PHOSPHATE EFFECTIVENESS

Quality of Phosphorus in Mixed Fertilizers as Revealed by Solubility in Water, Neutral Ammonium Citrate, and Alkaline Ammonium Citrate Solutions

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In 145 commercial mixed fertilizers, total P_2O_5 differed little from A.O.A.C.-available P_2O_5. In contrast to the A.O.A.C.-available P_2O_5, the percentage of total P_2O_5 that was water-soluble was very low in many of the samples. Among fertilizer grades containing 4.4% or less P (10% or less P_2O_5), none had a mean water-soluble P_2O_5 content that exceeded 41.3% of the total. Approximately 65% of the phosphorus in these samples was available according to the alkaline ammonium citrate procedure. By utilizing the relationship between the agronomic effectiveness of the phosphate in ammoniated ordinary superphosphate and its solubility in alkaline ammonium citrate and in water, as established by previous research, estimates were made of the effectiveness of the P_2O_5 in the commercial fertilizers studied. These estimates indicated that many of these samples are inferior phosphatic fertilizers; however, the A.O.A.C. method of determining available P_2O_5 did not distinguish between the high-quality and low-quality fertilizers.

A HIGH PERCENTAGE of the mixed fertilizers sold in the United States are formulated with ammoniated ordinary superphosphate. Although ammoniation is a very beneficial formulation process in the production of granulated mixed fertilizers, it decreases the water solubility of phosphorus in ordinary superphosphate by converting monocalcium phosphate into ammonium phosphate, dicalcium phosphate, and more basic calcium phosphates which are predominantly hydroxyapatite (1). As a result of ammoniation, much of the phosphorus in commercial mixed fertilizers is insoluble in water (3, 5, 11). For example, Clark et al. (5), in a survey conducted in 1955-6, found that less than half of the A.O.A.C.-available phosphorus in mixed fertilizers was water soluble and that one fourth of the mixed fertilizers had less than 30% of the A.O.A.C.-available phosphorus in water-soluble form.

Ammoniating ordinary superphosphate to a high degree [4 to 8 pounds of NH_3 per 8.8 pounds of P (20 pounds of P_2O_5)] greatly reduces the effectiveness of the phosphorus for crop production; however, this loss in effectiveness is not reflected in the A.O.A.C. method for determining available phosphorus (13, 14, 16). Because of this discrepancy, the A.O.A.C. method has been criticized by several workers (2, 12, 13, 16).

Many foreign countries, including most of the European Common Market countries, use alkaline ammonium citrate for evaluation of the water-insoluble fraction of the fertilizers rather than neutral ammonium citrate as specified by the A.O.A.C. Using an alkaline ammonium citrate procedure employed in the Netherlands (10), Hignett and Brabson (7) examined the water-insoluble phosphorus in mixtures of dicalcium phosphate and basic calcium phosphate and in several mixed fertilizers containing ammoniated ordinary superphosphate. They found dicalcium phos-

phate to be almost completely soluble in alkaline ammonium citrate, and the basic calcium phosphate (predominantly hydroxyapatite) to be almost completely insoluble. The alkaline ammonium citrate-soluble phosphorus in the fertilizers containing ammoniated ordinary superphosphate decreased as the degree of ammoniation increased. As a result of their work, Hignett and Brabson concluded that the Netherlands alkaline ammonium citrate method (N.A.A.C.) should be useful in assessing the value of water-insoluble phosphorus in fertilizers. Work in Mississippi has shown this to be true for ammoniated ordinary superphosphate (16).

Therefore, a study was initiated to determine the quality of the phosphatic component in mixed fertilizers presently sold in Mississippi by determining A.O.A.C.-available phosphorus, N.A.A.C.-available phosphorus, and water-soluble phosphorus.

