

The System $\text{NH}_3\text{-ZnO-H}_3\text{PO}_4\text{-H}_4\text{P}_2\text{O}_7\text{-H}_2\text{O}$ at 25°

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Equilibrium solubilities in the system $\text{NH}_3\text{-ZnO-H}_3\text{PO}_4\text{-H}_4\text{P}_2\text{O}_7\text{-H}_2\text{O}$ and solubilities of zinc in simulated ammonium polyphosphate liquid fertilizers were measured at 25° . The equilibrium concentration of zinc increased irregularly from

0.7 to 2.7% ZnO as the pH was raised from 5 to 6.1. A concentration of zinc of 1.5% ZnO appears to be a practicable maximum for ammonium polyphosphate liquid fertilizers that are to be stored.

In recent years, ammonium phosphate liquid fertilizers have been used as macronutrient carriers for the important micronutrient zinc. Liquid fertilizer manufacturers have attempted to produce ammonium polyphosphate solutions containing 2-4% ZnO by the addition of zinc metal or zinc salts. Because chemical reactions between zinc and the macronutrient compounds, particularly ammonium orthophosphates that are always present in polyphosphate solutions, form relatively insoluble zinc phosphates (Lehr, 1972) the results have been erratic. A study was made of the solubilities in the ammonium portion of the system $\text{NH}_3\text{-ZnO-H}_3\text{PO}_4\text{-H}_4\text{P}_2\text{O}_7\text{-H}_2\text{O}$ at 25° to determine the factors that influence the amount of zinc that can be added to ammonium polyphosphate liquid fertilizers.

The solubilities at 25° of the ammonium orthophosphates (D'Ans and Schreiner, 1910; Muromtsev, 1937; Muromtsev and Nazarova, 1938; Vol'fkovich *et al.*, 1940) and pyrophosphates (Farr and Fleming, 1965; Farr and Williard, 1971; Frazier *et al.*, 1973) have been reported, as has also the solubility of zinc pyrophosphate in unsaturated ammonium pyrophosphate solutions (McCullough and Hatfield, 1972). In this study of the five-component system containing ammonia, zinc, and ortho- and pyrophosphate, compositions were determined for the invariant-point solutions with which three ammonium phosphates and one zinc ammonium phosphate or two ammonium phosphates and two zinc ammonium phosphates were in equilibrium. A few compositions on tie lines between these invariant points were determined also.

MATERIALS AND PROCEDURE

The equilibrium mixtures were prepared by dissolving reagent $\text{NH}_4\text{H}_2\text{PO}_4$, ZnO, and NH_4OH and recrystallized $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ in H_2O to form solutions to which the desired saturating solid phases were charged until an excess was present in euhedral crystalline form. The zinc reagents used in this study were ZnNH_4PO_4 , $\text{Zn}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$, and $\text{Zn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$; their preparation and characterization were reported previously (Frazier *et al.*, 1965, 1966). When the quasi-equilibrium condition was established, the mixtures were rotated in a water bath at $25.0 \pm 0.1^\circ$ for 4 weeks to attain true equilibrium after which the liquid phases were sampled for analysis and the solids were re-examined microscopically to be sure that the desired solid phases were still present at the end of the equilibration period. The results are shown in Table I.

A new dimorph of $\text{Zn}(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot \text{H}_2\text{O}$ (form II) was prepared at pH 4.7-4.8 in pure form suitable for chemical analysis and crystallographic characterization; typical compositions are shown in Table II. The X-ray powder diffraction data for the new dimorph are shown in Table III, and its characteristic infrared absorption bands are shown in Table IV. The new dimorph,

$\text{Zn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O-II}$, crystallizes as small monoclinic prisms, class $2/m$; they often display a tabular habit (100 or 001) that makes them similar in appearance to $(\text{NH}_4)_2\text{HPO}_4$. Optically, the crystals are biaxial (-), with $2V = 78^\circ$ (calcd) and refractive indices $N_\alpha = 1.526$, $N_\beta = 1.532$, and $N_\gamma = 1.536$. The $OAP = 010$, with $Y = b$, but the habit and small size of the crystals prevented accurate determination of the extinction positions on 010. The new dimorph has a calculated density of 2.18 g/cm^3 , and, like form I, is insoluble in water.

