

# Ultra-High-Analysis $\text{NH}_3$ -P-S and $\text{NH}_3$ -P-O Reaction Products

## Development and Agronomic Evaluation

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Ultra-high-analysis fertilizer products containing up to 42% N and 51% P (117%  $\text{P}_2\text{O}_5$ ) and 3% S were made in bench-scale equipment by gas-phase reaction of  $\text{NH}_3$ , P, and S. These products were essentially inert as sources of N and P for corn. Other lower analysis products (7 to 28% N, 26 to 42% P, and 12 to 56% S) higher in solubility and availability for corn were made by reacting  $\text{NH}_3$  and  $\text{P}_4\text{S}_{10}$ . Gas-phase reaction products of  $\text{NH}_3$ , P, and O (air) containing 15 to 21% N and 32 to 39%

P (73 to 90%  $\text{P}_2\text{O}_5$ ) varied widely in water solubility, depending on temperature and retention time in a two-stage reactor. Response by corn to N and P in these highly condensed phosphate products usually increased with water solubility. The water-insoluble fractions hydrolyzed rather easily in hot water. The solubilized N and P in the resulting low-analysis solutions were about equally available as N in ammonium nitrate and P in concentrated superphosphate.

Interest in ultra-high-analysis fertilizer products stems largely from high handling and transportation costs. These costs are much higher per unit of plant nutrients in low-analysis than in high-analysis fertilizers. Increasing use of anhydrous  $\text{NH}_3$  for direct application in agriculture and use of  $\text{NH}_3$  and elemental P in fertilizer manufacture are examples of this economic fact.

High-analysis ammonium polyphosphates were made by gas-phase reactions of  $\text{NH}_3$  and  $\text{P}_2\text{O}_5$  (Stinson *et al.*, 1956). A representative product containing 17% N and 32% P was an effective soluble source of N and P in agronomic tests. It is also conceivable that other highly concentrated but slightly soluble fertilizer products might be shipped as fertilizer intermediates and then solubilized near the point of fertilizer use. This situation led to research and development by TVA on  $\text{NH}_3$ -P-S and  $\text{NH}_3$ -P-O reaction products. This paper summarizes crop response to N and P in these experimental products in comparison with standard fertilizer sources. Other possible ultra-high-analysis fertilizer products which have been investigated include phosphorus nitrides (Huffman *et al.*, 1954) and phosphorus hydrides (Hunter, 1968).

### MATERIALS AND METHODS

**Fertilizer Reaction Products.** Partial chemical analyses of the products made by the TVA Applied Research Branch and compared in the various greenhouse pot experiments are shown in Table I.

The gas-phase  $\text{NH}_3$ -P-S reaction products were highly insoluble and essentially inert, as shown by subsequent pot tests with corn. However, nearly complete hydrolysis of these products was accomplished by steam under pressure (600 p.s.i.g.) in 4 hours at 250° C. or in 1 hour at 275° C. (910 p.s.i.g.). Products somewhat lower in plant nutrient were then made by reacting  $\text{NH}_3$  and  $\text{P}_4\text{S}_{10}$  (Table I). Water solubility of various products varied from 10 to 95%.

In making the  $\text{NH}_3$ -P-S-products,  $\text{H}_2\text{S}$  was produced as a by-product which would have to be recovered to make any process economical. Substitution of  $\text{O}_2$  from air for S, however, eliminated the  $\text{H}_2\text{S}$  problem and lowered the raw materials cost.

For the  $\text{NH}_3$ -P-O reaction products, gaseous  $\text{NH}_3$ , P, and air were metered into reactors in amounts calculated to form diamidophosphoric acid,  $\text{PO}_2\text{H}(\text{NH}_2)_2$ . The white powdered precipitates were collected in an electrostatic precipitator.

Products made at 450° and 1000° C. were largely water-soluble, but very hygroscopic. Products made at atmospheric pressure, temperatures of 700° to 800° C., and a retention time of 1 second were stable dry powders varying in water solubility (Table I). The products could be completely hydrolyzed by heating with water at 130° C. (25 p.s.i.g.) for 2 hours or at 100° C. for about 3 hours at atmospheric pressure.