Table I. Summary of Solubility Data

Fertilizer Grade	No. of Samples	Total P (P_2O_5), Mean %	Portion of Total P_2O_5, Per Cent					
			A.O.A.C.-Available		N.A.A.C.-Available		Water-Soluble	
			Mean	Range	Mean	Range	Mean	Range
4-4.4-5.8 (4-10-7)	7	4.62 (10.58)	95.1	90.7-97.3	58.0	23.4-92.3	28.9	3.6-64.1
4-5.2-10 (4-12-12)	6	5.49 (12.59)	94.7	92.7-96.1	80.0	49.7-96.8	55.5	24.9-66.7
5-4.4-4.2 (5-10-5)	25	4.69 (10.75)	93.6	85.7-99.2	53.3	26.4-93.1	23.9	3.2-76.1
5-4.4-8.3 (5-10-10)	13	4.61 (10.57)	96.1	91.8-99.5	69.5	49.9-93.3	37.6	11.0-61.2
6-3.5-6.6 (6-8-8)	30	3.90 (8.93)	94.7	86.9-97.6	48.2	26.2-81.1	26.0	5.7-62.7
6-5.2-10 (6-12-12)	6	5.45 (12.48)	95.2	90.5-97.2	72.5	46.3-88.2	50.3	27.1-70.6
6-10.5-20 (6-24-24)	7	10.21 (23.41)	96.2	90.2-98.4	90.7	85.7-97.0	74.9	67.1-85.0
8-3.5-6.6 (8-8-8)	8	3.99 (9.15)	96.1	94.7-98.1	57.5	42.4-84.0	41.3	24.7-67.2
9-5.2-10 (9-12-12)	13	5.50 (12.61)	96.6	94.3-99.1	75.7	55.0-89.6	54.6	33.2-82.1
12-3.5-6.6 (12-8-8)	7	3.87 (8.87)	95.9	93.5-99.1	56.7	48.9-77.1	39.9	22.9-61.5
12-5.2-10 (12-12-12)	14	5.67 (13.00)	97.2	95.0-99.2	82.7	70.0-92.7	63.4	46.2-81.7
13-5.7-11 (13-13-13)	9	5.96 (13.66)	97.3	96.1-98.9	88.4	65.7-96.9	74.2	39.5-92.5

Experimental Procedure

Collection of Samples. The commercial mixed fertilizers examined in this study were obtained from the Mississippi State Chemical Laboratory. These were samples of fertilizers sold in Mississippi during the 1959–60 fiscal year. The percentages of total P_2O_5 and A.O.A.C.-available P_2O_5 were also obtained from the State Chemical Laboratory. Analyses were made according to official A.O.A.C. procedures (4).

In collecting the mixed fertilizers, an attempt was made to obtain a sample of the most important fertilizer grades sold by each manufacturer or guarantor operating in Mississippi. The 145 samples obtained represented 27 manufacturers or guarantors, most of whom also operate in other states, and comprised 12 grades. Probably most of these fertilizers were formulated with ammoniated ordinary superphosphate, especially those grades containing 4.4% or less P (10% or less P_2O_5).

Laboratory Methods. The total and A.O.A.C.-available P_2O_5 percentages reported in this paper are those obtained from the State Chemical Laboratory. The water-soluble phosphorus contained in the fertilizers was extracted by the A.O.A.C. official method (4), and the phosphorus in solution was determined by the molybdovandophosphoric acid method (8). The N.A.A.C.-available phosphorus was extracted by the official method of the Netherlands (10), the citrate was destroyed with a perchloric acid–nitric acid mixture (2:1), and phosphorus was determined by the molybdovandophosphoric acid method (8).

Results

A summary of total P_2O_5, A.O.A.C.-available P_2O_5, N.A.A.C.-available P_2O_5, and water-soluble P_2O_5 for each grade is shown in Table I.

Total and A.O.A.C.-Available P_2O_5. There was very little difference between total P_2O_5 and A.O.A.C.-available P_2O_5 contained in the fertilizers. Among the 145 mixed fertilizers, there were only five samples in which more than 10% of the total P_2O_5 was classified as unavailable by the A.O.A.C. method. In most samples, more than 94% of the total phosphorus was available according to the A.O.A.C. method.

Water-Soluble P_2O_5. In direct contrast to the A.O.A.C.-available phosphorus, the water-soluble phosphorus was very low in many of the samples tested. Some samples contained almost no water-soluble phosphorus as shown by the ranges in Table I. Among the fertilizer grades containing 4.4% or less P (10% or less P_2O_5), none had a mean water-soluble P_2O_5 content that exceeded 41.3% of the total. In mixed fertilizers containing greater than 4.4% P (10%
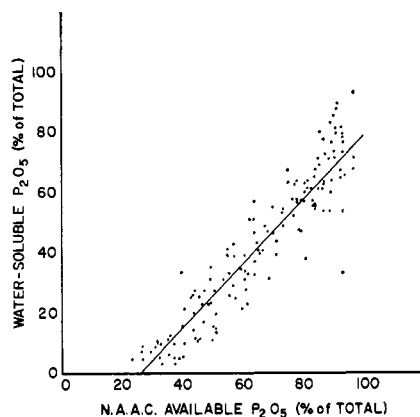