ZINC BEHAVIOR IN FERTILIZER SOLUTIONS

Ammonium polyphosphate liquid fertilizers usually are not saturated solutions at room temperature, and they also vary in pH and polyphosphate content. Hence, the solubilities of zinc in fertilizer solutions may differ from those determined under conditions of equilibrium in saturated solutions.

To obtain data more closely related to conditions in commercial fertilizer practice, ammonium polyphosphate solutions were prepared with grades (% N-% P_2O_5 -% K_2O) roughly in the range 10-34-0 to 11-37-0, and these solutions, with different pH values and different proportions of ortho- and pyrophosphates, were saturated with ZnO. The compositions of the final solutions and the corresponding precipitated solid phases are shown in Table V and plotted in Figure 1.

In preparing liquid fertilizers containing zinc, it has been common practice to add 4% Zn as ZnO to solid ammonium polyphosphate with a grade of about 15-60-0. On dissolution and further ammoniation to form a 10-34-0 solution, the solution should ideally contain 2.3% Zn (2.8% ZnO). If the stored solid absorbs moisture, however, the ZnO reacts with the solid ammonium polyphosphate, which is a mixture of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_3\text{HP}_2\text{O}_7$. The solid zinc salt on the surface will then be ZnNH_4PO_4 and $\text{Zn}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ if the pH is below 4.8 and $\text{Zn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O-I}$ if the pH is between 4.8 and 5.9. Dimorph $\text{Zn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O-II}$ has not been observed as a solid phase on the zinc-treated solid ammonium polyphosphates. When these salts are dissolved to prepare ammonium polyphosphate liquid fertilizers, the amount of zinc in solution after a reasonable mixing time is determined by the rate of solution and solubility of these newly formed zinc reaction products rather than by the solubility characteristics of ZnO.

To measure these rates, liquid mixtures that had pH 6.0 and grade 10-34-0-2ZnO, and in which 30% of the P_2O_5 was present as pyrophosphate, were prepared from $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_3\text{HP}_2\text{O}_7$, H_2O , NH_4OH , and either ZnNH_4PO_4 , $\text{Zn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$, or $\text{Zn}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ as the source of zinc. A similar set of mixtures was prepared in which 50% of the P_2O_5 was present as pyrophosphate, and all the mixtures were allowed to stand at room temperature ($25\text{-}27^\circ$). The mixtures prepared with $\text{Zn}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ formed clear solutions within 4 hr, and to each of the six mixtures there was added an additional amount of the respective zinc salt to double the zinc content to 4% ZnO. The mixtures then

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Table I. The System NH₃-ZnO-H₃PO₄-H₄P₂O₇-H₂O at 25°

