

by 12, 13, and 14, depending upon the fertilizer analysis. In the case where no phosphoric acid or diammonium phosphate is used, the unit cost increases as over-all analysis increases. However, in some cases, by changing raw materials, the unit cost of making a higher analysis material becomes less. For instance, at a recycle value of 1, a 14-14-14 grade fertilizer can be produced at a lower unit cost than 13-13-13 where no phosphoric acid is used by including 400 pounds of phosphoric acid in the formulation. In addition, this will produce an increase in production rate and plant nutrient of about 8%. This graph illustrates that another factor to be considered is the cost of changing to higher analysis products in terms of changes in raw materials

and the increased production rate in terms of plant nutrient that can be realized.

The various ways in which a series of formulations can be evaluated from the standpoint of economics of raw material costs gives the manufacturer a sound basis from which to decide on changes in his operations. He will be able to decide upon a formulation and make changes after estimating the effect of changes in production rate with changes in recycle. He can evaluate the advantages of adding new raw materials in terms of increased profits as opposed to the cost of installing new equipment.

It should be emphasized that the foregoing example is a study of a particular location and cannot be used to generalize

the economic effects of diammonium phosphate and phosphoric acid.

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Literature Cited

- (1) Payne, J. H., Daniels, S. D., *J. Agr. Food Chem.* **4**, 925 (1956)
- (2) Payne, J. H., Webber, R. T., *Ibid.*, **8**, 164 (1960).

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FERTILIZER SOLUTIONS ANALYSIS

Determination of Total Nitrogen and Nitrogen Distribution in Fertilizer Solutions

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A fairly rapid yet accurate procedure was developed for the analysis and sampling of nitrogen fertilizer solutions. The Kjeldahl distillation for ammonia content and the use of Devarda alloy treatment, with Kjeldahl distillation, for nitrate content were found satisfactory. For urea content, modifications of the urease hydrolysis technique were made. A convenient and reproducible sampling procedure was tested.

DURING THE FORMULATION of high nitrogen content fertilizer solutions, containing more than one compound as a source of nitrogen, it is necessary to know the concentration of each nitrogen compound in the solution. This information is desirable for estimation of vapor pressure and salting-out properties and for assurance that the total nitrogen content is acceptable.

High nitrogen fertilizer solutions may contain urea, ammonium nitrate, and ammonia in any combination, covering a fairly wide range of total nitrogen content. For characterization of a solution containing all three compounds, three analyses on some combination of either three components or two components and a total is required in general. To devise the most accurate and rapid sampling and analytical technique, a number of methods (1, 2, 5, 10) were considered, evaluated, and investigated.

The determination of total nitrogen by the familiar Kjeldahl technique, as given in the standard methods of the Association of Official Agricultural Chemists including the most recent revisions (1, 6, 7), could not be used, because of the time required and the poor accuracy and precision obtained when prepared mixtures were analyzed. Although excellent results could be obtained, by various modifications of the recommended Kjeldahl procedures for the analyses of the pure components of the mixture alone, the determination of the total nitrogen was discarded as too time-consuming. For consistent results, however, work completed during the course of this study indicated that urea samples might require a fairly dilute digestion and nitrate samples would require almost anhydrous conditions for best recovery (Table I).

For rapid estimation of urea alone, the urease enzymatic hydrolysis method

of Fox and Geldard (3) as modified by Smith, Dock, and Rich (9) appeared very promising if analysis time could be reduced and/or if accuracy could be improved. The latest method (7) using the enzymatic hydrolysis of urea to ammonium carbonate is a variation of the method by Smith, Dock, and Rich but the back-titration employed represents no basic improvement. However, with considerable reliance upon the literature cited, a method satisfactory with regard to both speed and precision was developed.

For the determination of ammonia and the ammonia from the urea, if present, a distillation of the ammonia from the caustic solution into a boric acid solution was adopted. For samples containing only ammonia and urea, a single acid titration of the solution followed by a urease hydrolysis and analysis of the neutralized solution appeared to be excellent.