Use of a two-stage reactor, the first at about 575° and the second at 800° C., produced wet solids when the reaction time was 0.5 second. Retention times of 2, 3, and 5 seconds in the first stage and of 0.5, 1.0, and 1.5 seconds in the second stage resulted in white, dry powders which by petrographic, x-ray, infrared, or chromatographic examination appeared to be largely mixtures of amorphous gels of highly condensed polyphosphates and unidentified compounds having PN and PNO linkages (TVA, 1968).

Retention time was 2.0 seconds in the first stage and 0.5 second in the second stage for products P-10 and P-11. Solutions produced by hydrolyzing these products were rather low in plant nutrient content (Table I), and the P was present largely as condensed phosphates.

**General Greenhouse Procedure.** Commercial hybrid corn (*Zea mays*) was grown in experiments 1 to 4 and 6 on Hartsells fine sandy loam or Montview silt loam, which were severely deficient in both N and P. Three kilograms of soil was used per pot, and adequate amounts of nutrients for good plant growth other than N or P under test were applied uniformly for all treatments in all experiments. The soils were limed to pH 6.2 to 6.5 with a 2 to 1 mixture of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . N or P sources were mixed throughout the soil unless otherwise indicated. Water was added to 0.3-atm. moisture percentage as needed during growth. After a growth period of 7 to 8 weeks, corn forage was cut at the soil surface, dried, weighed, ground, and analyzed for total N or P.

In experiment 5 annual ryegrass (*Lolium multiflorum*) was grown in pots containing 6.5 kg. of Mountview silt loam. The grass was clipped at a height of 5 cm. at 2-week intervals for eight clippings. Dry weights and content of P for each clipping were determined.

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**Table I. Partial Chemical Analyses by AOAC Methods of Reaction Products and Standard Fertilizers**

N or P Source	Reaction Conditions	Total N, %	Water-Soluble N, % of Total	Total P, %	Water-Soluble P, % of Total	Total S, %	Fertilizer Grade	Experiments in Which Compared
Gas-phase reaction of NH <sub>3</sub> , P, and S								
P-1	500° C., atmospheric pressure	39.9	...	50.1	...	5.1	39-114-0	1
P-2	350° C., atmospheric pressure	39.0	...	47.7	...	10.6	39-109-0	2
Reaction of NH <sub>3</sub> and P <sub>4</sub> S <sub>10</sub>								
P-3	250° C., atmospheric pressure	17.6	97	26.0	81	34.5	17-59-0	3
P-4	300° C., atmospheric pressure	25.3	13	34.9	17	23.1	25-79-0	3
P-5	300° C., CuSO <sub>4</sub> added	21.5	23	32.2	30	26.5	21-73-0	3
P-6	450° C., CuSO <sub>4</sub> added	23.3	9	39.0	15	11.2	23-89-0	3
Reaction of NH <sub>3</sub> , P, and O (air)								
P-7	700° to 800° C. for 1 sec.	21.5	20	36.3	19	...	21-83-0	4
P-8	800° C. for 3 sec.	19.4	70	37.0	61	...	19-84-0	4
P-9	575° C. for 2 sec.; 800° C. for 1 sec.	18.7	26	39.7	23	...	18-90-0	5
P-10	575° C. for 2 sec.; 800° C. for 0.5 sec.	19.0	20	38.4	20	...	19-87-0	...
P-11	575° C. for 2 sec; 800° C. for 0.5 sec.	15.0	90	31.9	90	...	15-73-0	...
P-10 solution	Water at 100° C.	2.7	100	4.7	100	...	3-10-0	6
P-11 solution	Water at 25° C.	2.7	100	5.8	100	...	3-13-0	6
Standard sources								
AN (NH <sub>4</sub> NO <sub>3</sub> )		35.0	100	...	...	...	35-0-0	1-4, 6
CSP (concentrated superphosphate)		...	...	21.7	88	...	0-49-0	1, 3-6
MAP (NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> )		12.2	100	27.0	100	...	12-62-0	5
NP (nitric phosphate)		19.6	100	8.7	23	...	19-9-0	5

