Figure 1. Sectional photograph of granules of mixed fertilizer made with granular triple superphosphate

this grade is very difficult unless some granular material is used in the formulation. It was believed that the granular superphosphate would be helpful in promoting granulation of low-nitrogen grades by providing nuclei around which granules would form (*5*).

In one test the triple superphosphate was granular and the other ingredients were nongranular; in another test, only the potassium chloride was in granular form. Sulfuric acid, in the amount of 135 pounds per ton of product, was added as a further aid to granulation. The results showed that the granular triple superphosphate was as effective as granular potassium chloride in promoting granulation; the on-size (−6 +28 mesh) recoveries were 82 and 88%, respectively. The difference was attributed to the fact that there was more potassium chloride than triple superphosphate in the formulation.

Of the products made with granular triple superphosphate, the triple superphosphate granules formed the nucleus of almost every particle. Figure 1 is a photograph of cross sections of particles of a 5–20–20 grade made with dark-colored granular triple superphosphate.

Storage Properties

Granular triple superphosphates made from electric-furnace and wet-process phosphoric acids were inspected after 6 months of storage. The bag set was judged to be medium to hard after storage, but none of the products showed lumps after the standard drop test designed to simulate normal handling of the bags. There was no evidence of bag rot. All of the materials tested had been allowed to cure in open-pile storage for 1 or 2 weeks prior to bagging. Product bagged directly from the pilot plant without curing rotted the bags, presumably, because of the higher free acid content of the fresh material. The granular triple superphosphate remained entirely free from caking and was free flowing in open-pile storage for several weeks.

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NITROGEN SOLUTIONS ANALYSIS

Rapid Method for Determination of Urea in Nitrogen Solutions

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Application of an enzyme, urease, makes possible a direct method for analyzing urea in water solutions of urea, ammonium nitrate, and ammonia. This method has given fast, accurate, and reliable results.

Current methods for determining urea in nitrogen solutions are time-consuming, require constant attention, and are subject to inaccuracies. The procedure outlined here provides a rapid method, which requires no special equipment and can be performed by plant operating personnel. Analyses can be completed within 30 minutes after sampling, with a maximum error of 1%.

In setting up a sequence of analyses for aqueous solutions of ammonia, ammonium nitrate, and urea, a wide choice of methods for the individual components is available.

A volumetric method for ammonia and the AOAC formaldehyde procedure for ammonium nitrate (*1*) were selected as the standard methods of analysis for these components. These methods are simple to perform, rapid, require no special equipment, and give reliable results.

Considerable thought was given to the selection of a method for urea. The precipitation with xanthydrol is specific, and accurate for urea (*13*), but is time-consuming. The gasometric methods—release of nitrogen by use of sodium nitrite or sodium hypobromite—while rapid, need special equipment and are reported to be inaccurate (*3*). The Kjeldahl procedures are widely used, but they have several disadvantages. To obtain the nitrogen in an analyzable form, a digestion period is needed to break down the urea, the addition of a reducing agent is necessary because of the presence of nitrate, and a distillation step is required to collect the ammonia. The introduction of the reducing agent causes considerable foaming in both the digestion and distillation steps, necessitating attention to prevent carry-over.

In the enzymatic method, an enzyme, urease, is used to decompose urea into ammonia and carbon dioxide. The ammonia can then be determined by titration and converted into a urea value.

The employment of urease in urea analyses is not novel, but apparently has not been reported previously in connection with nitrogen solutions. Urease has been used for over 40 years in clinical analyses pertaining to urea (*8, 9, 14*). The urea content of blood (*7*), urine (*5*), body organs (*4*), and milk (*12*) has been determined by the use of urease. Other applications of urease to determine urea have been in mixed animal feeds (*2, 11*), mixtures of cyanamide compounds (*6*), and ammoniated dentifrices (*10*).

By means of the volumetric methods for ammonia and ammonium nitrate and the urease method for urea, a nitrogen solution containing these three components can be analyzed within 0.5 hour after the sample has been obtained.

Reagents

Standard sulfuric acid solution, 0.5*N*. In the standardization, methyl purple indicator is used.

Urease solution, 2% aqueous slurry. Using methyl purple indicator, neutralize the solution with standard sulfuric acid. (After preparation, the material must be refrigerated if it is to be stored. Urease solution, which has been refrigerated for a week, has been used successfully).