Letter	pH	Compn of liquid phase, wt %					Pyro P ₂ O ₅ , % of total P ₂ O ₅	Equil. solid phase ^a
		(NH ₄) ₂ O	ZnO	P ₂ O ₅				
				Total	Pyro			
A	3.8	13.4	0.22	34.1	23.4	69	N ₂ P ₂ , NP, Zn ₃ N ₂ P ₄	
	4.1	15.9	0.40	37.0	26.6	72	N ₂ P ₂ , NP, Zn ₃ N ₂ P ₄	
	4.4	16.8	0.55	38.1	27.7	73	N ₂ P ₂ , NP, Zn ₃ N ₂ P ₄	
	4.5	17.2	0.60	38.7	28.4	73	N ₂ P ₂ , NP, Zn ₃ N ₂ P ₄	
B	4.7	19.4	1.1	41.4	31.2	75	N ₂ P ₂ , NP, Zn ₃ N ₂ P ₄ , ZnN ₂ P ₂ -II	
C	4.8	20.0	1.2	42.2	32.3	76	N ₂ P ₂ , NP, ZnN ₂ P ₂ -II, ZnN ₂ P ₂ -I	
D	4.9	20.5	0.82	42.3	31.9	75	N ₂ P ₂ , N ₃ P ₂ , NP, ZnN ₂ P ₂ -I	
	5.5	21.9	1.1	41.7	25.9	62	N ₃ P ₂ , NP, ZnN ₂ P ₂ -I	
E	5.8	22.5	1.3	41.7	23.2	56	N ₃ P ₂ , NP, N ₂ P, ZnN ₂ P ₂ -I	
F	5.9	22.6	2.4	41.0	25.6	62	N ₃ P ₂ , N ₂ P, ZnN ₂ P ₂ -I, ZnN ₆ P ₄	
	6.0	22.7	2.0	40.6	25.6	63	N ₃ P ₂ , N ₂ P, ZnN ₆ P ₄	
G	6.1	22.6	1.4	39.9	26.1	65	N ₃ P ₂ , N ₄ P ₂ , N ₂ P, ZnN ₆ P ₄	
	6.4	21.9	1.9	36.9	23.2	63	N ₄ P ₂ , N ₂ P, ZnN ₆ P ₄	
	7.0	21.0	2.4	33.3	20.5	62	N ₄ P ₂ , N ₂ P, ZnN ₆ P ₄	
H	7.4	20.5	2.6	31.8	19.0	60	N ₄ P ₂ , N ₂ P, ZnN ₆ P ₄ , ZnNP	
	7.9	20.1	1.0	28.7	14.9	52	N ₄ P ₂ , N ₂ P, ZnNP	
I	8.6	20.0	0.9	27.2	13.3	49	N ₄ P ₂ , N ₂ P, N ₃ P, ZnNP	
J	8.9	18.7	1.7	25.3	16.5	65	N ₄ P ₂ , N ₃ P, ZnNP	

^a NP = NH₄H₂PO₄, N₂P = (NH₄)₂HPO₄, N₃P = (NH₄)₃PO₄·3H₂O, N₂P₂ = (NH₄)₂H₂P₂O₇, N₃P₂ = (NH₄)₃HP₂O₇·H₂O, N₄P₂ = (NH₄)₄P₂O₇, ZnN₂P₂-I = Zn(NH₄)₂P₂O₇·H₂O-I, ZnN₂P₂-II = Zn(NH₄)₂P₂O₇·H₂O-II, Zn₃N₂P₄ = Zn₃(NH₄)₂(P₂O₇)₂·2H₂O, ZnN₆P₄ = Zn(NH₄)₆(P₂O₇)₂·6H₂O.

Table II. Preparations of Zn(NH₄)₂P₂O₇·H₂O-II

No.	Composition, %				mol/mol of P ₂ O ₅		
	ZnO	(NH ₄) ₂ O	P ₂ O ₅	H ₂ O (diff.)	ZnO	(NH ₄) ₂ O	H ₂ O
XR1768	27.7	17.3	47.9	7.1	1.01	0.99	1.17
XR1798	28.8	17.1	47.7	6.4	1.06	0.98	1.06
Stoichio- metric	27.74	17.72	48.39	6.13	1.00	1.00	1.00

were allowed to stand at room temperature with daily shaking for 30 days, after which the zinc contents of the clear supernatant solutions were determined. The results are shown in Table VI.

DISCUSSION OF RESULTS

The equilibrium data for the system NH₃-ZnO-H₃PO₄-H₄P₂O₇-H₂O in Table I are plotted in Figure 2 with data from Table V to show the fields of stability of the five zinc ammonium phosphates. Although the ratio of ortho- to pyrophosphate in the unsaturated solutions (Table V) varied considerably, the boundaries of the regions of the important zinc salts were fairly definitely fixed. One trend observed was that with an increase in the proportion of orthophosphate the invariant point X (Figure 2), at which ZnNH₄PO₄, Zn(NH₄)₆(P₂O₇)₂·6H₂O, and Zn(NH₄)₂P₂O₇·H₂O-I are in equilibrium, moves toward the point F. This movement enlarges the region of stability of ZnNH₄PO₄.

