

FERTILIZER ANALYSIS

Rapid Determination of Nitrogen and Phosphorus Pentoxide in Ammonium Phosphate Fertilizer Solutions

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A rapid method for determination of total nitrogen and phosphorus pentoxide in a fertilizer solution of ammonia and phosphoric acid has been developed to assist plant operators in controlling neutralization. This method is based on the fact that the 8-24-0 solution is a mixture of diammonium and monoammonium phosphates. The diammonium phosphate is titrated to monoammonium phosphate, which is boiled in the presence of excess standard alkali to liberate the ammonia and then back-titrated with standard acid to form monosodium phosphate. Values are accurate within 10 parts per thousand.

THE INCREASE IN THE PRODUCTION OF LIQUID FERTILIZERS in the western and midwestern states has been due largely to the availability of raw materials and the development of relatively low-cost equipment for their production. Many improvements have been made in the design of liquid fertilizer plants. Equipment manufacturers are now offering plants varying from small scale batch to large scale continuous-flow types.

The procedure employed for the manufacture of liquid fertilizers in either batch or continuous-flow plants is essentially (1) neutralization of the phosphoric acid solution by ammonia, in either its anhydrous or aqueous form, and (2) addition of water-soluble salts to produce the desired formulas.

Steps 1 and 2 may be carried out singly or simultaneously. In both systems the ammoniation of the phosphoric acid is controlled to the 1-3-0 N:P₂O₅ weight ratio. The procedure for compounding

the liquid mixes and their physical properties have been discussed by Langguth and others (1) and Slack, Driskell, and Schaffer (2).

Many large scale producers of liquid fertilizers prefer to produce the 1-3-0 ratio ammonium phosphate solution—8-24-0—by the continuous neutralization process. This solution may be used as a base mix for formulating a diversity of grades or used as such, as a fertilizer. Although the instrumentation of these plants provides a high degree of accuracy there is need for a simple analytical method which will enable the manufacturer to control the operation. The following titration method is applicable only to solutions derived from ammonia and phosphoric acid.

Theory

The ratio of nitrogen to phosphorus pentoxide in the ammonium phosphate

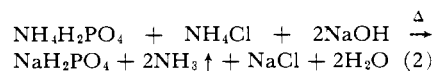
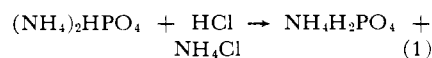
fertilizer solution is between that of mono- and diammonium phosphates.

Solution	N:P ₂ O ₅ Ratio	pH of Soln. (Diluted to 1%)
1. Monoammonium phosphate	1 to 5	4.6
2. Ammonium phosphate fertilizer solution (example 8-24-0)	1 to 3	7.1
3. Diammonium phosphate	1 to 2.5	7.6

The method proposed is based on the fact that the 1-3-0 ratio fertilizer solution is composed of a mixture of mono- and diammonium phosphates, the relative quantities of which may be determined by titration. It would theoretically be possible to titrate the diammonium phosphate to monoammonium phosphate with standard acid and

then titrate all the monoammonium phosphate with standard alkali to form sodium ammonium phosphate. However, in the titration to form sodium ammonium phosphate the solution becomes buffered and the end point is difficult to detect. The proposed method, which is a modification of these titrations, has distinct end points.

The diammonium phosphate is titrated with standard acid to form monoammonium phosphate and ammonium chloride (Equation 1). The monoammonium phosphate is then converted to monosodium phosphate by boiling off the ammonia in an excess of standard alkali and back-titrating with standard acid to form monosodium phosphate and sodium chloride (Equation 2).



Equipment and Reagents

Equipment includes two self-filling, reservoir-type burets of 50-ml. capacity, and two specific gravity hydrometers having an over-all length of 300 mm. (11.8 inches) with specific gravity scales: $A=1.000$ to 1.220 , $B=1.200$ to 1.420 . These hydrometers require about 250 ml. of liquid for submersion.

A hydrometer jar with a height of 300 mm. and a diameter of 50 mm. or greater, 5-, 25-, and 50-ml. pipets, 250-ml. beakers, stirring rods, glass beads, a hot plate, and beaker tongs are also used.