Figure 1. Relationship between N.A.A.C.-available P_2O_5 and water-soluble P_2O_5

Table II. Average Relative Effectiveness of P_2O_5 in Mixed Fertilizers Sold in Mississippi, 1959–60

Fertilizer Grade	Estimated Average Rel. Effectiveness (OSP = 100)
4–4.4–5.8 (4–10–7)	56
5–4.4–4.2 (5–10–5)	51
5–4.4–8.3 (5–10–10)	69
6–3.5–6.6 (6–8–8)	45
8–3.5–6.6 (8–8–8)	55
12–3.5–6.6 (12–8–8)	55
Av.	55

P_2O_5), more of the phosphorus was water soluble; however, in 20% of these fertilizers less than half of the total phosphorus was water soluble. According to Lawton et al. (9) and several other agronomists (6, 11), a minimum of 40% of the phosphorus should be water soluble for many fertilization practices. Only 54% of the total samples tested and 27% of samples in fertilizer grades containing 4.4% or less P (10% or less P_2O_5) met this criterion.

N.A.A.C.-Available P_2O_5. The N.A.A.C.-available phosphorus was also very low for many of the samples tested. Approximately 35% of the phosphorus contained in the samples was unavailable when judged by European standards. This figure increases to 45% when only the samples in grades containing 4.4% or less P (10% or less P_2O_5) are considered.

There was a linear relationship between percentage of the total P_2O_5 which was water-soluble and the percentage of the total P_2O_5 which was N.A.A.C.-available (Figure 1). The equation for the line shown in Figure 1 was calculated by linear regression analysis to be $Y = 1.08X - 28.5$, where Y is the predicted per cent of the total phosphorus which will be water soluble when X per cent is N.A.A.C.-available. The linear correlation coefficient (r) between the two sets of values was 0.93. Since the data of Hignett and Brabson (7) show a linear

relationship between N.A.A.C.-available P_2O_5 and water-soluble P_2O_5 in ammoniated ordinary superphosphate, the high linear correlation obtained here lends support to the contention that most of these samples were formulated by processes involving the ammoniation of ordinary superphosphate.

The values given in Table I indicate that a large difference exists between the A.O.A.C. and N.A.A.C. methods of determining available phosphorus. A.O.A.C.-available P_2O_5 varied only from 86 to 99% of total P_2O_5 as N.A.A.C.-available P_2O_5 varied from 23 to 98%. Dicalcium phosphate was found by Hignett and Brabson (7) to be almost completely soluble in alkaline ammonium citrate; thus, the phosphorus classified as unavailable by the N.A.A.C. method must be present in compounds more basic than dicalcium phosphate. Although calcium phosphates more basic than dicalcium phosphate generally are less effective as phosphatic fertilizer than the soluble phosphates (12, 15), this difference in effectiveness was not indicated by the A.O.A.C. method of determining available P_2O_5.

Estimates of Fertilizer Effectiveness. Extensive field experiments in Mississippi have established the relationship between N.A.A.C.-available P_2O_5 and relative effectiveness (expressed as per cent superphosphate equivalents) of ammoniated ordinary superphosphates (16). This work was done using ordinary superphosphates with known degrees of ammoniation, and consisted of 43 experiments with three different crops over a 5-year period. In all of these experiments, the phosphate fertilizers were band-placed, and sufficient nitrogen and potassium were applied to provide adequate and uniform amounts to all treatments. Several rates of unammoniated ordinary superphosphate were included in each experiment to describe the response to added phosphorus and to serve as a standard for comparison. The relationship thus established was expressed by the following linear regression equation: $Y = 1.14X - 10.1$, where Y is the predicted effectiveness of the fertilizer relative to ordinary superphosphate when X per cent of the total P_2O_5 is N.A.A.C.-available.

