equivalent to the calculated amount of metaphosphoric acid had hydrolyzed. This slower velocity was similar to the velocity of hydrolysis of the calcium pyrophosphate alone. This test confirmed the presence of pyrophosphate and metaphosphate in accordance with the reaction just given.

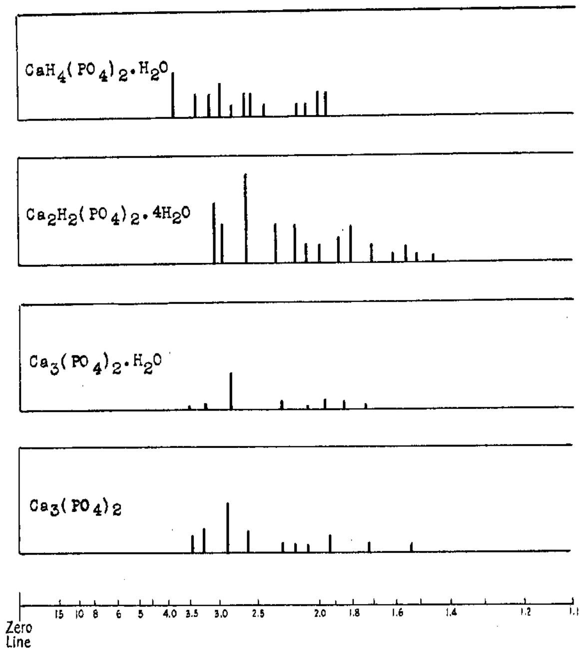

FIGURE 1. DIAGRAMS OF X-RAY PATTERNS OF PHOSPHATES

Length of lines indicates estimated intensity of diffraction spectra lines Mo. radiation. λ = 0.712 Å. *R* = 20 cm.

TABLE III. EFFECTS OF TEMPERATURE AND PERIOD OF HEATING ON LOSS OF WEIGHT OF MONOCALCIUM PHOSPHATE MONOHYDRATE

(Loss of 7.14 per cent is equivalent to 1 mole water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° *C.*	*Hours*	%
99 to 101	27	6.32
90 to 101	256	6.93
90 to 101	334	6.93
103	5	6.73
109	5	7.14
119	5	7.25
134	5	7.31
147	5	7.39
151	5	7.41
203	1	10.83
203	3	11.66
203	18	13.74
203	63	14.91
203	158	15.66
203	254	15.90
203	373	16.27
203	492	16.30
203	587	16.33
203	730	16.40
203	855	16.81
203	974	17.54
203	1165	17.59
203	1362	17.60
203	1658	17.60
325	204	21.78
900 to 910	1/3	22.40
900 to 910	4	23.16
950 to 970	7	23.80
950 to 970	30	33.47
950 to 970	49	36.77
950 to 970	82	40.56
950 to 970	127	42.07
950 to 970	170	42.35
950 to 970	176	42.34

When the monocalcium phosphate monohydrate was heated at 325° C. for 204 hours, a loss in weight equivalent to 3 molecules of water took place. This loss can be accounted for by a complete change from orthophosphate to metaphosphate in accordance with the following equations:

$$2CaH_4(PO_4)_2.H_2O = Ca_2P_2O_5 + 2HPO_3 + 5H_2O$$
$$Ca_2P_2O_7 + 2HPO_3 = Ca_2P_2O_7 + P_2O_5 + H_2O$$
$$Ca_2P_2O_5 + P_2O_5 = 2Ca(PO_3)_2$$

To study the effect of higher temperatures for short and long periods of time, samples of the salt were heated for about 20 minutes, and also for 4 hours, over a Bunsen burner at approximately 900° to 910° C., and then for longer periods over Méker burners at approximately 950° to 970° C. until the weights were constant. The data obtained (Table II) show that at the temperature of a Bunsen burner the equivalent of 3 molecules of water is removed in about 20 minutes, and when the temperature is raised to that of a Méker burner, the equivalent of approximately 3 more molecules of water is removed gradually over a period of 170 hours. The total loss was equivalent to 6 molecules of water. A loss in weight (49.6 per cent) equivalent to 7 molecules of water can be accounted for by the equation:

$$2CaH_4(PO_4)_2.H_2O + \text{heat} = Ca_2P_2O_7 + P_2O_5\uparrow + 6H_2O\uparrow$$

in which case both phosphoric anhydride and water are removed. This is in disagreement with Hinds (*18*), who states that metaphosphate is the final product when monocalcium and dicalcium phosphate are heated. A further loss in weight equivalent to 1 molecule of water might have taken place at a higher temperature.