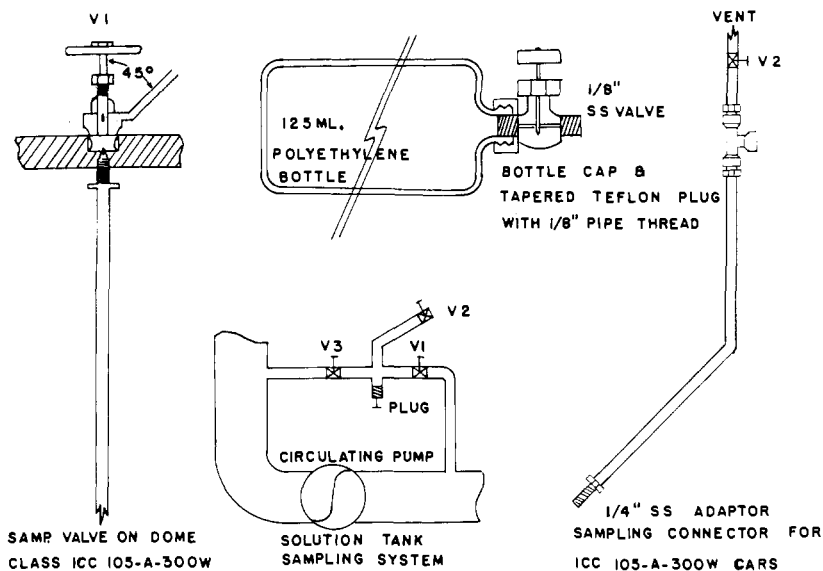


Figure 1. Fertilizer solution sampling system

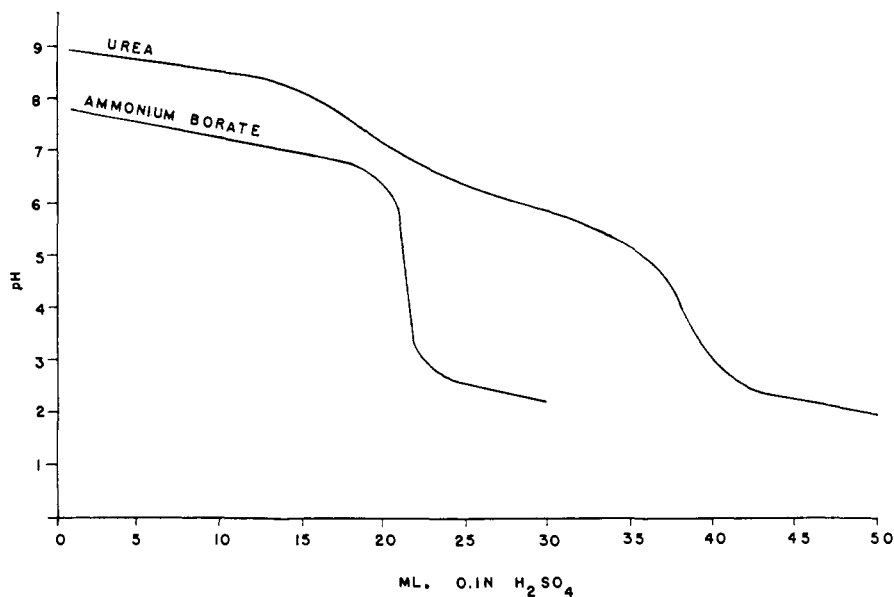


Figure 2. Titration of hydrolyzed urea and ammonium borate

For the determination of nitrate content, when present, a satisfactory analysis would be obtained by treating the sample solution, after removal of ammonia, with Devarda alloy and again distilling into a boric acid solution (7).

Experimental

Apparatus and Special Reagents. Sulfuric acid solution, 0.1*N*, standardized.

Urease powder, Fisher Scientific Co., U-21.

Devarda alloy, Mallinckrodt G-234.

Kjeldahl distillation apparatus (Precision Scientific), two and six place.

pH Meter, Beckman Model H-2.

Procedure. Carefully weigh a sample containing not more than 1.0 gram of ammonia into a 500-ml. volumetric

flask. Dilute to the mark with distilled water.