To estimate the effectiveness of the commercial fertilizer grades containing 4.4% or less P (10% or less P_2O_5) using the above relationship, it was assumed that all samples examined in these grades contained ammoniated ordinary superphosphate. This is a reasonable assumption in view of the widespread use of ordinary superphosphate for formulating low-analysis fertilizer grades. The estimated average relative effectiveness of these fertilizer grades is shown in Table II. These data show that the estimated average effectiveness of these relatively low-analysis fertilizers is quite low.

For control purposes, a method more discriminating than the present A.O.A.C. procedure is needed to serve as a basis for quality control for fertilizer manufacturers and for protection of the consumer.

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NUTRIENT CONSERVING AGENTS

The Loss of 2-Chloro-6-(trichloromethyl)-pyridine from Soil

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2-Chloro-6-(trichloromethyl)pyridine applied to soil as an intimate mixture is lost by two exponential processes. One is volatilization and the other is degradation to 6-chloropicolinic acid. Of four soils studied, the half time of the slowest degradation process is only 22 days at 20° C. The half time of the most rapid is 4 days at 20° C.

2-CHLORO-6-(trichloromethyl)-pyridine (N-Serve, trademark of The Dow Chemical Co.), nutrient conservor, is a compound proposed for use as a nitrogen-conserving agent (2). When used in this manner, the compound would be applied to soil along with fertilizers containing ammonium ions to inhibit microbial oxidation and subsequent leaching loss. Hence, both volatilization from the soil and action of soil microflora might have a considerable effect on the length of time the plant was exposed to the chemical and on the residue levels which might subsequently be found in crop plants. To evaluate the relative importance of these different processes, the work described was initiated.

Reagents

6-Chloropicolinic Acid. Dissolve 10 grams (.045 mole) of 2-chloro-6-(trichloromethyl)pyridine in 50 grams (0.41 mole) of 80% (by weight) sulfuric acid and heat under reflux at 130° C. for 2 hours. During this time, hydrogen chloride is evolved freely by the solution. Cool the flask and contents to room temperature and add 100 grams of crushed ice. Place the flask in a refrigerator maintained at 4° C. for several hours and then filter off the resulting precipitate.

Recrystallization to constant melting point from the minimum volume of hot 50% (by weight) methanol yields 4.5 grams (.029 mole) of 6-chloropicolinic acid melting at 194°–195° C. (dec.). Reported melting point, about 190° C. (7). Calculated for $C_6H_4ClNO_2$: C, 45.7%; H, 2.56%. Found: C, 45.8%; H, 2.77%.

6-Chloropicolinic-C^{14} Acid. To a solution of 1 mmole of n-butyllithium in 6 ml. of dry ether at −40° to −35° C., add rapidly and with stirring a solution of 361 mg. (2.44 mmoles) of 2,6-dichloropyridine. Stir the mixture at this same temperature for 5 minutes. Carbonate with 1 mmole of carbon-C^{14} dioxide at −78° C. and continue stirring at this temperature for 2 more hours.

Permit the reaction mixture to warm to room temperature and add 20 ml. of water. Separate the aqueous phase from the ether phase and wash the aqueous with three equal portions of ether. Transfer the remaining aqueous phase to a small liquid extractor, saturate with sodium chloride, and adjust the pH to 2.2 with 6N hydrochloric acid. Extract with chloroform for 2 hours, and evaporate the chloroform extract to dryness on a steam bath to obtain 132 mg. of product (85%) melting at 191°–192° C. The infrared spectrum is identical to that of 6-chloropicolinic acid prepared by the hydrolysis of 2-chloro-6-(trichloromethyl)pyridine.

2-Chloro-6-(trichloromethyl)-C^{14}-pyridine. Seal 132 mg. (0.85 mmole) of 6-chloropicolinic-C^{14} acid in a 6-inch borosilicate-glass test tube with 1 gram of phosphorus pentachloride and heat at 170° C. for 32 hours. Cool the reaction mixture to room temperature and pour onto 5 grams of crushed ice. Make alkaline with 6N sodium hydroxide solution and extract with four successive 5-ml. portions of ethanol-free ether. Dry the ether extracts over anhydrous magnesium sulfate and assay for product by means of its ultraviolet absorption spectrum: λ_{max} is 270 mμ; E_{max} is 4190. The yield is approximately 183 mg., representing a 94% conversion of the 6-chloropicolinic-C^{14} acid.

The melting point of the product isolated from preliminary runs was 66°–68° C.; there was no depression of melting point when mixed with an authentic