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Determination of free phosphoric acid in superphosphate

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DETERMINATION OF FREE PHOSPHORIC ACID IN SUPERPHOSPHATE

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Water soluble phosphoric acid in ordinary superphosphate and double (or triple) superphosphate consists of mainly monocalcium phosphate, but it also contains one to several per cent free phosphoric acid. Both free acid and water are the essential components in order to know the change in curing or to estimate the reduction of posphoric acid in manufacture of mixed fertilizer.

In 1954 NAKAMURA and the author (1) studied about the determination of free water. However, there have been few reports about free phosphoric acid, though many papers on volumetric or colorimetric determination of phosphoric acid have been published. The tentative method in Japan, titrating water soluble matter with sodium hydroxide using methyl orange as indicator (2), is not so good, because the neutral point is indistinct and rather high result is gained by the effect of coexistence of monocalcium phosphate and water soluble fluorine. And many extraction methods with organic solvents, such as ether (3—5), absolute alcohol (6), neutral acetone (7,8) and acetone-ether mixture of equal volume (9) in place of water, have been proposed; but such methods have some defects and are too troublesome to be practical.

In this work, solubilities of components of superphosphate in several solvents were investigated and the practical and precise procedure was established.

Solubilities of Components of Superphosphate in Organic Solvents

1. Sample. Each sample was passed through 500μ (32 meshes) sieve after drying, and the composition is shown in Table 1.

a) Monocalcium phosphate monohydrate [Ca$(H_2PO_4)_2 \cdot H_2O$]: C.P. grade product was recrystallized from 50% phosphoric acid solution, washed with acetone-ether mixture (1:1) and dried in sulfuric acid desiccator (10).

b) Dicalcium phosphate dihydrate [CaHPO$_4 \cdot$ 2H$_2$O]: Calcium chloride solution was added equivalently to diammonium phosphate solution adjusted to pH 4 with phosphoric acid and the precipitate was washed with water and dried at room temperature.

c) Tricalcium phosphate monohydrate [Ca$_3$(PO$_4$)$_2 \cdot$ H$_2$O]: A little excess calcium nitrate solution was added dropwise to trisodium phosphate solution, and the precipitate was washed with water and dried at 60°C (11).

d) Calcium sulfate dihydrate [CaSO$_4 \cdot$2H$_2$O]: Ammonium sulfate solution was added equivalently to calcium chloride solution, and the precipitate was washed with water and

Table 1. Composition of Sample

Sample	CaO	P$_2$O$_5$	SO$_3$	P$_2$O$_5$/CaO	SO$_3$/CaO	H$_3$PO$_4$
	%	%	%			%
Ca(H$_2$PO$_4$)$_2 \cdot$H$_2$O	22.29 (22.25)	56.30 (56.31)		2.53 (2.53)		
CaHPO$_4 \cdot$2H$_2$O	32.53 (32.59)	41.29 (41.24)		1.27 (1.27)		
Ca$_3$(PO$_4$)$_2 \cdot$H$_2$O	51.10 (51.26)	43.48 (43.25)		0.85 (0.84)		
CaSO$_4 \cdot$2H$_2$O	32.53 (32.57)		46.37 (46.50)		1.43 (1.43)	
CaSO$_4$	41.22 (41.19)		58.77 (58.81)		1.43 (1.43)	
H$_3$PO$_4$ aq. (A)		62.13				85.79
H$_3$PO$_4$ aq. (B)		32.66				45.10
H$_3$PO$_4$ aq. (C)		14.85				20.50

Note: Figures in parentheses indicate theoretical values.