**Table II. Uptake of N and P by Corn from Ammonia-Pentasilfide Reaction Products and from a Standard Source of N or P (Experiment 3)**

N and/or P Source and Water-Soluble N and P, % of Total	P Applied, Mg./Pot	Crop Uptake of P		Relative Effectiveness <sup>a</sup>		N Applied, Mg./Pot	Crop Uptake of N		Apparent Recovery of Applied, N, %	
		Crop 1, mg./pot	Total 2 crops, mg./pot	Crop 1	Both crops		Crop 1, mg./pot	Total 2 crops, mg./pot	Crop 1	Both crops
P-3 (97N, 81P)	60	30	49			150	177	207		
	120	40	62	97b	87b	300	282	317	62b	66b
	240	52	84			600	475	530		
P-4 (13N, 17P)	60	23	41			150	132	168		
	120	31	51	36c	37c	300	157	195	19c	22c
	240	43	68			600	224	273		
P-5 (23N, 30P)	60	26	43			150	124	157		
	120	35	56	39c	40c	300	169	203	20c	24c
	240	43	70			600	227	281		
P-6 (9N, 15P)	60	21	37			150	115	148		
	120	23	40	15d	15d	300	126	157	6d	5d
	240	30	47			600	147	176		
CSP (88P) or AN (100N)	60	37	56			150	211	242		
	120	39	66	100a	100a	300	302	336	75a	75a
	240	57	93			600	560	595		
No P or no N	0	18	33	...	...	0	112	145	...	...

<sup>a</sup> Based on coefficients obtained from a curvilinear model.

Dry matter and nutrient uptake responses were evaluated in terms of appropriate linear or curvilinear models. Mean values or response curves having the same letter in tables or figures are not different at the 5% level of statistical significance.

**EXPERIMENTS CONDUCTED AND RESULTS**

**Gas-Phase Reaction Products of NH<sub>3</sub>, P, and S (Experiments 1 and 2).** In one series of pots in experiment 1 the

fine powdered reaction product and concentrated superphosphate (CSP) were compared as sources of P mixed with the soil to supply 0, 60, 120, and 240 mg. of P per pot. In a second series, the product was compared with ammonium nitrate (AN) as sources of N mixed with the soil to supply 0, 100, 200, 400, and 800 mg. of N per pot.

In 8 weeks of growth, dry corn forage yields were increased from 5 grams per pot with no applied P to 36 grams with 240 mg. of P as CSP and from 11 grams with no applied N to 54 grams with 800 mg. of N as AN.

Table III. Uptake of N and P by Corn from NH<sub>3</sub>-P-O Reaction Products (Experiment 4)

N and/or P Sources and Water-Soluble N and P, % of Total	P Applied, Mg./Pot	Crop Uptake of P, Mg./Pot				N Applied, Mg./Pot	Crop Uptake of Applied N, Mg./Pot	Apparent Recovery of Applied N, %
		-35-Mesh		-6 + 9-Mesh				
		Crop 1	2 crops	Crop 1	2 crops			
P-7 (20N, 19P)	60	11	20	12	23	250	163	37b
	120	18	30	18	33	500	257	
	240	28	52	35	60			
P-8 (70N, 61P)	60	11	21	11	21	250	173	38b
	120	16	29	17	33	500	261	
	240	27	50	33	59			
CSP (88P) or AN (100N)	60	24	37	19	35	250	261	76a
	120	40	64	38	61	500	453	
	240	53	90	58	93			
No P or no N	0	4	9	...	...	0	71	...

However, there was no growth response to either N or P in the reaction product.

Series of pots were then set up for experiment 2 in which AN and the reaction product were mixed with the soil to supply 0, 100, 200, 400, and 800 mg. of N 90 days before planting, 60 days before, and at time of planting corn. Three successive crops of corn forage produced total dry matter yields of 16 to 18 grams per pot with no applied N, with increasing yields up to 57 grams with AN. Again, the reaction product produced no increase in growth, nor did it release any appreciable N to the crops. Thus, the reaction product was essentially inert, even with soil incubation and repeated cropping.

