

Table II. Comparison to Published Values of Infant Foods by Category

Food	No. of samples	This paper		Kamm et al. (1965)		
		Nitrate nitrogen, ppm		No. of samples	Nitrate nitrogen, ppm	
		Range	Av			Range
Fruits	10	4-13	8	22	0-7	2
Desserts	5	3-6	5			
Puddings	2	7-10	9	5	0.8-11	4
Cereals	4	8-12	10	22	0.4-48	13
Egg products + custards	4	5-17	11	13	0.9-11	4
Dairy products	1		8	9	0-7	3
Meats	7	8-11	10	15	1-11	4
Meat dinners	10	8-14	10	20	0.9-16	7
Vegetables	10	12-483	97	61	0.2-492	68

Table III. Comparison to Published Values of Infant Foods over 20 ppm Nitrate Nitrogen

Food	This paper, nitrate nitrogen, ppm	No. of samples	Kamm et al. (1965) nitrate nitrogen, ppm	
			Range	Av
Green beans	41	3	16-71	37
Garden vegetables	51	5	19-62	41
Spinach	117	5	244-379	312
Squash	215	5	10-93	64
Beets	483	6	144-492	222
Mixed vegetables	(12)	2	21-24	22
Carrots	(15)	8	15-38	23
Graham crackers	Not tested	1		48
Wax beans	Not tested	2	73-129	101

(different lot numbers) were found to contain 41 and 80 ppm of nitrate nitrogen. This could be caused by a difference either in the amount of water added or the nitrate content of the beans themselves. While the cause of the difference is of interest, the real concern is with the nitrate nitrogen content of the food as it is consumed. It is the authors' experience that most baby food is consumed directly from the jar.

Vegetables are generally found to be highest in nitrate nitrogen. A survey of nitrate content of vegetables by Boswell et al. (1967) also showed fairly high values for some of the same vegetables reported here. Boswell et al. also note that the nitrate content of vegetables is influenced by such factors as plant variety, maturity at harvest, climate, geography, and fertilization. These factors could account for the large differences found in different samples of the same vegetable.

Since the development of this method, another method using the nitrate electrode has come to the attention of the authors. The method of Milham et al. (1970) employs a buffer to eliminate interferences and would appear to also be adaptable for a rapid-screening method for baby food.

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Preparation and Characterization of Some Long-Chain Ammonium Polyphosphates

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The preparation and characterization of four polymorphic forms of long-chain ammonium polyphosphates and an ammonium hydrogen polyphosphate are described. Single-crystal data are given for three of the polymorphs and for the new ammonium hydrogen polyphosphate salt.

Although crystalline long-chain ammonium polyphosphates are not produced as fertilizers, their high nutrient content and apparent complete availability as plant food make them interesting as potential fertilizer materials. Their reactions with the soils need further study.

The crystalline long-chain ammonium polyphosphates are similar in many respects to the well-known sodium and potassium Kurrol's salts. Thilo and Dostál (1959) showed that compounds with the general composition ABX_3 tend

to exist in several polymorphic forms. Both the ammonium and alkali metal long-chain polyphosphates belong to this group and occur in several polymorphic modifications. Most of the earlier work was with the alkali metal polyphosphates. Four temperature-dependent polymorphs of KPO_3 (Von Jost and Schulze, 1971) and three forms of $NaPO_3$ (Inorganic Index to the Powder Diffraction File, 1972) are known to exist. Structural analysis of these and a series of other polyphosphates with metaphosphate composition have shown that the polyphosphate anion consists of interconnected PO_4 tetrahedra forming "infinite" linear polyphosphate chains. Altogether, six different structural arrangements of the polyphosphate chains have been determined (Thilo, 1965).