Solubility and Reaction. For a review of the literature pertaining to the solubility of monocalcium phosphate monohydrate, the reader is referred to articles by Cameron and Hurst (*7*), Sanfourche and Focet (*22*), Seidell (*23*), and Stoklasa (*24*).

The effect of shaking for different periods of time on the solubility was studied first. The salt was added to water and carbon dioxide–saturated water at the rate of 25 and 50 grams per liter, respectively. The suspensions were placed on a shaker, and aliquots taken after 3, 9, 24, and 48 hours, filtered, and then analyzed for phosphorus. The results are given in Table IV. These data indicate that shaking for 3 hours was sufficient for equilibrium to take place in both solvents.

Table IV. Effects of Period of Shaking and Amount of Salt Added on Solubility of Monocalcium Phosphate Monohydrate in Water and Carbon Dioxide–Saturated Water

(Ratio of P_2O_5 to CaO in salt is 2.53)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	*G./l.*	*G./l.*	%	*G./l.*	%	
Water	24	10.0	9.92	99.2	10.00	100.0	2.52
	24	12.0	10.80	90.0	11.80	98.3	2.32
	24	20.0	18.90	94.5	18.70	93.5	2.55
	3	25.0	23.85	95.5	...	...	..
	9	25.0	23.85	95.5	...	...	..
	24	25.0	23.85	95.5	...	...	..
	48	25.0	23.85	95.5	...	...	..
	3	40.0	36.60	91.5	...	...	..
	24	100.0	87.17	87.2	79.90	79.9	2.78
CO_2–saturated water	3	14.0	13.97	99.7	13.82	98.8	2.56
	3	14.5	14.50	100.0	14.00	96.5	2.64
	3	16.0	15.40	96.7	15.80	99.0	2.48
	3	17.0	17.00	100.0	16.65	98.0	2.59
	24	20.0	17.80	89.0	19.40	97.0	2.33
	14	25.0	24.70	98.7	23.20	93.0	2.71
	3	50.0	46.80	93.5	...	...	..
	9	50.0	46.80	93.5	...	...	..
	24	50.0	46.80	93.5	...	...	..
	48	50.0	46.80	93.5	...	...	..
	24	75.0	62.00	82.5	61.00	81.3	2.58
	24	100.0	86.70	86.7	77.00	77.0	2.86

The influence of ratio of salt to solvent on solubility was studied by adding 10 to 100 grams of salt to a liter in the case of water, and 14 to 100 grams in the case of carbon dioxide–saturated water. The results of analyses for phosphorus and calcium in solution are given in Table IV, and show that all the added phosphate dissolved when 10 grams of salt were added per liter of water at 25° C. Beyond this, the percentage of salt which dissolved decreased, but the actual amount increased greatly.

In the case of carbon dioxide–saturated water, all the added phosphate dissolved at 25° C. when 14 grams of salt per liter were added. The percentage of salt that dissolved decreased as the quantity of salt added was increased, while the actual amount increased. As the amount of salt added to both solvents increased, the ratio of P_2O_5 to CaO in the solution increased, showing that some decomposition was taking place, and that a more insoluble calcium salt was being formed and left out of solution. Stoklasa (*24*) believed that the process of decomposition could be represented as follows:

$$X\ CaH_4(PO_4)_2.H_2O + H_2O = (X - 1)\ CaH_4(PO_4)_2.H_2O + CaHPO_4 + 2H_2O + H_3PO_4$$

When *X* equals 4, the undecomposed quantity would be 75 per cent, and the decomposed 25 per cent.

The effect of concentration of monocalcium phosphate monohydrate in filtered water solutions on reaction is shown in Table V. The solution having the highest ratio of P_2O_5 to CaO had the lowest pH. The acidity increased with increasing concentrations of dissolved salt.