Antifoam agent, octyl alcohol, or any of the common antifoam agents.

Method of Sampling

The sample line is equipped with a needle valve and a piece of aluminum tubing just long enough to reach within 0.5 inch of the bottom of a 500-ml. volumetric flask.

Fill a 500-ml. volumetric flask approximately $^2/_3$ full with distilled water and weigh to the nearest 0.1 gram on a pan balance. Purge the line well before sampling and then shut off. Wipe the sample line clean, crack the valve, and introduce approximately 100 grams of sample into the flask under the surface of the water. Stopper the flask and allow to come to room temperature before reweighing. After weighing, dilute to the mark with distilled water and mix well. All analyses can be made by taking appropriate aliquots of this solution.

Determination of Urea

Transfer an appropriate aliquot to a 500-ml. Erlenmeyer flask containing 100 ml. of distilled water and neutralize with standard acid to the methyl purple end point. Add 5 ml. of urease solution for each 0.1 gram of urea expected. Warm the sample to, but not exceeding, 40° C. After warming, allow the sample to stand for 20 minutes at room temperature to give the urease sufficient time to degrade the urea to ammonia and carbon dioxide. Add two drops of the antifoam agent and, while swirling it vigorously, titrate the sample with standard acid to the methyl purple end point. One milliliter of 0.5*N* acid is equivalent to 0.015 gram of urea.

Discussion

To establish the validity of this method, two points were investigated. First, six samples of reagent grade urea were analyzed. Urea can be determined with an accuracy to 0.8% of the urea present (Table I). The next step was the analysis of solutions containing free ammonia and ammonium nitrate plus urea. Solutions were prepared in the laboratory on a weight basis using solid urea and ammonium nitrate, distilled water, and anhydrous ammonia. Weighings were made on a pan balance with weight accuracy to 0.1 gram. Five solutions were prepared and analyzed according to the procedure outlined above. Table II shows that the method was accurate within 1% with apparently no interference from either free ammonia or ammonium nitrate.

In establishing this test method, one of the major considerations given was to the time element, as the test would be used for product quality control on a batch process. Table III presents results of tests made to determine the quantity of urease necessary to break down the urea in a reasonable time—0.8 gram of urease per 1 gram of urea will complete the degradation in 20 minutes at 40° C.

The method has now been in use for about $1^1/_2$ years and has proved very satisfactory for control testing. A statistical analysis of results obtained covering the past several months of this period is given below as average difference in 339 duplicate analyses by weight per cent of urea present.

All analyses	0.12
0–15% urea	0.06
15–40% urea	0.15
Over 40% urea	0.18

Table I. Urea Recovery by Urease Method

Gram Urea, Theory	Gram Urea, Found	Recovery, %
0.5074	0.5031	99.2
0.5074	0.5056	99.6
0.5074	0.5074	100.0
0.2030	0.2034	100.2
0.0641	0.0635	99.1
0.0641	0.0641	100.0

Analyses were made on duplicate samples from each batch and good reproducibility was obtained.

Interference

This test method has been in laboratory use under routine conditions and no interfering materials have been encountered. It has been used to a limited extent on complete liquid fertilizers and thus far has given satisfactory results.

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Table II. Urea in Nitrogen Solutions

Free Ammonia, Wt. % Calcd.	Ammonium Nitrate, Wt. % Calcd.	Urea, Wt. % Calcd.	Urea, Wt. % Found	Difference	Error, %
19.0	65.6	5.72	5.79	+0.07	1.2
			5.86	+0.14	2.4
25.0	55.0	9.55	9.55	0.00	0.0
			9.54	−0.01	0.1
20.0	56.9	10.23	10.16	−0.07	0.7
			10.21	−0.02	0.2
18.5	59.1	10.77	10.60	−0.17	1.6
			10.61	−0.16	1.5
4.4	None	35.73	35.63	−0.10	0.3
			35.54	−0.19	0.5
			Av.	0.09	0.8

Table III. Urease Concentration Needed for Urea Breakdown

(Samples contained 0.5074 gram urea)

2% Urease, Ml.	Time, Min.	Temp., °C.	Recovery, %	Urease/Urea
10	20	40	93.9	0.4
10	30	40	96.3	0.4
20	20	40	99.8	0.8
20	20	40	99.8	0.8