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Table 2. Solubility of Phosphates in Organic Solvents

(P$_2$O$_5$ mg/100 ml of solvent)

Calcium phosphate	Calcium sulfate	Water	Solvent				
			Ether	Acetone	Acetone-ether mixture	Methanol	Ethanol
		g					
	—	—	0.3	2.1	1.1	107.3	2.2
	—	0.2	4.2	12.6	9.2	161.1	22.4
Ca(H$_2$PO$_4$)$_2$·H$_2$O 1 g	CaSO$_4$·2H$_2$O 1.5 g	—	0.1	1.4	0.8	56.6	1.8
		0.2	2.8	7.0	6.1	81.1	16.8
	CaSO$_4$ 1.2 g	—	0.0	0.4	0.2	50.2	0.8
		0.2	1.9	5.0	3.2	79.5	10.1
CaHPO$_4$·2H$_2$O 1 g	—	—	0.0	0.2	0.1	0.5	0.3
	—	0.2	0.0	0.2	0.1	0.5	0.4
Ca$_3$(PO$_4$)$_2$·H$_2$O 1 g	—	—	0.0	0.0	0.0	0.0	0.0
	—	0.2	0.0	0.0	0.0	0.0	0.0

dried at 60°C (12).

e) Anhydrous calcium sulfate (Anhydrite) [CaSO$_4$]: Calcium sulfate dihydrate (d) was dried at 400°C after previous drying at 150°C.

f) Phosphoric acid solutions: A, B and C solutions were prepared by diluting c.p. grade phosphoric acid.

2. Experimental and results. After 1 g of mono-, di-, or tricalcium phosphate was shaken for 30 min respectively with 100 ml of each of organic solvents, *i.e.*, acetone, acetone-ether mixture (1 : 1), methanol, and ethanol, soluble phosphoric acid in the filtrate was determined by the molybdate volumetric method (13). And

in this procedure the effect of coexistence of water or calcium sulfates with these phosphates was also investigated. Results obtained are shown in Table 2.

Solubilities of phosphorus in five solvents were generally shown as the following order:—

ether < acetone-ether mixture < acetone < ethanol < methanol.

But tricalcium phosphate was entirely insoluble in all solvents, and dicalcium phosphate, a little soluble. On the other hand, solubility of monocalcium phosphate coexistent with water was greater than that without water, because hydrolysis of monocalcium phosphate might produce free phosphoric acid, while its solubility

Table 3. Recovery of Free Phosphoric Acid by Organic Solvents (1)

(P$_2$O$_5$/100 ml of solvent)

Calcium phosphate	Calcium sulfate	Phosphoric acid solution			Ether			
		Taken	P$_2$O$_5$ (a)	H$_2$O	Amount of recovery (b)	Difference (b-a)	Ratio (b/a)	Amount of recovery (c)
		g	mg	mg	mg	mg	%	mg
	—	(A) 0.16	99.4	22.7	95.8	−3.6	96.4	99.9
	—	(B) 0.30	98.0	164.7	95.4	−2.6	97.3	98.6
	—	(C) 0.50	74.2	397.5	72.0	−2.2	97.0	74.8
Ca(H$_2$PO$_4$)$_2$·H$_2$O 1 g	CaSO$_4$·2H$_2$O 1.5g	(A) 0.16	99.4	22.7	93.0	−6.4	93.6	99.7
		(B) 0.30	98.0	164.7	94.8	−3.2	96.7	98.5
		(C) 0.50	74.2	397.5	71.5	−2.7	96.4	74.6
	CaSO$_4$ 1.2g	(A) 0.16	99.4	22.7	92.7	−6.7	93.3	99.3
		(B) 0.30	98.0	164.7	94.3	−3.7	96.2	98.2
		(C) 0.50	74.2	397.5	71.4	−2.8	96.2	74.4

decreased when calcium sulfate, especially anhydrite, was added.

In the second experiment, each of three phosphoric acid solutions (cf. Table 1) was added respectively to 1 g of monocalcium phosphate in the extraction with five solvents in order to know the recovery of free phosphoric acid. Results are shown in Table 3.

Amount of recovery of free phosphoric acid in the case of dilute phosphoric acid addition was higher than in the concentrated one treatment, and as regards the kind of solvents, it was generally shown as the following order:—

ether<acetone-ether mixture<acetone<ethanol<methanol.