Table V. Reaction of Water Solutions of the Three Phosphates

Phosphate	Salt Added	Salt Dissolved, Based on Phosphorus in Solution	pH of Solution
	G./l.	*G./l.*	
Monocalcium phosphate monohydrate	10.0	9.92	3.62
	100.0	87.17	2.49
Dicalcium phosphate tetrahydrate	0.5	0.196	6.00
	1.0	0.16	6.55
Tricalcium phosphate monohydrate	0.5	0.0137	6.22
	5.0	0.0307	6.41

Dicalcium Phosphate Tetrahydrate

Preparation. A review of the literature pertaining to the preparation of dicalcium phosphate tetrahydrate indicates that the temperature at which evaporation takes place (*3*, *6*) and the use of proper washing solutions (*13*) are the most important factors to be considered.

The writer prepared the pure crystalline salt in accordance with the method outlined by DeSchulten (*13*). Anhydrous commercial dicalcium phosphate was dissolved in 25 per cent acetic acid solution at 50° C. The filtered solution was evaporated at 25° to 33° C. under a hood, where circulation was aided with a fan. The salt which collected on the side of the beaker was pushed down into the solution. When about 75 per cent of the added salt had crystallized, the crystals were crushed somewhat and the liquid filtered off. The crystalline mass was then washed by decantation ten times with absolute alcohol and finally five times with absolute ether. After drying at room temperature, the crystals were ground to pass a 20-mesh sieve and the product used for determinations of properties.

Composition and Crystal Properties. The results of analyses of the dicalcium phosphate tetrahydrate for phosphorus and calcium are given in Table I, and agree well with the theoretical values of the tetrahydrate salt.

The crystals were pale yellow rhomboidal plates with the sharper corners broken off in many instances, which is in agreement with the observations of DeSchulten (*13*). Results of examination of the crystals under the petrographic microscope are given in Table II, and check very closely with those of Koehler (*19*).

The x-ray diffraction pattern of this salt represented in Figure 1 had more prominent lines than those of the other salts, and it also differed in position of the lines.

Loss of Water and Transformation upon Heating. Results of the effect of heating dicalcium phosphate tetrahydrate for long periods of time at temperatures of 40°, 75°, 110°, 200°, and 950° to 970° C. are given in Table VI. When the salt was heated for approximately 690 hours at 40° C., a loss equivalent to 0.6 molecule of water resulted. The salt gradually lost 1.5 molecules of water when heated at 108° C. for approximately 270 hours. Almost maximum loss occurred within 5 hours when it was heated at 200° C., only a slight additional loss occurring upon further heating, which shows that the salt reaches a stable point quickly at this temperature. When it was heated at 950° to 970° C. for 27 hours, a loss equivalent to nearly 5 molecules of water occurred, which can be accounted for by transformation to the pyrophosphate.

The salt was also heated for short periods—that is, for 5 hours—at temperatures ranging from 40° to 325° C. The results are given in Table VI. There was a gradual loss of water with rise in temperature. The partially hydrated salt was not stable over any temperature range between 40° and 200° C. The first 2 molecules of water were gradually

TABLE VI. EFFECTS OF TEMPERATURE AND PERIOD OF HEATING ON LOSS OF WEIGHT OF DICALCIUM PHOSPHATE TETRAHYDRATE

(Loss of 5.23 per cent is equivalent to 1 mole of water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° *C.*	*Hours*	%
40	5	0.08
40	48	0.60
40	96	0.78
40	192	1.89
40	312	2.35
40	621	3.23
40	687	3.57
66	5	1.32
75	15	2.08
75	36	2.70
75	60	3.07
75	108	3.58
75	352	3.52
85	5	2.15
95	5	3.95
105	5	4.87
108	5	5.57
108	11	5.81
108	57	6.41
108	151	7.04
108	270	7.56
108	335	7.60
110	5	6.07
134	5	7.70
150	5	10.45
175	5	13.66
184	5	19.80
200	12	19.57
200	24	19.63
200	49	19.70
230	5	19.80
255	5	19.97
277	5	20.03
310	5	20.25
325	5	20.41
950 to 970	1	25.61
950 to 970	9	25.76
950 to 970	27	25.80

driven off over the temperature range of 40° to 150° C. There was some indication that the third and fourth molecules are removed at the same temperature, or at least within a narrow range of temperature. The first molecule of water was driven off at approximately 108° C., the second at 150° C., and the third and fourth at 150° to 185° C. Dragunov (*14*) reported a loss equivalent to nearly 4 molecules of water by heating the dry salt at 150° C. for only 20 minutes. Davies (*12*) also observed that there was no definite temperature at which the salt lost its water of crystallization.