Reagents needed are 1.0*N* sodium hydroxide, 1.0*N* hydrochloric acid, and mixed indicator made from 2 parts of 0.1% water-soluble methyl red plus 5 parts of 0.1% water-soluble bromocresol green.

Procedure

Fill the hydrometer jar, determine specific gravity, and immediately pipet 5 ml. of this solution into a 250-ml. beaker. Add 25 ml. of water, 3 drops of mixed indicator, and several glass beads to the beaker. Titrate the solution with 1*N* hydrochloric acid to a red end point and record the milliliters of acid as *A*. Pipet a 50-ml. aliquot of 1*N* sodium hydroxide to the beaker, stir, and boil on the hot plate until no odor of ammonia can be detected. Remove the beaker from the hot plate and titrate with hydrochloric acid without cooling, to the same red end point. Record milliliters of acid as *B*.

Calculations

The amount of sodium hydroxide consumed in titration *B* is equivalent

Materials Used ^a	Analysis	
	% N	% P ₂ O ₅
Monoammonium phosphate	12.2	61.5
Diammonium phosphate	21.1	53.8

Soln. No.	N:P ₂ O ₅ Ratio		Analysis			
	Calculated	Determined	Calculated		Determined	
			% N	% P ₂ O ₅	% N	% P ₂ O ₅
Series I						
1	1 - 5.09	1 - 5.06	4.88	24.8	4.88	24.7
	1 - 5.09	1 - 5.09			4.87	24.8
2	1 - 3.91	1 - 3.84	6.00	23.3	6.01	23.1
		1 - 3.88			6.00	23.3
3	1 - 3.47	1 - 3.50	6.58	22.9	6.55	22.9
		1 - 3.47			6.57	22.8
4	1 - 3.10	1 - 3.08	7.16	22.3	7.25	22.3
		1 - 3.10			7.28	22.6
5	1 - 2.53	1 - 2.55	8.30	21.0	8.28	21.1
		1 - 2.53			8.31	21.0
	Av. difference	0.02			0.03	0.1
Series II						
1			7.00	21.0	7.02	20.7
					6.99	21.0
2			8.00	24.0	8.00	23.8
					8.00	23.9
3			9.00	27.0	9.03	26.8
					9.02	26.9
			Av. difference		0.01	0.1

^a Produced by Victor Chemical Works, Chicago, Ill.

to the total quantity of ammonia present, as shown in Equation 2. The sodium hydroxide required for reaction with the ammonium chloride formed in Reaction 1 is equal to the milliliters of 1*N* hydrochloric acid in titration *A*. Thus, subtracting the milliliters of hydrochloric acid (titration *A*) from the milliliters of sodium hydroxide consumed ($50-B$) gives the amount of sodium hydroxide consumed in the formation of the monoammonium phosphate shown in Equation 2. This in turn can be calculated to phosphorus pentoxide.

The equations used in determining the percentage of nitrogen and phosphorus pentoxide present are

$$\% \text{ N} = \frac{(50.0 - B) \times 1.4}{5 \times \text{specific gravity of soln.}}$$

$$\% \text{ P}_2\text{O}_5 = \frac{[50.0 - (B + A)] \times 7.1}{5 \times \text{specific gravity of soln.}}$$

Preparation of Known Solutions

Two series of ammonium phosphate solutions were prepared from crystalline mono- and diammonium phosphates of known composition. Series I contained solutions which varied in their nitrogen-phosphorous pentoxide ratio; Series II

was taken at a constant nitrogen-phosphorus pentoxide ratio, but varied in concentration.

Results and Discussion

The procedure is relatively simple and has been designed to be carried out by trained plant personnel.

The nitrogen and phosphorus pentoxide values of this method are accurate within 10 parts per thousand. This method therefore has sufficient precision to warrant its use in controlling the production of the ammonium phosphate solutions. The exact composition of the solutions as required by state fertilizer regulations should be determined by approved analytical procedures.

Literature Cited

- (1) Langguth, R. P., Payne, J. H., Jr., Arvan, P. G., Sisler, C. C., Brautigam, G. F., Jr., J. AGR. FOOD CHEM. 3, 656-62 (1955).
- (2) Slack, A. V., Driskell, J. C., Schaffer, H. B., Jr., Division of Fertilizer and Soil Chemistry, 128th Meeting, ACS, Minneapolis, Minn., September 1955.

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