The data in Table I are plotted in Figure 3 to show the relation between pH and the solubility of zinc in concentrated ammonium polyphosphate solutions. In addition to the general increase in solubility with a rise in pH from 3.8 to 7.4, there are abrupt increases in solubility at pH 4.7 where the equilibrium solid phases contain two zinc salts—Zn₃(NH₄)₂(P₂O₇)₂·2H₂O and Zn(NH₄)₂-P₂O₇·H₂O—and at pH 5.9 where the solid phases

Table III. X-Ray Powder Diffraction Data^a for Zn(NH₄)₂P₂O₇·H₂O-II

<i>d</i> , Å	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀
9.12	8	2.97	18	1.987	9
7.81	100	2.92	49	1.957	5
6.98	97	2.78	6	1.951	4
6.67	18	2.70	2	1.922	7
5.86	17	2.67	1	1.907	4
5.36	3	2.61	44	1.892	5
5.12	6	2.56	18	1.872	7
5.01	2	2.55	15	1.817	7
4.74	33	2.50	5	1.791	7
4.62	3	2.48	5	1.774	3
4.12	9	2.45	1	1.762	2
3.99	2	2.422	4	1.716	3
3.91	10	2.404	5	1.698	5
3.84	16	2.375	2	1.678	4
3.75	28	2.327	7	1.642	6
3.62	10	2.315	6	1.637	5
3.48	15	2.288	5	1.616	4
3.37	10	2.268	3	1.606	4
3.33	36	2.221	3	1.580	3
3.29	56	2.140	5	1.506	6
3.26	33	2.094	2	1.451	3
3.23	28	2.035	15	1.427	5
3.14	16	2.006	4	1.403	4
3.00	26				

^a Sample side loaded, with spinel as internal standard. Data obtained with X-ray diffractometer with Cu K_α radiation, λ = 1.54178 Å. Intensities measured as peak heights above background and expressed as per cent of strongest line.

also include two zinc salts—Zn(NH₄)₂P₂O₇·H₂O and Zn(NH₄)₆(P₂O₇)₂·6H₂O. Most liquid fertilizers have a pH near 6, so that the abrupt changes in solubility of zinc in the short pH range 5.8–6.1 go far toward explaining the large variations in zinc solubilities that have been

Table IV. Infrared Absorption Spectrum of Zn(NH₄)₂P₂O₇·H₂O-II

cm ⁻¹	I ^a	cm ⁻¹	I ^a	cm ⁻¹	I ^a
3375	m	1457	m	730	w
3205	m	1399	m	674	w
3150	sh	1145	s	602	w
2970	m	1064	s	584	m
2830	m	1022	s	544	m
1675	w	1000	m	525	sh
1649	w	927	s	494	m
1476	m	910	s		

^a s = strong, m = medium, w = weak, sh = shoulder.

reported by commercial formulators of liquid fertilizers. The low zinc content at point I in Figure 3, which is the invariant point at which ZnNH₄PO₄, (NH₄)₄P₂O₇, (NH₄)₂HPO₄, and (NH₄)₃PO₄·3H₂O are in equilibrium, was unexpected; it does not conform with the generally

accepted idea that the solubility of zinc increases with a rise in pH above 7.0, supposedly because of the formation of soluble zinc ammine complexes. This region is not of interest in fertilizer technology and was not explored.

As shown in Figure 1, the equilibrium concentration of zinc in simulated ammonium polyphosphate liquid fertilizers increases irregularly from 0.7% ZnO at pH 5 to 2.7% ZnO at pH 6.11 and, as shown in Figure 3, the solubility of zinc in the equilibrium five-component system increases as the number of saturating zinc salts increases. For example, in solutions with which two zinc salts and two ammonium phosphates are in equilibrium (points B, C, F, and H) the concentration of dissolved zinc is almost twice that in solutions with which one zinc salt and three ammonium phosphates are in equilibrium (points D, E, G, and I).

Thus, for liquid fertilizer compositions, the invariant-point solution with a pH near 6.11 (Table V, Figure 1), in which 56% of the P₂O₅ is present as pyrophosphate and with which three zinc salts and one ammonium phosphate are in equilibrium, should contain somewhat more than