SOLUBILITY AND REACTION. For a review of the literature pertaining to the solubility of dicalcium phosphate tetrahydrate, the reader is referred to the articles by Cameron and Seidell (*8*), and Cameron and Hurst (*7*).

The effect of duration of period of shaking on solubility was studied first. The salt was added to water and to carbon dioxide-saturated water at rates of 0.12 and 1 gram per liter, respectively. The suspensions were placed on the shaker and aliquots taken after 3, 9, 24, 48, 72, and 96 hours. Results of analyses for phosphorus in the filtered solutions are given in Table VII. Equilibrium was attained after the solutions had been shaken for 72 hours, which is a much longer period than was required by monocalcium phosphate.

The influence of ratio of salt to solvent on solubility was next investigated. Different amounts of salt ranging from 0.12 to 1 gram per liter were added to water, and amounts ranging from 0.266 to 5 grams per liter were added to carbon dioxide-saturated water. The results of analyses for phosphorus and calcium in filtered solutions are given in Table VII. Maximum solubility in water at 25° C. was attained with only 0.5 gram of salt per liter. The ratios between the amounts of phosphorus and calcium which dissolved show that some hydrolysis took place. Approximately 0.2 gram per liter of the salt is soluble in water according to the phosphorus determination. These results are higher than those reported by Seidell (*23*), and lower than those reported by Comey and Hahn (*11*).

The solubility of the salt in carbon dioxide-saturated water was found to be highest when 3 or 4 grams of salt were added per liter. A slightly lower solubility was found when 5 grams per liter were added. Slightly larger proportionate amounts of calcium than of phosphorus were dissolved. These results differ from those obtained in water where larger proportionate amounts of phosphorus than of calcium were dissolved. It is not apparent why the solubility was less when 5 grams of salt were added per liter than when 3 or 4 grams were added. These results for carbon dioxide-saturated water are higher than those given by both Seidell (*23*) and Comey and Hahn (*11*). The ratio of P_2O_5 to CaO in solution agreed better with the formula requirements in the case of carbon dioxide-saturated solutions than in the case of water solutions, indicating less hydrolysis in the former.

TABLE VII. EFFECTS OF PERIOD OF SHAKING AND AMOUNT OF SALT ADDED ON SOLUBILITY OF DICALCIUM PHOSPHATE TETRAHYDRATE IN WATER AND CARBON DIOXIDE-SATURATED WATER

(Ratio of P_2O_5 to CaO in salt is 1.27)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	*G./l.*	*G./l.*	%	*G./l.*	%	
Water	3	0.12	0.037	30.8	....	..	..
	9	0.12	0.044	36.7	....	..	..
	24	0.12	0.057	47.5	....	..	..
	48	0.12	0.061	50.7	....	..	..
	72	0.12	0.067	55.7	....	..	..
	96	0.12	0.067	55.7	....	..	..
	72	0.50	0.179	36.0	0.139	27.8	1.65
	72	0.50	0.196	39.2	0.128	25.6	1.94
	72	1.00	0.160	16.0	0.135	13.5	1.50
CO_2-saturated water	3	0.266	0.132	49.5	0.133	50.0	1.26
	3	0.570	0.219	38.5	0.243	42.7	1.14
	3	1.0	0.513	51.3	....	..	..
	9	1.0	0.610	61.0	....	..	..
	24	1.0	0.750	75.0	....	..	..
	48	1.0	0.660	66.0	....	..	..
	72	1.0	0.777	77.7	....	..	..
	96	1.0	0.777	77.7	....	..	..
	72	3.0	0.820	27.3	0.8400	27.9	1.24
	72	4.0	0.818	20.5	0.8460	21.1	1.23
	72	5.0	0.685	13.7	0.7200	14.4	1.21

The effect of concentration of dicalcium phosphate in water solutions on the reaction is shown in Table V. The solutions of highest concentration had the lowest pH. Another factor that probably affected the values was the ratios of P_2O_5 to CaO in solution. The pH values of dicalcium phosphate solutions, as would be expected, are much higher than those of the monocalcium phosphate. Zinzadze (*31*) obtained a pH of 7.5 for a freshly prepared solution.