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Table I. X-ray Powder Diffraction Patterns of CAPP^a

Form I				Form II				Form V				Form VI	
d_{obsd}	d_{calcd}	I/I_0	hkl	d_{obsd}	d_{calcd}	I/I_0	hkl	d_{obsd}	d_{calcd}	I/I_0	hkl	d_{obsd}	I/I_0
6.89	6.873	9	210	6.02	6.020	55	020	6.86	6.856	54	020	6.62	100
6.03	6.019	100	220	5.70	5.699	100	110	5.61	5.596	100	110	5.60	85
5.41	5.398	69	040	4.39	4.407	8	120	3.67	3.664	60	130	5.36	89
4.37	4.367	2	101	3.99	3.999	12	011	3.43	3.430	75	111	4.328	9
3.81	3.811	48	211	3.47	3.466	6	021		3.428		040	3.988	20
3.73	3.734	3	131	3.40	3.402	37	111	3.06	3.065	11	200	3.762	67
3.58	3.575	14	410	3.225	3.235	19	200	2.805	2.800	15	131	3.685	2
3.495	3.492	45	041	3.110	3.124	3	210	2.793	2.798	9	220	3.655	15
3.425	3.436	24	420	3.050	3.056	45	121	2.688	2.690	19	041	3.534	14
3.315	3.325	4	301	3.003	3.010	2	040	2.356	2.352	13	221	3.474	91
3.238	3.237	32	430	2.912	2.915	25	031	2.284	2.285	2	061	3.296	12
3.10	3.071	5	151	2.729	2.729	7	140		2.285		240	3.220	11
2.888	2.883	9	251	2.515	2.519	11	230	2.171	2.170	3	002	3.175	18
2.823	2.830	10	061		2.515		211	2.136	2.143	4	012	3.141	6
	2.818		411	2.450	2.454	14	041		2.141		160	3.003	14
2.780	2.777	3	161	2.362	2.365	12	221	2.080	2.069	2	022	2.853	13
2.750	2.749	14	421	2.292	2.295	3	141	2.023	2.023	3	112	2.826	6
2.644	2.644	15	431	2.094	2.094	8	051	1.871	1.867	5	132	2.808	5
2.536	2.554	3	460		2.088		012	1.83	1.833	1	042	2.748	19
	2.515		441	2.018	2.015	5	102		1.832		311	2.681	17
2.418	2.417	12	600	1.992	1.992	2	151	1.719	1.715	2	222	2.662	7
2.353	2.358	4	620	1.916	1.917	1	160		1.714		331	2.501	9
2.291	2.291	29	630		1.910		122	1.698	1.689	2	261	2.476	8
	2.290		002	1.899	1.900	3	330	1.638	1.638	1	350	2.386	10
2.238	2.240	5	022		1.898		311	1.417	1.415	3	332	2.354	7
	2.231		541	1.830	1.831	3	321		1.415		332	2.286	41
2.141	2.140	7	222	1.755	1.758		251					2.194	3
	2.134		601		1.754	3	212					2.162	4
2.108	2.109	3	650		1.753		340					2.115	2
	2.108		042	1.707	1.705	1	260					1.946	2
1.906	1.906	3	422	1.678	1.674	1	142					1.834	2
1.867	1.867	2	262	1.623	1.622	2	232					1.654	3
	1.866		352		1.620		341					1.441	3
1.526	1.527	1	003	1.549	1.545	1	152						
				1.503	1.502	1	351						
				1.467	1.469	2	360						
					1.466		322						
				1.429	1.428	1	252						
				1.351	1.351	1	342						
					1.351		441						

^a Cu K α radiation, $\lambda = 1.54178$ Å, d spacings observed from diffractometer tracing. Intensities measured as peak heights above background and expressed as percent of strongest line.

The existence of a water-insoluble ammonium polyphosphate of high molecular weight was first described by Tammann (1892) who erroneously named the salt ammonium decametaphosphate. Frazier et al. (1965) isolated a crystalline long-chain ammonium polyphosphate (CAPP) from ammoniated superphosphoric acid and published its x-ray powder diffraction pattern. The existence of several polymorphic forms of CAPP was first pointed out by Shen et al. (1969) who described methods of preparation of the different forms.