In the extraction with methanol or ethanol, the ratio of recovery was over 100% and the extract contained evidently a part of phosphorus in monocalcium phosphate. But coexistence of calcium sulfate, especially anhydrite, tended to decrease the solubility of monocalcium phosphate. From the results of chemical analysis and X-ray diffraction method, KRUGEL (14) and HILL (10) reported that calcium sulfate in superphosphate is mainly anhydrite accompanied with small amounts of dihydrate. On the other hand, the recovery in the extraction with ether was incomplete and monocalcium phosphate was rather more soluble in acetone than in acetone-ether mixture (cf. Table 2). Accordingly, acetone-ether mixture will be the best solvent in the

extraction of free phosphoric acid in both ordinary superphosphate containing monocalcium phosphate and anhydrite, and double one containing no calcium sulfate.

In these experiments, neither calcium nor sulfate was found in the filtrate, and so it is sure that these solvents hardly dissolve calcium sulfate or calcium in monocalcium phosphate.

Free Phosphoric Acid in Commercial Fertilizer

1. Sample. Commercial ordinary superphosphates (a and b) and double superphosphate (c) passed through 500μ sieve were used, and these compositions are shown in Table 4.

2. Phosphoric acid extracted with several solvents. After 2 g of sample was shaken for 30 min respectively with 100 ml of solvent, phosphoric acid in the filtrate was determined by titrating with 0.1 N sodium hydroxide or by volumetric method (13). Results of the determination are shown in Table 5.

Amount of extracted phosphoric acid was evidently different according to the kind of solvents. The order of dissolving power was generally similar to that in the chemicals experiments (cf. Table 2 and Table 3). It is supposed that extraction with ether was incomplete, because its figures were the lowest; while the analytical values obtained by extraction with methanol and ethanol were higher than that in the case of water. And when

Table 3. Recovery of Free Phosphoric Acid by Organic Solvents (2)
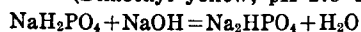(P_2O_5/100 ml of solvent)

Solvent										
Acetone		Acetone-ether mixture			Methanol			Ethanol		
Difference (c-a)	Ratio (c/a)	Amount of recovery (d)	Difference (d-a)	Ratio (d/a)	Amount of recovery (e)	Difference (e-a)	Ratio (e/a)	Amount of recovery (f)	Difference (f-a)	Ratio (f/a)
mg	%	mg	mg	%	mg	mg	%	mg	mg	%
+0.5	100.5	99.5	+0.1	100.1	205.1	+105.7	206.3	101.9	+2.5	102.5
+0.6	100.6	98.1	+0.1	100.1	191.9	+ 93.9	195.8	101.2	+3.2	103.3
+0.6	100.8	74.5	+0.3	100.4	174.5	+100.3	235.2	78.9	+4.7	106.3
+0.3	100.3	99.4	0.0	100.0	195.4	+ 96.0	196.6	101.5	+2.1	102.1
+0.5	100.5	98.0	0.0	100.0	203.0	+105.0	207.1	99.8	+1.8	101.8
+0.4	100.5	74.4	+0.2	100.3	172.3	+ 98.1	232.2	76.4	+2.2	103.0
−0.1	99.9	99.2	−0.2	99.8	170.9	+ 71.5	171.9	100.9	+1.5	101.5
+0.2	100.2	97.7	−0.3	99.7	172.0	+ 74.0	175.5	99.5	+1.5	101.5
+0.2	100.3	74.2	0.0	100.0	156.4	+ 82.2	210.8	76.0	+1.8	102.4

ertilizer is extracted with water, methanol or ethanol, monocalcium phosphate in superphosphate seems to be remarkably soluble in sample c, which contains no calcium sulfate. Accordingly, acetone or acetone-ether mixture, especially the latter, should be the best solvent in the extraction of free phosphoric acid in superphosphate. In this experiment also, neither calcium nor sulfate was found in the filtrate treated with organic solvents as seen in Table 2 and Table 3; and so it will be certain that, no free sulfuric acid was contained in commercial superphosphate.