Table V. Solubility of Zinc in Simulated Ammonium Polyphosphate Liquid Fertilizers

pH	Compn of liquid phase, wt %					Pyro P ₂ O ₅ , % of total P ₂ O ₅	Equil. solid phase ^a
	(NH ₄) ₂ O	ZnO	P ₂ O ₅				
			Total	Pyro			
4.8	17.5	0.8	38.0	12.1	32	NP, Zn ₃ N ₂ P ₄ , ZnN ₂ P ₂	
5.0	16.0	0.7	32.8	15.1	46	NP, ZnN ₂ P ₂	
	16.8	0.9	34.5	18.0	52	NP, ZnN ₂ P ₂	
	17.8	0.9	36.6	21.3	58	NP, ZnN ₂ P ₂	
	19.9	0.9	40.8	27.5	67	NP, ZnN ₂ P ₂	
	19.7	0.9	40.5	31.4	78	ZnN ₂ P ₂	
5.23	16.2	1.3	32.9	12.1	37	ZnNP	
5.4	17.8	2.1	34.9	14.5	42	NP, ZnNP, ZnN ₂ P ₂	
	18.6	1.2	36.1	16.0	46	NP, ZnN ₂ P ₂	
	19.4	1.2	37.7	20.6	55	ZnN ₂ P ₂	
	19.6	1.1	38.2	26.1	68	ZnN ₂ P ₂	
	20.0	1.0	39.0	29.5	76	ZnN ₂ P ₂	
5.56	20.0	1.9	38.0	18.1	48	NP, ZnNP, ZnN ₂ P ₂	
5.7	19.5	1.8	36.5	15.9	44	ZnNP	
	21.1	1.3	39.4	24.1	61	ZnN ₂ P ₂	
	19.7	1.4	36.8	24.0	65	ZnN ₂ P ₂	
5.78	21.4	1.4	42.8	23.7	55	ZnN ₂ P ₂	
5.97	18.6	1.3	33.3	12.2	37	ZnNP	
6.0	20.4	1.6	36.6	15.5	43	N ₂ P, ZnNP	
	21.9	2.1	39.3	22.4	57	ZnN ₂ P ₂	
	20.7	2.1	37.2	24.7	66	ZnN ₂ P ₂ , ZnN ₆ P ₄	
	21.7	1.6	38.9	29.6	76	N ₃ P ₂ , ZnN ₂ P ₂ , ZnN ₆ P ₄	
	21.8	2.7	38.5	21.3	56	ZnNP, ZnN ₆ P ₄	
6.11	21.8	2.7	38.5	21.3	56	ZnNP, ZnN ₆ P ₄	
6.3	22.2	1.4	38.2	25.8	68	N ₄ P ₂ , ZnN ₆ P ₄	
6.35	20.3	2.8	34.1	18.8	55	ZnNP, ZnN ₆ P ₄	
6.36	19.7	1.3	33.0	12.2	37	ZnNP	
6.45	19.7	2.0	32.9	15.3	46	ZnNP	
6.50	19.9	1.3	32.7	15.7	48	N ₂ P, ZnNP	
6.57	21.4	2.3	35.7	21.1	59	ZnNP, ZnN ₆ P ₄	
6.6	20.9	2.7	34.9	19.0	55	N ₂ P, ZnNP	
	21.6	1.6	36.0	23.4	65	N ₄ P ₂ , ZnN ₆ P ₄	
	19.9	1.8	33.1	24.6	74	N ₄ P ₂ , ZnN ₆ P ₄	
7.0	19.8	1.7	30.5	15.3	50	N ₂ P, ZnNP	
	20.2	2.0	33.6	21.5	64	N ₄ P ₂ , ZnN ₆ P ₄	
7.2	19.7	2.0	30.5	16.7	55	N ₂ P, ZnNP	
7.4	20.5	2.6	31.8	19.0	60	N ₄ P ₂ , N ₂ P, ZnNP, ZnN ₆ P ₄	
7.5	19.8	1.3	29.4	15.1	51	N ₂ P, ZnNP	
7.9	20.1	1.0	28.7	14.9	52	N ₄ P ₂ , N ₂ P, ZnNP	

^a NP = NH₄H₂PO₄, N₂P = (NH₄)₂HPO₄, N₃P₂ = (NH₄)₃HP₂O₇, N₄P₂ = (NH₄)₄P₂O₇, ZnNP = ZnNH₄PO₄, Zn₃N₂P₄ = Zn₃(NH₄)₂(P₂O₇)₂·2H₂O, ZnN₂P₂ = Zn(NH₄)₂P₂O₇·H₂O, ZnN₆P₄ = Zn(NH₄)₆(P₂O₇)₂·6H₂O.