EXPERIMENTAL SECTION

Methods. All chemicals for the study were reagent grade and were used without further purification. The samples characterized by x-ray and petrographic examinations were shown to consist of only one phase before chemical analysis. Phosphorus was determined gravimetrically as the quinolinium molybdophosphate and nitrogen by distillation of ammonia from a sodium hydroxide solution (AOAC, 1970).

The x-ray powder diffraction patterns were recorded on a Philips diffractometer with a proportional counter and Ni-filtered Cu K α radiation ($\lambda = 1.5478$ Å). Unit-cell and space-group data were determined from both precession and Weissenberg photographs. The densities of the crystals were measured by flotation in mixtures of acetone and bromoform.

Refractive indices were measured with a polarizing microscope by the immersion method. Estimated standard deviations in refractive indices are ± 0.002 .

Preparation of CAPP. Crystalline long-chain ammonium polyphosphates were prepared by the method of McCullough and Sheridan (1972) from a series of less condensed ammonium phosphates by thermal dehydration in an atmosphere of ammonia. The process is simple and straightforward and appears to be associated with a gradual loss of water. The starting material can be ortho-, pyro-, tripoly-, or higher polyphosphate-containing reagents.

Portions of the less condensed phosphates were heated in a tube furnace in an atmosphere of anhydrous ammonia. Temperatures were measured by a thermocouple inside the tube.

Preparation of CAPP by this method appears to be associated with the initial formation of an amorphous phase which slowly converts into crystalline CAPP salts upon continued heating. This amorphous material is assumed to consist of mixtures of polyphosphates with intermediate chain lengths, whereas the chain length in the well-crystallized salts is thought to approach infinity.

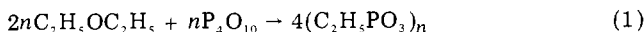
The mechanism of the dehydration process thus seems to be that of a gradual buildup in the concentration of polyphosphates with intermediate chain lengths which will polymerize into extremely long chains as more water is

removed during continued heating.

The rate of dehydration below 200 °C is extremely slow, and the products prepared at those temperatures always contain considerable amounts of amorphous material. The process becomes appreciably faster at higher temperatures; however, the last traces of water are difficult to remove and the products often contain a small amount of the amorphous phase.

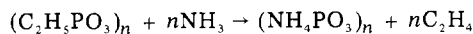
To study the different polymorphic forms of CAPP free from this amorphous material, the following method of preparation was developed.

Reagent P₄O₁₀ was treated with ethyl ether to form the ethyl ester of metaphosphoric acid (Thilo and Woggon, 1954). The overall equation for this reaction may be expressed as:



The ester is prepared by boiling 2 mol of the ether with 1 mol of P₄O₁₀ under reflux for 2 h.

The ester is an oily substance which reacts quantitatively with anhydrous ammonia at temperatures above 150 °C, according to eq 2.



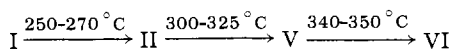
The reaction was carried out by heating the ester in a tube furnace in a flowing atmosphere of anhydrous ammonia. (The gas given off by the reaction (Thilo and Dostal, 1959) burned with an intense light color which is characteristic of burning ethylene gas.)

PHASE TRANSITIONS AMONG CAPP POLYMORPHS

When crystalline long-chain ammonium polyphosphates are prepared as described here, the product will usually contain mixtures of various polymorphic forms. However, it was found that the individual forms could be prepared relatively pure within selected temperature ranges except for form VI which was always associated with small amounts of form V.

The formation of the different modifications is temperature dependent. Lower temperature polymorphs were converted to higher forms by raising the temperature, and the process appeared to be irreversible. All polymorphs were found to be moderately stable and nonhygroscopic when exposed to air at room temperature.

The following phase transformations were observed to take place within the indicated temperature ranges when heating the various forms at 1 atm of ammonia pressure.



These transformations were found to be rather sluggish, and tempering times of up to 20 h sometimes were necessary to convert one form completely to another. This is one reason why such phase changes are difficult to detect by short-term thermal analysis. The x-ray powder diffraction patterns of these four forms of long-chain ammonium polyphosphates are shown in Table I.