Tricalcium Phosphate Monohydrate

PREPARATION. A review of the literature pertaining to the preparation of tricalcium phosphate monohydrate shows that a pure salt will precipitate in an alkaline solution when the theoretical ratio of P_2O_5 to CaO is present (*29, 30*), and in an acid solution but above pH 5.5 if a very low ratio of P_2O_5 to CaO is present (*5*).

Tricalcium phosphate monohydrate was prepared as follows in approximately 15-gram quantities:

Sixteen and four-tenths grams of disodium phosphate ($Na_2HPO_4.12H_2O$) were dissolved in 2 liters of water contained in a 3-liter round-bottomed flask. An equivalent quantity of calcium chloride was dissolved in 750 cc. of water and placed in a separatory funnel connected to the mouth of the flask. The stopcock of the funnel was so adjusted that the contents flowed into the flask in about 48 hours. The flask was supported in a water bath maintained at 65° to 70° C., and the contents were kept agitated by means of a stream of carbon dioxide-free air which entered through a fine capillary that extended to the bottom of the flask. During the course of a day, approximately 500 cc. of water evaporated, necessitating the addition of a like amount. Special care was taken to maintain the pH between 7 and 8 by adding dilute ammonium hydroxide as required. At the end of 48 hours, the precipitate was allowed to settle and the supernatant liquid poured off. Twelve portions were prepared in this manner, mixed together, and the mass washed free of chlorides by decantation, using small quantities of water. The salt was air-dried and ground to pass a 20-mesh sieve, and then used for determinations of its properties.

COMPOSITION AND CRYSTAL PROPERTIES. Results of analyses for phosphorus and calcium of tricalcium phosphate monohydrate are given in Table I, and agree well with the theoretical values of the monohydrate.

The crystals were too small for petrographic study, but x-ray diffraction patterns of both freshly prepared salt and of salt which had been heated for 25 hours at 950° to 970° C. were obtained, and are represented in Figure 1. The lines in the pattern of the heated salt were closer together and were also more prominent than those of the freshly prepared salt, which shows that the molecular planes in the crystal were brought closer together when the crystal was heated. Since in these patterns a number of the prominent lines of mono- and dicalcium phosphate were absent the crystalline properties exhibited were not due to admixtures of mono- and dicalcium phosphates. The exhibition of crystalline properties by tricalcium phosphate monohydrate is in agreement with the work of Zinzadze (*31*) and Gerlach (*17*). Cameron and Seidell (*8*), working prior to the advent of the x-ray method, were unable to establish the crystalline nature of this salt. These patterns, as would be expected, differ from those which Tromel (*27*) obtained for oxyapatite and hydroxyapatite.

LOSS OF WATER AND TRANSFORMATION ON HEATING. Results of heating tricalcium phosphate monohydrate for short and long periods of time are given in Table VIII. When the salt was heated for 5-hour periods at 65° and 100° C., the loss in weight was very small. This stability of the salt at temperatures around 100° C. was also observed by Zinzadze (*31*). The salt lost weight equivalent to 0.91 molecule of water when heated at 950° to 970° C. for 5 hours. An additional loss of only 0.06 water molecule took place when the same samples were heated for 21 hours more at this high temperature, which is in agreement with the results of Sanfourche (*21*).