It is recommended that instead of methyl orange, dimethyl yellow and phenolphthalein are used as indicators in titration with 0.1 N sodium hydroxide, because in the first stage of titration, color change of dimethyl yellow is more distinct than that of methyl orange, and in the second stage, the point of color change is able to be distinguished very easily by using phenolphthalein. The chemical equations in these titrations are represented as follows:
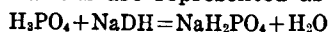
$H_3PO_4 + NaDH = NaH_2PO_4 + H_2O$
(Dimethyl yellow, pH 2.9-4.0),
$NaH_2PO_4 + NaOH = Na_2HPO_4 + H_2O$
(Phenolphthalein, pH 8.2-9.8).

And amount of free phosphoric acid calculated from volume of standard solution in the end point by phenolphthalein, was close to the value obtained by molybdate method as shown in Table 5.

3. Effect of dehydration. In the extraction with organic solvents, a part of monocalcium phosphate was inclined to be hydrolysed when free water was coexistent in fertilizer, as suggested from results in Table 2 and Table 3. Therefore, 2 g of each sample dehydrated by several different methods, was extracted respectively with 100 ml of acetone-ether mixture, and the filtrate was evaporated to dryness, diluted with water, and titrated by the above-mentioned two stages method. Results obtained are shown in Table 6.

Free phosphoric acid of dehydrated sample was generally lower than that of non-treated sample. The values of 100°C-dried sample were the lowest, those of 65°C-dried samples in both ordinary and fanned air-bath were considerably lower, and a little lower values were obtained in the case of vacuum-desiccation method. A portion of monocalcium phosphate in superphosphate is hydrolysed by free water to dicalcium

Table 4. Composition of Sample

| Sample | H₂O | | P₂O₅ | | | | | pH |
	Total*	Free**	Total (T)	Citrate-soluble*** (C)	Water-soluble (W)	C/T	W/T	
	%	%	%	%	%	%	%	
a	10.20	8.90	16.25	16.22	14.66	99.8	90.2	2.8
b	9.89	8.18	20.53	20.21	19.52	98.4	95.1	2.6
c	13.30	11.74	44.89	43.76	41.75	97.5	93.0	3.0

* 100±1°C, 8 hr (13).
** 65±1°C, 5 hr (1).
*** Soluble in PETERMAN's ammonium citrate solution (13).

Table 5. Free Phosphoric Acid in Fertilizer

(% as P₂O₅)

| Solvent | Ether | | Acetone | | Acetone-ether mixture | | Methanol | | Ethanol | | Water |
Sample	Method	Titra-tion*	Volu-metric	Titra-tion*	Volu-metric	Titra-tion*	Volu-metric	Titra-tion*	Volu-metric	Titra-tion*	Volu-metric	Titra-tion**
a	1.75	1.76	3.41	3.44	3.08	3.10	4.96	4.96	3.98	4.09	3.56
b	4.42	4.48	6.61	6.66	6.31	6.31	7.98	7.99	7.33	7.39	6.43
c	1.40	1.48	2.58	2.57	2.41	2.45	5.93	5.91	3.88	3.90	3.84

* Dimethyl yellow and phenolphthalein were used as indicators.
** Dimethyl yellow was used as indicator.