Transfer a 25-ml. aliquot of the solution to a 250-ml. iodine flask and add 15 ml. of distilled water. Neutralize the solution to pH 4.0 using a recently buffered pH meter. (If only urea and ammonia are present in the sample, this titration could be used for ammonia estimation.) Then add 50 ± 2 mg. of the urease powder from a calibrated dipper. Swirl the solution in the flask to effect suspension of the powder, then add 50 ml. of boiling, distilled water. Stopper the flask and allow it to stand for 30 minutes. Add 1 drop of capryl or octyl alcohol and titrate again to pH 4.0 using standard acid solution. During titration do not use mechanical stirring. Calculate the urea nitrogen content by:

% urea nitrogen =

$$\frac{[(A)(B) - F] \times 1.401 \times 500}{(\text{wt. of sample})(25)}$$

where *A* = ml. of standard acid used for titration

B = normality of standard acid used

F = blank factor, $(A)(B) = F$, for titration of 50 mg. of urease powder

After determination of urea, add 3 ml. of standard acid to the solution titrated above. Transfer the solution completely to an 800-ml. Kjeldahl flask and add sufficient distilled water to obtain a total volume of 300 ml. Carefully pour 50 ml. of a 50% sodium hydroxide solution down the neck of the flask so that the caustic solution forms a layer underlying the solution in the flask. Connect the flask to the Kjeldahl distillation assembly, swirl the flask, and heat to distill approximately 125 ml. of distillate into a 50-ml. boric acid solution (5% by weight). Titrate the boric acid solution with standard acid to pH 4.7. Calculate the distillable nitrogen by:

% distillable nitrogen =

$$\frac{(A - B)N \times 1.401 \times 500}{(\text{wt. of sample})(25)}$$

where *A* = ml. of acid used for titration of sample

B = ml. of acid used for titration of blank (blank solution is water and 50 mg. of urease powder treated as a sample)

N = normality of standard acid

Immediately after the determination of the distillable nitrogen, add to the Kjeldahl flask approximately 125 ml. of distilled water and 5.0 grams of Devarda alloy, carefully wrapped in a nitrogen-free filter paper. As soon as the initial reaction in the flask starts to subside, apply heat, distill, and collect 125 ml. of distillate in a 50-ml. boric acid solution, titrate, and calculate nitrate nitrogen as above for distillable nitrogen, by using an appropriate blank correction.

Ammonia nitrogen =

$$(\text{distillable nitrogen}) - (\text{urea nitrogen})$$

Total nitrogen =

$$(\text{distillable nitrogen}) + (\text{nitrate nitrogen})$$

Sampling. For the analysis of fertilizer solution, during or following blending, a sample must be taken of a material which can have a considerable vapor pressure. To obtain reproducible samples from mixing or blending tanks, modifications were made of the sampling method of Greene (4) as presented in Figure 1.

To sample, first fill the polyethylene bottle about one third with distilled

water. Squeeze it to force the water to just below the base of the valve. Close it and weigh the bottle and its content. Open valves V_1 and V_3 in the pump bypass, with the plug in place, and close V_2 . When circulating solution is at the proper temperature, close valves V_3 and V_1 , open valve V_2 , and remove the plug. Insert the sample bottle in place of the plug, close valve V_2 , and open valves V_3 and V_1 . After about 2 minutes, carefully open the valve on the sample bottle, just for the period required to allow the bottle to return to normal bottle shape. Close valves V_3 and V_1 , open valve V_2 , remove the sample bottle, and replace the plug. Clean the sample bottle valve and reweigh the bottle and contents. Follow a similar procedure for sampling tank cars. For 49 samples of high vapor pressure urea-ammonia solutions analyzed during April of 1959, the average difference between duplicate samples and the analyses for urea was 0.09% and for ammonia 0.08%.

Discussion

The accuracy and precision of the urea determination for urea are demonstrated in Table II for a series of samples taken from a lot of recrystallized urea and samples taken from a crude urea where urea was determined by both Kjeldahl analysis and analyses for impurities. The analyses were made by nine different analysts with no more than two analyses made at any one time. The accuracy and precision of the procedure for a urea and ammonia mixture are indicated in Table III, while Table IV gives the results for two urea-ammonia-nitrate mixtures. The mixtures used in this study were prepared by blending, by weight, recrystallized urea, ammonium sulfate (Fisher Scientific Co. primary standard A-938), and recrystallized potassium nitrate.