TABLE VIII. EFFECTS OF TEMPERATURE AND PERIOD OF HEATING ON LOSS OF WEIGHT OF TRICALCIUM PHOSPHATE MONOHYDRATE

(Loss of 5.48 per cent is equivalent to 1 mole of water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° *C.*	*Hours*	%
65	5	0.60
108	5	0.96
325 to 335	24	3.03
950 to 970	5	4.96
950 to 970	14	5.15
950 to 970	21	5.24
950 to 970	25	5.24

SOLUBILITY AND REACTION. The influence of ratio of salt to solvent on solubility of tricalcium phosphate monohydrate was studied by Cameron and Seidell (*9*), and Cameron and Hurst (*7*), while Gaarder (*16*), and Osugi et al. (*20*) studied the effect of reaction of the solution on solubility of the salt.

In order to study the effect of period of shaking on solubility, the salt was added to water and to carbon dioxide-saturated water at rates of 0.008 and 0.3 gram per liter, respectively. The suspensions were shaken and samples taken after 3, 9, 24, 48, 72, 96, and 120 hours, filtered, and then analyzed for phosphorus. The results are given in Table IX. The water solutions and the carbon dioxide-saturated solutions came to equilibrium at the end of 96 and 3 hours' shaking, respectively.

TABLE IX. EFFECTS OF PERIOD OF SHAKING AND AMOUNT OF SALT ADDED ON SOLUBILITY OF TRICALCIUM PHOSPHATE MONOHYDRATE IN WATER AND CARBON DIOXIDE-SATURATED WATER

(Ratio of P_2O_5 to CaO in salt is 0.84)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	*G./l.*	*G./l.*	%	*G./l.*	%	
Water	3	0.008	0.0015	18.7	....	...	..
	9	0.008	0.0018	22.5	....	...	..
	24	0.008	0.0024	30.0	....	...	..
	48	0.008	0.0036	45.0	....	...	..
	72	0.008	0.0040	50.0	....	...	..
	96	0.008	0.0048	60.0	....	...	..
	120	0.008	0.0048	60.0	....	...	..
	24	0.111	0.0097	8.7	....	...	..
	120	0.500	0.0137	2.7	0.0237	4.7	0.49
	48	1.110	0.0158	1.4	....	...	..
	120	5.000	0.0307	0.61	0.0241	0.48	1.06
CO_2-saturated water	24	0.121	0.058	48.0	0.060	49.5	0.81
	3	0.300	0.1480	49.3	....	...	..
	9	0.300	0.1480	49.3	....	...	..
	24	0.300	0.1480	49.3	....	...	..
	24	0.300	0.1420	47.4	0.145	48.5	0.82
	3	0.500	0.1480	29.6	0.149	29.8	0.84
	24	1.000	0.1970	19.8	0.204	20.4	0.82
	24	2.000	0.2010	10.1	0.217	10.8	0.79
	24	4.000	0.2300	5.75	0.235	5.9	0.82

The influence of ratio of salt to solvent on solubility was studied by adding from 0.008 to 5 grams of salt in the case of water, and 0.12 to 4 grams in the case of carbon dioxide-saturated solutions. The results of analyses for phosphorus and calcium are given in Table IX. The maximum solubility of the salt at 25° C. in water was 0.031 gram per liter on the basis of the phosphorus in solution, when 5.0 grams of salt per liter were added. Since more phosphorus than calcium dissolved, the residue, of necessity, became a more basic phosphate than tricalcium phosphate. Cameron and Hurst (*7*) obtained similar results.

The maximum solubility of tricalcium phosphate monohydrate in carbon dioxide-saturated water was approximately 0.23 gram of salt per liter on the basis of the phosphorus in solution, and slightly higher on the basis of the calcium in solution. This solubility was attained when 4 grams of salt were added to a liter of carbon dioxide-saturated water. The ratio of P_2O_5 to CaO in solution was very close to that of the formula. The solubility obtained is within the limits given by Seidell (*23*).

The effect of concentration of the salt in water solutions on reaction is given in Table V. These solutions had higher pH values than solutions of the monocalcium phosphate, but approximately the same as solutions of dicalcium phosphate. The values obtained are slightly lower than those of Zinzadze (*31*), who observed a pH of 6.8 in water solution.