CHARACTERIZATION OF CAPP

When CAPP compounds are prepared according to the general procedures described here the crystals are too small for single-crystal x-ray examinations, with the exception of form II. However, it was found that by tempering any of the three forms I, II, or V, or their mixtures in evacuated sealed glass tubes at temperatures between 400 and 450 °C large fibrous crystals could be grown from the melt by slow cooling to room temperature. These crystals were separated from the amorphous phase in which they were embedded by washing with concentrated ammonium hydroxide solution.

Table II. Composition, Crystallographic, and Optical Data of Chain Ammonium Polyphosphates

Form	Emp. form.	Composition, wt % of total				Crystal system	Cell param. (angles), Å (deg)			Space group	No. of form. units in unit cell	Density, g/cm ³ (D _m /D _x)	Refractive indices		
		Exptl	Theor.				a (α)	b (β)	c (γ)				α	β	γ
I	NH ₄ PO ₃	14.2	31.1	14.4	31.9	Orthorhombic	14.50 (90.0)	21.59 (90.0)	4.58 (90.0)	P _{abm} or P _{ab2}	16	1.79/1.797	1.487	1.490	1.498
II	NH ₄ PO ₃	14.1	31.4	14.4	31.9	Orthorhombic	6.47 (90.0)	12.04 (90.0)	4.24 (90.0)	P ₂ , 2 ₁ , 2 ₁	4	1.92/1.952	1.526	1.527	1.536
V	NH ₄ PO ₃	14.1	31.8	14.4	31.9	Orthorhombic	6.13 (90.0)	13.71 (90.0)	4.34 (90.0)	P _{mnb} or P ₂ nb ₂	4	1.79/1.765	1.482	1.490	1.497
	NH ₄ H(PO ₃) ₂	8.0	35.8	7.9	35.0	Triclinic	7.687 (96.6)	15.112 (97.5)	4.845 (83.9)	P ₁ or P ₁	4	2.15/2.126	1.544	1.557	1.566

Table III. X-ray Diffraction Pattern of $\text{NH}_4\text{H}(\text{PO}_3)_2$

d_{obsd}	d_{calcd}	I/I_0	hkl	d_{obsd}	d_{calcd}	I/I_0	hkl
7.58	7.588	100	100	2.698	2.699	1	$\bar{1}\bar{5}0$
6.53	6.529	2	$\bar{1}10$	2.639	2.638	3	221
5.10	5.096	5	$\bar{1}20$	2.532	2.533	<1	310
4.33	4.353	4	130	2.496	2.492	2	060
4.25	4.283	2	$\bar{1}\bar{1}1$	2.356	2.356	2	$\bar{3}01$
	4.226		0 $\bar{2}1$	2.324	2.323	5	012
4.00	4.000	3	$\bar{1}30$	2.306	2.308	4	0 $\bar{6}1$
3.85	3.852	<1	021		2.305		$\bar{1}60$
3.84	3.840	<1	101	2.259	2.259	1	$\bar{2}41$
3.794	3.794	<1	200	2.176	2.176	3	260
3.754	3.752	1	$\bar{1}\bar{1}1$		2.176		$\bar{3}30$
3.690	3.688	1	111	2.125	2.125	3	$\bar{1}61$
3.642	3.639	1	0 $\bar{3}1$	2.064	2.068	3	321
3.601	3.600	1	210	2.038	2.039	2	$\bar{2}51$
3.520	3.516	4	220	2.006	2.011	1	$\bar{3}40$
3.469	3.466	2	1 $\bar{2}1$		2.000		260
3.373	3.368	16	121	1.880	1.880	2	420
3.267	3.266	11	$\bar{2}20$	1.843	1.844	<1	222
3.202	3.237	2	$\bar{1}40$		1.843		421
	3.189		$\bar{2}11$	1.819	1.819	<1	062
3.170	3.163	2	201	1.780	1.780	3	052
3.100	3.101	22	0 $\bar{4}1$	1.719	1.720	1	152
	3.095		$\bar{1}31$	1.695	1.695	1	401
3.063	3.076	1	$\bar{2}21$	1.634	1.634	1	252
	3.040		$\bar{1}31$	1.580	1.581	3	460
2.995	3.008	3	$\bar{2}11$		1.581		461
				1.506	1.506	2	521
2.892	2.893	4	$\bar{2}30$	1.499	1.500	3	501
2.806	2.809	3	041	1.400	1.400	1	412
2.767	2.767	<1	211		1.400		511
2.726	2.727	2	1 $\bar{4}1$	1.391	1.392	1	362