Early in the study it was realized that a small blank correction was required for each titration. However, this observed blank could be considered constant for any one given lot of urease and any one given lot of Devarda alloy, if the same amounts of each reagent were used in every test.

Direct addition of the urease as a powder to the solution eliminated the need for preparation of usual urease suspensions which change effectiveness with age and require almost constant attention for blank value. Under the conditions given for the enzymatic hydrolysis, 50 mg. of the urease powder could easily convert up to 0.35 gram of urea in 30 minutes.

The end points of the titrations were selected on the basis of curves prepared by plotting pH vs. acid used during the titration of numerous samples of varying size and composition (Figure 2). To

Table I. Total Nitrogen Recovery vs. Method Used for Analysis

Sample	Nitrogen, %			
	Theoretical	1958 ^a	1959 ^a	Present work
Ammonium sulfate	21.18	21.20	21.08	21.08
	21.18	21.13	21.24	21.14
Urea	46.55	46.47	46.21	46.43
	46.55	46.58	46.26	46.51
Potassium nitrate	13.86	13.33	13.67	13.71
	13.86	13.35	13.73	13.94

^a AOAC revised method for the year indicated.

Table II. Urea Recovery Data vs. Sample and Operator

Operator	Urea, %			
	Crude Urea, Considered 97.71%		Recrystallized Urea, Considered 100%	
1	97.75	97.71	99.96	99.93
2	97.65	97.54	99.92	100.08
3	97.51	97.50	100.28	100.07
4	97.66	97.63	100.00	100.10
5	97.53	97.35	99.89	99.94
6	97.93	97.91	100.02	99.91
7	97.73	97.57
8	97.74	97.82
9	97.71	97.73
	Av.	97.66		100.00
	Std. error	±0.15		±0.11

supplement the pH meter, suitable indicators were also tested and evaluated. For the titration of ammonia in boric acid solution, the mixed indicator solution of Sher (8) seemed the most satisfactory with regard to sharpness of color change, change at desired pH, and additional warning color change before the actual end point. For titration of the hydrolyzed urea, a comparable indicator was desired. After trial of several indicators, a mixed indicator solution prepared as follows gave fairly good results.

Table III. Nitrogen Recovery from a Prepared Blend Containing Ammonia and Urea

Nitrogen, %		
Urea	Ammonia	Total
19.95	13.73	33.68
19.85	13.52	33.37
19.96	13.56	33.49
19.86	13.43	33.40
19.87	13.41	33.28
Av.	19.90	13.53
Std. error	±0.053	±0.13
		±0.15

Table IV. Nitrogen Recovery from Prepared Blends Containing Urea, Ammonia, and Nitrate

	Blend to Contain 28.0% N				Blend to Contain 32.0% N			
	Nitrogen, % in							
	Urea	Ammonia	Nitrate	Total	Urea	Ammonia	Nitrate	Total
	14.62	6.76	6.69	28.07	16.46	7.84	7.70	32.00
	14.64	6.66	6.69	27.99	16.48	7.59	7.62	31.69
	14.58	6.70	6.70	27.98	16.47	7.73	7.49	31.69
	14.61	6.54	6.64	27.79	16.61	7.75	7.91	32.27
	14.65	6.64	6.95	28.24	16.63	7.56	7.68	31.87
Av.	14.62	6.66	6.73	28.01	16.53	7.69	7.68	31.90
Std. error	±0.02	±0.06	±0.12	±0.16	±0.08	±0.12	±0.15	±0.17

Carefully weigh out 0.20 gram of 4 - (4 - dimethylamino - 1 - naphthylazo) - 3-methoxybenzenesulfonic acid powder (Eastman) into a small beaker. Add exactly 5.18 ml. of 0.100N sodium hydroxide solution and 0.22 gram of indigo carmine powder (Fisher Scientific Co.), and then dilute to 100 ml. with distilled water. Use four drops of indicator for each analysis and take the end point of the titration as the color change from green through gray to a faint purple.

The data in the tables, with the ex-

ception of Table II, were obtained with the pH meter. For Table II, pH meter and indicator were used indiscriminately.