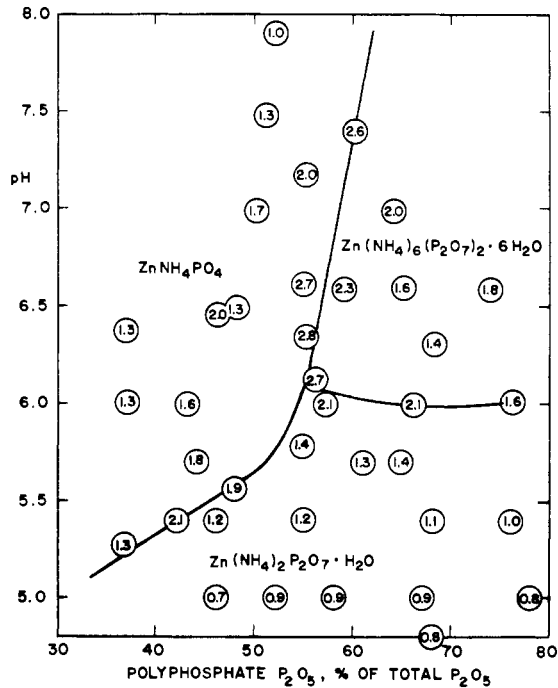


Figure 1. Equilibrium zinc contents and solid phases of zinc-containing simulated ammonium polyphosphate liquid fertilizers. Numbers in circles denote ZnO content, per cent.

Table VI. Dissolution of Zinc Phosphates in 10-34-0 Ammonium Polyphosphate Solutions with pH 6 at 25°

Pyro P ₂ O ₅ , % of total P ₂ O ₅	Zinc phosphate added ^a	ZnO, %, in final soln ^b
30	ZnNH ₄ PO ₄	0.50
	Zn(NH ₄) ₂ P ₂ O ₇ ·H ₂ O	0.66
	Zn ₃ (NH ₄) ₂ (P ₂ O ₇) ₂ ·2H ₂ O	2.4
50	ZnNH ₄ PO ₄	0.86
	Zn(NH ₄) ₂ P ₂ O ₇ ·H ₂ O	0.62
	Zn ₃ (NH ₄) ₂ (P ₂ O ₇) ₂ ·2H ₂ O	2.3

^a In amount to supply 4.0% ZnO. ^b After standing for 30 days with daily manual shaking.

2.7% dissolved ZnO. This high concentration of zinc can be maintained, however, only with very close control of the solution composition, so that a lower concentration of dissolved zinc, probably 1.5% ZnO, appears to be a practicable maximum for ammonium polyphosphate liquid fertilizers.

The data in Figure 3 show that 1.5% ZnO is a safe level that will not cause precipitation above pH 5.9 and should be easily solubilized at the higher pH (about 6.3) and temperature (120-150°F) where most liquids are produced. Likewise, Figure 1 shows that at pH 6, a concentration of 1.5% ZnO will be stable down to 35% polyphosphate and possibly lower since most 10-34-0 liquids will have already become saturated with (NH₄)₂HPO₄ at this polyphosphate level (see pH 6.0, Table V).

The results (Table VI) of the equilibration tests simulating the dissolution of solid ammonium polyphosphate fertilizers showed that Zn(NH₄)₂P₂O₇·H₂O and ZnNH₄PO₄ dissolve very slowly and will not produce the equilibrium solubility of zinc in 30 days at room temperature. The data in Table V show that at pH 6.0 the minimum equilibrium solubility of zinc in ammonium polyphosphate fertilizer solutions is 1.6% ZnO. Thus, Zn(NH₄)₂P₂O₇·H₂O is an undesirable reaction product