Table 6. Effect of Dehydration

Sample	Non-treated	100±1°C, 3 hr		65±1°C, 5 hr		65±1°C, 2 hr (in fanned air-bath)		Under vacuum (15 mm Hg) in H₂SO₄ desiccator 24 hr (20°C)	
	Free-P₂O₅	Loss of wt.	Free-P₂O₅*	Loss of wt.	Free-P₂O₅*	Loss of wt.	Free-P₂O₅*	Loss of wt.	Free-P₂O₅*
	%	%	%	%	%	%	%	%	%
a	3.08	10.20	1.96	8.90	2.57	8.84	2.68	8.92	2.09
b	6.31	9.89	5.02	8.18	5.85	8.19	5.81	8.24	6.15
c	2.41	13.30	1.15	11.74	1.98	11.56	1.89	11.84	2.40

* Extracted with acetone-ether mixture.

phosphate and free phosphoric acid. The reaction is represented by the following equation :—

$$Ca(H_2PO_4)_2 \cdot H_2O + H_2O \rightleftharpoons CaHPO_4 \cdot 2H_2O + H_3PO_4.$$
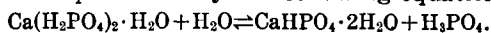
This reversible reaction proceeds to the left side by dehydration, which brings about the resultant decrease of free phosphoric acid. And the decrease appears to be accelerated by the procedure of heating. Accordingly, the method of extracting non-treated sample with acetone-ether mixture that dissolves little monocalcium phosphate coexistent with water and can recover almost 100% of free phosphoric acid, is recommended, as the procedure of previously dehydrating sample brings about some decrease of free phosphoric acid.

4. Effects of fluoride and sulfate. MATSUI (16) and HIRANO (17) reported that most fluorine in rock phosphate reacted in manufacture of superphosphate and a part of it volatilized as silicon tetrafluoride or hydrogen fluoride, while the residual existed in product. Accordingly, the effect of fluorine should be considered in the titration of phosphoric acid, as the soluble fluorine exists probably as fluosilicic acid or hydrofluoric acid in product. Therefore, total, water soluble, and acetone-ether mixture soluble

Table 7. Fluorine
(% in sample)

Sample	Total -F	Water soluble-F	Acetone-ether mixture soluble-F	
			Evaporated to dryness with NaOH	Without addition of alkali
a	1.05	0.27 (25.7)	0.05 (4.8)	0.00
b	1.56	0.19 (12.2)	0.05 (3.2)	0.00
c	1.70	0.36 (21.2)	0.06 (3.5)	0.00

Note: Figures in parentheses indicate ratios to total-F.

fluorines in samples were determined colorimetrically by aluminum-hematoxylin method (18). Results are shown in Table 7.

Since water soluble fluorine was more than 10% of total one, positive error by coexistence of the fluorine should not be negligible in the extraction with water. And the existence of fluosilicic acid would accelerate the indistinctness of neutral point indicated by methyl orange. On the other hand, acetone-ether mixture soluble fluorine was only several per cent of total and it was completely volatilized when the acidic filtrate was evaporated to dryness, and so there is no effect of it in the procedure.

In regard to the effect of sulfate, there is no free sulfuric acid in superphosphate, as calcium sulfate is formed in the presence of monocalcium phosphate, and only trace of sulfate is contained in the solutions extracted with organic solvents; therfore, it will be unnecessary to investigate the effect of soluble sulfate in this procedure.

Summary and Conclusions

In order to establish the method of determination of free phosphoric acid in ordinary or double superphosphate, the solubility of calcium phosphates in organic solvents was determined, and the selection of solvents and the effect of free water or fluorine in commercial fertilizers were investigated. The results obtained are summarized as follows :

1) The order of phosphate dissolving power is shown generally as follows :
ether < acetone-ether mixture < acetone < ethanol < methanol.

Tricalcium phosphate is entirely insoluble in all solvents, whereas dicalcium phosphate a little

soluble. On the other hand, monocalcium phosphate is more soluble, but its solubility decreases when it is coexistent with calcium sulfate, especially anhydrite.

2) Recovery of free phosphoric acid by extraction with five solvents was determined and acetone-ether mixture (1 : 1) was found to be the best solvent.

3) As dehydration of sample before extraction brings about a decrease of free phosphoric acid, it is recommended that sample is extracted without drying.

4) Effect of coexistence of soluble fluorine is completely excluded, if the filtrate is evaporated to dryness after extraction.