Acknowledgment

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Literature Cited

(1) Assoc. Offic. Agr. Chemists, Wash-

- ington, D. C., "Official Methods of Analysis," 8th ed., 1955.
- (2) Cline, R. E., Fink, P. M., *Anal. Chem.* **28**, 47 (1956).
- (3) Fox, E. J., Geldard, W. J., *Ind. Eng. Chem.* **15**, 743-5 (1923).
- (4) Greene, P. A., Assoc. Offic. Agr. Chemists Meeting, October 1956, Washington, D. C.
- (5) Gullstrom, D. K., Demkovich, P. A., *J. Agr. Food Chem.* **7**, 26-7 (1959).
- (6) *J. Assoc. Offic. Agr. Chemists* **41**, 32 (1958).
- (7) *Ibid.*, **42**, 31-4 (1959).
- (8) Sher, I. H., *Anal. Chem.* **27**, 831-2 (1955).
- (9) Smith, J. A., Dock, D. G., Rich, R. W., *J. Agr. Food Chem.* **6**, 587-8

- (1958).
- (10) U. S. Department of Defense, Military Specifications, **MIL-U-10866A**, (Nov. 25, 1952).

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FERTILIZER TECHNOLOGY

Fineness of Commercial Florida Land Pebble and Other Phosphates Used in Superphosphate Manufacture

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Published collaborative studies were examined and screen analyses made on 16 samples of ground Florida land pebble to answer these questions: How reliable are routine screen analyses? How fine is the -200-mesh fraction? How coarse is the +100-mesh fraction? The precision of the -200-mesh determination, slightly less than half that of -100-mesh determination, corresponds with somewhat more than $\pm 2\%$ of the sample at 95% confidence. The average diameter of the -200-mesh (-74-micron) fraction is reduced by about one sixth in grinding from 50 to 85% finer than 200 mesh; the -50-micron fraction is not noticeably altered. The mean diameter of the +100-mesh fraction, excluding +32-mesh material, increases with the percentage of whole sample remaining on the 100-mesh sieve. The mean diameter of the -32-mesh fraction of the whole sample can be inferred from the percentage through the 200-mesh sieve to about 10 microns.

THE CURRENT TREND toward refinement in fertilizer processing brings a growing need for closer process control. Among demands of this kind is appraisal of the relative reactivity of acidulation grades of phosphate rock. Looking to this need one views the trade specifications that call for certain percentages to pass the 100- and 200-mesh sieves and queries: How reliable are the determined percentages? How fine is the -200-mesh fraction? How coarse is the +100-mesh fraction? Responses to these questions are the primary concern of this paper. The quest for information on those issues, however, draws attention to other matters that merit brief treatment. Noteworthy among the latter are the importance ascribable to rock varieties as a factor in the variability of screen analysis, a comparison of two procedures for determining screen fractions, and the prediction of the average particle of a lot of rock from the determination of one of the commonly sought screen fractions.

Materials and Procedures

The data for the determination of the precision of screen analyses were derived from a published collaborative study of methods for mechanical analysis of phosphate rock (5, 6). Results from both screen analyses and complete mechanical analyses performed in the authors' laboratories on a recent collection of commercially ground Florida land pebble phosphates were used to determine average particle size of screen separates.

Collaborative Study. The study covered two years. In the first year (5) two lots of Florida land pebble were analyzed in triplicate by seven laboratories for the percentages passing the 100-mesh sieve and the 200-mesh sieve (wet). In the second year (6) nine laboratories, including the above seven, using the same procedure analyzed four varieties of rock, including a Florida soft phosphate, a Tennessee brown rock, a Wyoming rock, and a fresh portion

from one of the lots of land pebble used the preceding year. Thus, 50 sets of triplicate determinations for each screen fraction were made on five rocks representing four varieties.

These five rocks are considered as a set typifying the ranges in physical character and analytical difficulty encountered in domestic ground phosphate rock. Grade and variety were not considered. This is desirable because the emphasis is on variability of determining two common screen fractions rather than one fineness per se. This course seems permissible because grade and variety can be factors only in so far as they influence the physical homogeneity and screenability of the rock.

Standard deviations of individual laboratory means were calculated and classified into frequency distributions, in order to evaluate laboratory performance on the basis of precision. Differences among laboratories were handled in a similar manner to show laboratory performance with respect to accuracy.