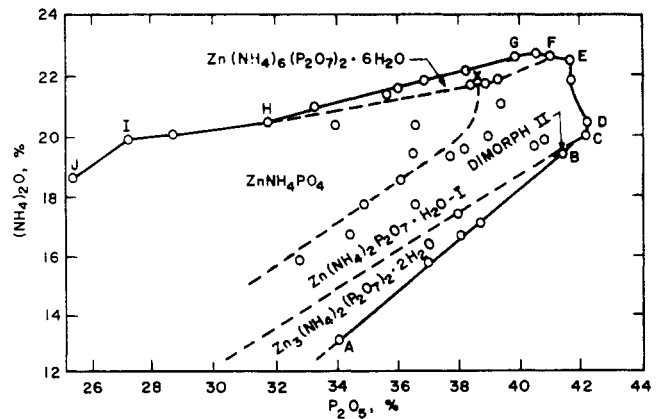


Figure 2. The system NH₃-ZnO-H₃PO₄-H₄P₂O₇-H₂O at 25° projected on the (NH₄)₂O-P₂O₅-H₂O face: A-B = N₂P₂ + NP + Zn₃N₂P₄; B-C = N₂P₂ + NP + ZnN₂P₂-II; C-D = N₂P₂ + NP + ZnN₂P₂-I; D-E = N₃P₂ + NP + ZnN₂P₂-I; E-F = N₃P₂ + N₂P + ZnN₂P₂-I; F-G = N₃P₂ + N₂P + ZnN₆P₄; G-H = N₄P₂ + N₂P + ZnN₆P₄; H-I = N₄P₂ + N₂P + ZnNP; I-J = N₄P₂ + N₃P + ZnNP. The designation of compounds is the same as in Table I.

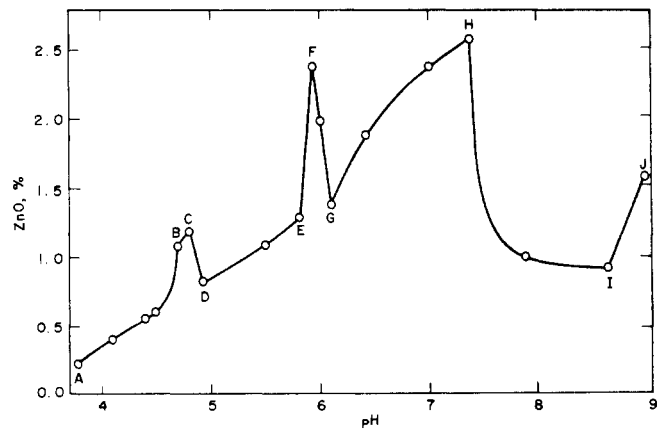


Figure 3. Effect of pH on the solubility of zinc in ammonium ortho- and pyrophosphate solutions. Letters on points are the same as those in Figure 2 and Table I.

when ZnO is added to solid ammonium polyphosphate that is to be used in the preparation of liquid fertilizers, and the presence of this salt as a solid phase in freshly prepared liquid fertilizers does not necessarily indicate that the solution is saturated with zinc. This conclusion is supported by the data in Figure 2 which indicate that the saturating zinc salt in 10-34-0 [18.5% (NH₄)₂O] and 11-37-0 [20.4% (NH₄)₂O] solutions is ZnNH₄PO₄.

In exploratory tests of the effect of fluorine on the solubility of zinc, ammonium fluoride was added to the invariant-point solutions D, E, and F (Table II, Figure 3) to provide a concentration of 1% F. The fluorine decreased the solubility of zinc slightly, showing that fluorine does not sequester zinc as it does magnesium and aluminum (Frazier *et al.*, 1972).

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COMMUNICATIONS

Improved Determination of Residues of Phorate and Its Principal Metabolites

Improvements in methodology for the determination of residues of phorate and its three principal metabolites are described. These refinements include chilling the sample during extraction to

prevent emulsion formation, using a microcolumn cleanup procedure resulting in economy of time and materials, and evaporating under nitrogen to preclude oxidation of phorate.

Problems were encountered in applying the method of Suett (1971) to the analysis of field-treated carrots for determining residues of phorate (*O,O*-diethyl *S*-[(ethylthio)methyl] phosphorodithioate) and three of its metabolites. The modifications described here considerably reduce the time needed for analysis, save materials, and prevent oxidation of the labile phorate.