5) The method of two steps titration using dimethyl yellow and phenolphthalein as indicators gives the distinct neutral point and the accurate value.

From the above-mentioned results, the following procedure is recommended :

Reagents

a) Acetone-ether mixture (1:1): Mix 500 ml of acetone with an equal volume of ether and keep it in glass-stoppered bottle at low temperature.

b) Standard NaOH solution: Prepare 0.1 N solution, standardize with sulfamic acid (dried in vacuum H_2SO_4 desiccator more than 24 hr) using bromthymol blue as indicator, and calculate phosphoric acid corresponding to 1 ml.

c) Indicator

  i) Bromthymol blue: Dissolve 0.1 g in 100 ml of 20% (by vol.) alcohol.

  ii) Dimethyl yellow: Dissolve 0.1 g in 100 ml of 90% (by vol.) alcohol.

  iii) Phenolphthalein: Dissolve 1.0 g in 100 ml of 95% (by vol.) alcohol.

Preparation of solution

Ordinary or double superphosphate: Weigh 2 g of sample passed through 500 μ (32 meshes) sieve in flask, add 100 ml of acetone-ether mixture (1:1), continuously agitate for 30 min (30–40 rounds per min), and filter the solution through dry filter paper.

Determination

Pipet 50 ml aliquot into beaker, evaporate it to dryness on water-bath, add *ca.* 50 ml of hot water, and mix thoroughly. Titrate with standard NaOH solution using one drop of methyl orange as the first indicator, and when the neutral point is reached, note the number of milliliters used, add 5 drops of phenolphthalein, and cotinue the titration without refilling the buret, until the faint pink color appears. Calculate free phosphoric acid from the total titration value from zero to the end point indicated by phenolphthalein.

$$ml\ 0.1\ N\ \text{NaOH} = 0.003549\ g\ P_2O_5$$

Note : Addition of dimethyl yellow may be omitted.

Literature Cited

(1) NAKAMURA, T. and YAMAZOE, F., *Bull. Nat. Inst. Agr. Sci.*, B, No. 3, 1 (1954).

(2) LEHRECKE, H., *Angew. Chem.*, 49, 620 (1936).

(3) HILL, W.L. and JACOB, K.D., *J. Assoc. Offic. Agr. Chemists*, 17, 487 (1934).

(4) HILL, W.L. and BEESON, K.C., *ibid.*, 18, 244 (1935).

(5) MEURICE, R., *Ann. chim. anal.*, 18, 229 (1936).

(6) Offic. Methods of Analysis in Fertilizers, Nat. Agr. Station, p. 18 (1936).

(7) SHUEY, P.M., *Ind. Eng. Chem.*, 17, 269 (1925).

(8) SHUEY, P.M., *Am. Fertilizer*, 93, No. 10, 7 (1940).

(9) MEPPEN, B. und SCHEEL, K.C., *Angew. Chem.* 50, 811 (1937).

(10) HILL, W.L., and HENDRICKS, S.B., *Ind. Eng. Chem.*, 28, 440 (1936).

(11) JACOB, K.D. *et al.*, *Ind. Eng. Chem. Anal. Ed.*, 4, 25 (1932).

(12) MELLOR, J.W., Comp. Treat. Inorg. Theor. Chem., Longmans, 3, 760 (1923).

(13) Offic. Methods of Analysis in Fertilizers, Misc. Public. Nat. Inst. Agr. Sci., B, No. 4 (1957).

(14) KRUEGEL, C. and RETTER, A., *Superphosphate*, 3, 57 (1930).

(15) Offic. Methods of Analysis, Assoc. Offic. Agr. Chemists, 8, 6 (1955).

(16) MATSUI, G. and MORI, H., *Kôgyô Kagaku Zasshi*, 19, 417 (1916).

(17) HIRANO, S. and SASUGA, H., *ibid.*, 62, 50 (1959).

(18) OKUNO, H., *Nippon Kagaku Zasshi*, 63, 23 (1942).