**NH<sub>3</sub>-P<sub>4</sub>S<sub>10</sub> Reaction Products (Experiment 3).** Four powdered reaction products and AN mixed with the soil to supply 0, 150, 300, and 600 mg. of N per pot were compared in one series of pots. In a second series the products and CSP mixed with the soil to supply 0, 60, 120, and 240 mg. of P were compared.

Total yields of dry corn forage from two successive crops grown over a 15-week period increased curvilinearly from 18 grams per pot with no applied P to a maximum of 93 grams per pot with 240 mg. of P as CSP. Essentially linear increases resulted with the less available source of P and with N applied from all sources. The yields were in the order CSP or AN > P-3 (250° C.) > P-4 = P-5 (300° C.) > P-6 (450° C.), the same order of decrease in water solubility of N or P in the various sources.

Uptake of N and of P by the two corn crops is given in Table II. Regression analyses showed that water solubility explained 97% of the variation in effectiveness for the two corn crops of the various fertilizers as sources of N and 92% of the variation as sources of P. Very little additional N was taken up by the second crop over that utilized by the first crop. However, the second crop obtained considerable amounts of P from all sources. Thus, the reaction products contained water-soluble N fractions which were readily available to corn and water-insoluble fractions which had a very low availability. Only the product made at the lowest temperature (250° C.) released nearly as much P as did CSP or as much N as did AN.

**NH<sub>3</sub>-P-O Reaction Products (Experiments 4, 5, and 6).** In experiment 4 two sizes (-35-and -6 + 9-mesh) of CSP and two NH<sub>3</sub>-P-O reaction products were evaluated as P sources, and both powdered products were compared with AN as sources of N. Total yields of two successive

crops of corn grown over a 16-week period increased linearly with amounts of P applied. Yields and uptake of P were in the order: fine NH<sub>3</sub>-P-O products < granular NH<sub>3</sub>-P-O products < fine CSP = granular CSP. A similar order was true for the evaluation as N sources by a single corn crop: NH<sub>3</sub>-P-O products < AN (Table III).

The markedly different water solubilities of N and P in products P-7 and P-8 were not found in later analyses of similar products. As was true for crop uptake of P in experiment 3, additional uptake of P by the second crop occurred with all sources.

In experiment 5 fine and granular monoammonium phosphate (MAP), nitric phosphate (NP), dicalcium phosphate (DCP), and a NH<sub>3</sub>-P-O reaction product (P-9) were compared as sources of P for eight clippings of annual ryegrass. As shown in Figure 1, total uptake of P by the eight clippings from the fine fertilizers were in the order: NH<sub>3</sub>-P-O reaction product << DCP = NP < MAP. The order for the granular fertilizers was DCP < NH<sub>3</sub>-P-O reaction product < NP << MAP. These results indicate that the water-insoluble fraction of the NH<sub>3</sub>-P-O product was much less available to grass than the water-insoluble fractions of DCP and NP, which are largely or entirely soluble in neutral ammonium citrate solution.

Two solutions prepared by hydrolysis of NH<sub>3</sub>-P-O reaction products were compared in experiment 6 with CSP as sources of P and with AN as sources of N for corn. The solutions were applied dropwise and CSP or AN as -6 + 9-mesh granules to soil in a layer in the pots and covered with 5 cm. of soil.

Slightly higher yields of corn forage (Figure 2) were obtained to P in the solutions than in CSP. This early growth response difference is a common result with granular or band-applied ammonium phosphates, as compared to superphosphates. The solutions were slightly poorer sources of N than was AN. Presumably, some of the N in the solutions was less available. The results indicated that all sources were satisfactory fertilizers for corn. The original P-10 and P-11 products were not included in this evaluation. No explanation is apparent for the marked difference in water solubility of these products.