Additional Comments on Reactions of the Three Phosphates

Contrary to first thought, it is to be noted that, depending on the conditions of the test, tricalcium phosphate may apparently give a slightly more acid reaction than dicalcium phosphate. This may be due to the formation of intermediate products or to insufficient time for equilibrium to be established. In order to obtain some further data on the reaction of these phosphates as they are commonly obtained, samples of such commercial products and others as were at hand were tested. In making these tests, 0.2 gram of the phosphate was placed in 20 cc. of carbon dioxide-free water, the suspension shaken 2 minutes, centrifuged, and the pH determined colorimetrically on 5 cc. of the clear supernatant liquid. The results are given in Table X. The pH of the different samples of the mono- and dicalcium phosphates did not vary greatly, as did the samples of tricalcium phosphate. Here again, the samples of tricalcium phosphate usually reacted more acid than did those of dicalcium phosphate.

TABLE X. REACTION OF VARIOUS SAMPLES OF THREE PHOSPHATES

Monocalcium Phosphate	pH
Author's preparation	4.3
Commercial preparation No. 1	3.3
Commercial preparation No. 2	3.0
Research laboratory preparation	3.1
Dicalcium Phosphate	
Author's preparation	7.3
Commercial preparation No. 1	7.2
Commercial preparation No. 2	6.9
Commercial preparation No. 3	6.8
Commercial preparation No. 4	7.0
Research laboratory preparation	6.8
Tricalcium Phosphate	
Author's preparation	6.6
Commercial preparation No. 1	3.6
Commercial preparation No. 2	5.4
Commercial preparation No. 3	6.6
Research laboratory preparation	6.9

Summary

The purpose of this investigation was to prepare mono-, di-, and tricalcium phosphates in pure crystalline form, and to establish the more important properties of these pure forms. The results are summarized as follows:

1. Crystalline monocalcium phosphate monohydrate was prepared by evaporating at 33° to 40° C. a water solution of phosphoric acid and calcium hydroxide having a P_2O_5 to CaO ratio of 5 to 1. The values of the refractive indices N_g, N_m, and N_p were found to be 1.5292, 1.5176, and 1.4932, respectively. It became anhydrous at 109° C., became a mixture of pyrophosphate and metaphosphate on heating for a long period at 203° C., was transformed into metaphosphate at 325° C., and lost weight equivalent to 6 molecules of water at 950° C. The solubility at 25° C. was 10 and 14 grams per liter in water and carbon dioxide–saturated water respectively, when the amount of salt added was limited to that which dissolved completely. However, when more salt was added than would dissolve, hydrolysis was evident. The pH of a water solution containing 10 grams of salt per liter was 3.62.

2. Dicalcium phosphate tetrahydrate was prepared according to the method of DeSchulten—that is, crystallization of the salt at 30° C. from a 25 per cent acetic acid solution to which anhydrous dicalcium phosphate had been added. The refractive indices N_g, N_m, and N_p were found to be 1.5576, 1.5457, and 1.5392, respectively. Heating the salt for 5-hour periods at 108°, 150°, and 150° to 185° C. caused a loss equivalent to 1 molecule, 2 molecules, and 3 to 4 molecules of water, respectively. It was transformed into pyrophosphate at 950° to 970° C. The solubility in water at 25° C. was in the range of 0.16 to 0.196 gram per liter, and in carbon dioxide–saturated water, 0.62 to 0.82 gram per liter. The pH values of water solutions containing 0.196 and 0.160 gram of salt per liter were 6.00 and 6.55, respectively.

3. Tricalcium phosphate monohydrate was prepared by the slow addition of calcium chloride solution to a constantly agitated alkaline solution of disodium phosphate, maintained at 65° to 70° C. An x-ray diffraction pattern indicated the product to be crystalline, but the crystals were too small for petrographic study. The salt was stable at 100° C. When heated at 325° C. for 24 hours and at 950° to 970° C. for 5 hours, it lost weight equivalent to 0.6 and 1 molecule of water, respectively. The solubility in water at 25° C. varied with the ratio of salt to water from less than 0.005 to more than 0.03 gram per liter, and in carbon dioxide–saturated water from 0.058 to 0.23 gram per liter. The pH values of water solutions containing 0.0132 and 0.0307 gram of salt per liter were 6.22 and 6.41, respectively.

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