EXPERIMENTAL SECTION

Apparatus. A Sorval Omni-Mixer with a 400-ml sample cup was used for sample extraction. Two gc columns were required: a 6 ft × 0.25 in. o.d. glass column packed with 3% OV-17 on 60–80 mesh Gas-Chrom Q for analysis of phorate and phorate oxygen analog (POA), and a 3 ft × 2 mm i.d. column containing 2.5% XE-60 on 60–80 mesh Gas-Chrom Q for analysis of phorate sulfoxide (PSO) and phorate sulfone (PSO₂) (Saunders and Getzin, 1973). The detector temperature was 200°; column oven temperatures were 195° for the OV-17 and 190° for the XE-60 column. The flow of nitrogen carrier gas was 90 ml/min; hydrogen, 200 ml/min; and air and oxygen, each 20 ml/min.

Reagents. Analytical standards of phorate, POA, PSO, and PSO₂ were supplied by American Cyanamid Co., Princeton, N.J. Nuchar C (Fisher Scientific) was acid washed by refluxing 100 g of charcoal with 500 ml of concentrated HCl for 1 hr, adding 500 ml of distilled water, and again refluxing 1 hr, cooling, and washing with distilled water until neutral to indicator tape. The charcoal was then transferred to a glass jar and heated overnight at 130°. Silane-treated glass wool (Applied Science Lab., Inc.) and Whatman CF11 cellulose powder were used in the microcolumn cleanup.

Procedure. A 50-g sample of shredded whole carrot, with 40 g of anhydrous Na₂SO₄ and 100 ml of chloroform-methanol (9:1, v/v), was blended for 3 min in the Omni-Mixer with the sample cup immersed in an ice water bath. The extract was filtered through a 150-ml Büchner funnel lined with glass fiber paper and fitted to a 250-ml graduated cylinder (Williams and Brown, 1973). The extraction was repeated twice with additional 50-ml portions of chloroform-methanol, and the extracts were pooled.

Ten per cent of the combined extracts, representing 5 g of carrot, was transferred to a 50-ml beaker and evaporated under a stream of nitrogen to about 0.5 ml. A cleanup column was prepared by plugging a Pasteur pipet with a small wad of silane-treated glass wool and adding a 4–5 cm layer of Nuchar C-Whatman CF11 cellulose powder (4:10, w/w). The packing was topped with a smaller plug of glass wool and prewashed with approximately 1 ml of

ethyl acetate. The concentrated extract was dissolved in 1 ml of ethyl acetate and transferred to the cleanup column using a Pasteur pipet. As the last of the sample entered the column packing, a total of 5 ml of ethyl acetate was added to strip the column of pesticide. All solvent which eluted after the prewash was collected in a concentrating tube and again evaporated to 0.5 ml under a stream of nitrogen. Each sample was chromatographed twice using a flame photometric detector in the phosphorus mode, first on the OV-17 column to determine phorate and POA and later on the XE-60 column for PSO and PSO₂.

RESULTS AND DISCUSSION

Recoveries from carrots untreated but fortified are shown in Table I. One of the earliest problems was to find a suitable gc column. Grant *et al.* (1969) reported direct determination of phorate and its metabolites including the oxygen analog sulfoxide and sulfone using a 5% DEGS column. However, we were unable to chromatograph these two oxygen analog metabolites even at the 1-μg level. Nor did we achieve satisfactory separation of phorate from POA or PSO from PSO₂, despite variations of column length and support loading. Such disparity of results may be partially explained by the work of Kruppa and Henly (1974). They found that, with conditioning, the DEGS in each column formed a distinct superpolyester and that conditioning was accompanied by severe bleeding of the liquid phase. Thus, each DEGS column was unique and its performance unpredictable. No one column was found which satisfactorily separated all four compounds. The

Table I. Recovery of Phorate and Three Metabolites from Untreated, Fortified Carrots^a

Fortifi- cation, ppm	Percentage recovery			
	Phorate	POA	PSO	PSO ₂
0.1	90.5	85.3	107.5	81.5
	88.9	91.3	80.0	88.6
	95.1 (91.5)	79.7 (85.4)	87.2 (91.6)	109.6 (93.3)
0.5	86.0	86.5	77.6	85.6
	1.0	92.9	90.1	83.1
		99.1 (96.0)	103.7 (96.9)	97.0 (90.1)

^a Average values are in parentheses.