#### DISCUSSION

Results from this investigation indicate the feasibility of producing fertilizer products of very high nutrient—up to 42% N and 51% P by gas-phase reactions of NH<sub>3</sub>, P, and S. However, these products were essentially inert

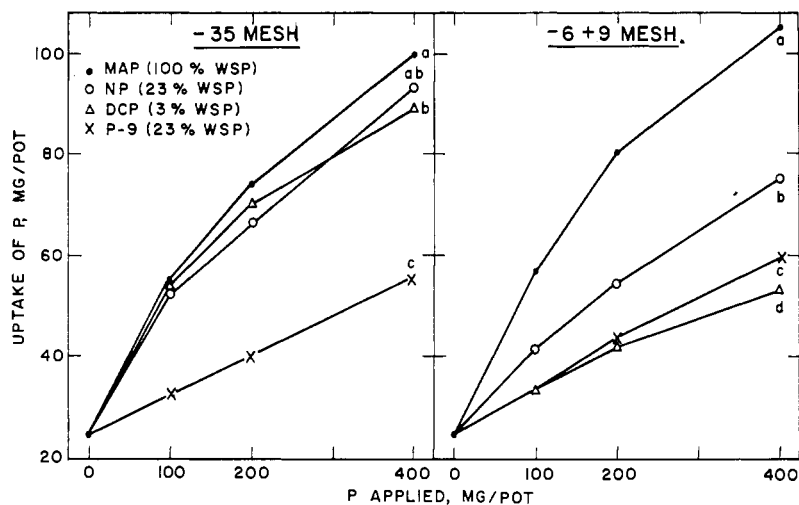


Figure 1. Total uptake of P by 8 clippings of ryegrass from granular and fine sources (experiment 5)

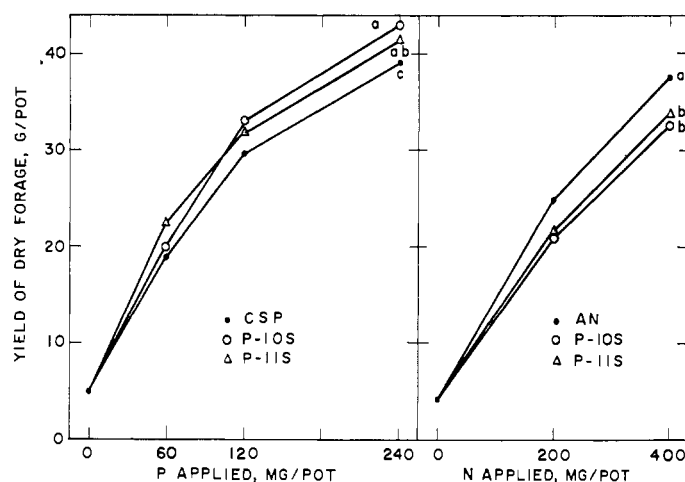


Figure 2. Yields of corn forage with solutions from two  $\text{NH}_3$ -P-O reaction products and CSP as sources of P and solutions and AN as sources of N (experiment 6)

as sources of N and P for crop growth. They could be solubilized by steam at rather high pressure.

Products made by gas-phase reaction of  $\text{NH}_3$ , P, and O (air) contained 15 to 21% N and 32 to 42% P (73 to 97%  $\text{P}_2\text{O}_5$ ). Crop response to N and P in these products increased in general with their water solubility. However, the poor agreement between solubility and crop response in some experiments indicates possible difficulties of AOAC methods for determining the solubility of these condensed phosphate products. Variations in rate of hydrolysis and dissolution probably affect the results.

The water-insoluble fractions could be hydrolyzed rather easily in hot water. The N and P in the resulting solutions were essentially as available as these nutrients in standard water-soluble sources.

Technology of producing these ultra-high-analysis fertilizer products is still in the bench-scale developmental stage and research by TVA chemical engineers is continuing.

#### LITERATURE CITED

- Huffman, E. O., Tarbutton, G., Elmore, K. L., Cate, W. E., Walters, H. K., Jr., Elmore, G. V., *J. Am. Chem. Soc.* **76**, 6239 (1954).  
 Hunter, F., "New Fertilizer Materials," p. 327, Noyes Development Corp., Park Ridge, N. J., 1968.  
 Stinson, J. M., Striplin, M. M., Jr., Brown, N. A., Seatz, L. F., *J. Agr. Food Chem.* **4**, 248 (1956).  
 Tennessee Valley Authority, Muscle Shoals, Ala., "New Developments in Fertilizer Technology," 7th Demonstration, p. 10, 1968.

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