The x-ray powder diffraction pattern of the crystals thus recovered indicated that the material consisted of about equal amounts of forms I and V. Apparently these two forms occur intimately mixed in the fibrous crystals. The presence of two phases with distinctly different unit-cell dimensions was apparent from the single-crystal x-ray diffraction patterns of these fibrous crystals. The powder diffraction patterns of forms I, II, and V were indexed from the unit-cell parameters determined from the single-crystal photographs and are shown in Table I, along with the unindexed pattern for form VI. Compositions and crystallographic and optical data are shown in Table II.

DISCUSSION

The powder diffraction patterns of forms I and II (Table I) agree fairly well with the data reported by Shen et al. (1969). Several lines in the earlier reported pattern of form V cannot be indexed by the single-crystal data. However, by careful examination of the diffraction data, it can be seen that all these lines correspond to rather strong reflections of other polymorphs (including the new form VI). Thus, it appears that the earlier reported pattern of form V includes reflections from other polymorphs. Form III, as reported by Shen et al. (1969), was not encountered in our study. The composition of this intermediate is not known.

Many lines in the powder diffraction pattern of form IV, as reported by Shen et al., are found in the new form VI, and it may be argued that these two patterns represent a difference in the degree of purity rather than an indication of the existence of two different polymorphic forms. However, the presence of two strong reflections at 6.62 and

5.60 Å in the form VI pattern which are missing in the pattern of form IV, and the presence of a strong reflection at 6.37 in form IV which is missing in the pattern of form VI, would indicate that these two patterns represent different compounds.

The x-ray powder diffraction pattern of form VI as reported in the present work consistently appeared when different forms of long-chain ammonium polyphosphates were heated in a stream of ammonia at temperatures of 340 to 350 °C.

Structural similarities between the four forms of CAPP described here and various forms of potassium Kurrol's salt are not immediately apparent from the x-ray powder diffraction patterns or single-crystal data available. Form V of CAPP has similar unit-cell dimensions and the same space group as one form of the potassium salt, $\text{KPO}_3\text{-II}$ (Von Jost and Schulze, 1971). However, the x-ray powder diffraction patterns of these two compounds are sufficiently different to indicate that these salts are not isomorphous.

PREPARATION OF $\text{NH}_4\text{H}(\text{PO}_3)_2$

A new salt with the empirical composition $\text{NH}_4\text{H}(\text{PO}_3)_2$ was prepared by treating P_4O_{10} with anhydrous ammonia at 450 °C followed by tempering of the amorphous reaction product in an evacuated sealed glass tube at 410 °C for several hours. The crystals that formed inside the tube upon slow cooling to room temperature were separated from an amorphous phase by washing with concentrated ammonium hydroxide solution.

About 20% of the crystalline phase was identified as CAPP form V; the other 80% was a well-crystallized compound with an x-ray powder diffraction pattern (Table III) different from any forms of CAPP. This new salt is a stable well-crystallized compound that melts at 520 °C. It was insoluble in water and was separated from CAPP by washing with dilute HCl. Infrared absorption spectra showed the presence of hydrogen and ammonium. Other absorption bands were consistent with the bands generally observed in long-chain polyphosphates (Corbridge, 1969). This observation together with the rather insoluble nature of the compound indicate that it has a chain structure.

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