phate in the residues as the temperature of defluorination was raised from 220° to 320° C. probably reflects the conversion of the primary orthophosphates to metaphosphates. The presence of the gangue from the rock phosphate in FG probably is the cause of the larger fraction of citrate-insoluble phosphate in defluorinated FG than in defluorinated FO.

These residues could be returned to the ammoniation step at any point subsequent to the removal of the high fluorine precipitate, and the phosphorus in the precipitate then would appear in the final product.

Ammoniation of Low-Fluorine Filtrates

When an extract of rock phosphate is completely ammoniated without removal of any intermediate precipitate, the precipitate at any degree of ammoniation is very finely divided and settles slowly from the mother liquor. When the precipitate that contains 90% of the fluorine is removed, however, subsequent precipitates are so granular and settle so rapidly that, in bench-scale work, homogeneous slurries were not maintained with vigorous agitation. The solids contents of grab samples of the effluent slurries from continuous ammoniations ranged from one-half to three times that in a homogeneous slurry.

Although troublesome in bench-scale work, the rapid settling of the precipitates from low-fluorine filtrates might be useful in large-scale operation. Intermediate precipitates could be removed by sedimentation between stages of ammoniation, and removal of the precipitates would facilitate control of the final stage of ammoniation and also minimize reversion of the precipitated dicalcium phosphate to more basic phosphates.

A low-fluorine filtrate (fluorine ratio, 0.011) that had been overadjusted with phosphoric acid to a net lime ratio of 1.8 was ammoniated completely in a single continuous stage with precipitation of all the calcium and formation of only dicalcium phosphate when the correct amount of ammonia was added and the terminal pH was 4. Addition of more than the correct amount of ammonia in either one or two continuous stages also precipitated all the calcium, but the precipitate contained less phosphorus—much of it present as calcium phosphates more basic than dicalcium phosphate.

Similar results were obtained with an adjusted filtrate in which the net lime ratio was 2.03 and the fluorine ratio was 0.015. With an adjusted filtrate in which the net lime ratio was 2.05 and the fluorine ratio was 0.036, however, significant amounts of basic calcium phosphates were formed when the terminal pH was raised above 2 and more than 60% of the phosphorus was precipitated. A slurry from this filtrate that had been ammoniated to pH 2 was ammoniated to pH 3.5 in a second continuous stage to precipitate the rest of the phosphorus without formation of much basic phosphate.

An unadjusted extract with a net lime ratio of 4.04 and a fluorine ratio of 0.013 could not be ammoniated in a single continuous stage past a pH of 1.5 without precipitation of basic calcium phosphate. At pH 1.5 90% of the ammonia requirement had been added and 80% of the phosphorus was precipitated. The slurry was ammoniated in one more continuous stage to precipitate the rest of the phosphorus at pH 4 by addition of a total of 110% of the ammonia requirement, but 10 to 20% of the phosphorus in the combined precipitate was in the form of basic calcium phosphates. Addition of carbon dioxide during the second stage did not prevent the precipitation of basic phosphates.

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FERTILIZER NITROGEN ANALYSES

Apparent Loss of Organic Nitrogen in Fertilizers Containing Urea and Natural Organics

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SPECIALTY FERTILIZERS with a fixed percentage of organic nitrogen, such as 10-6-4 fertilizer, used for golf courses, usually contain organic by-products known as natural organics. The latter are the source of both the water-insoluble organic and of the water-soluble organic nitrogen. Urea is used to increase the content of the water-soluble organic nitrogen.

Explanations were sought for the unexpectedly low percentages of organic nitrogen reported frequently by one company making such fertilizers. Erroneous weighing of the ingredients or segregation was not considered a sufficient reason for the analyses consistently lacking a few tenths of a per cent of organic nitrogen. Fertilizer grade urea is known to be practically free from mineral nitrogen as supplied by nitrates and ammonium salts. It had to be determined, whether the results indicated errors in the analytical procedure, or

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When special-purpose fertilizers containing natural organics and urea are analyzed, standard procedures often show lower organic nitrogen than calculated. This work was done to show whether the apparent shortage is due to the analytical procedure or to the hydrolysis of the urea or of the natural organic. Mixtures of natural organics and other fertilizer ingredients, with or without urea, were analyzed. Breakdown of urea was generally low. However, in fertilizers kept at 50° C. for 5 weeks 0.3 to 0.4% of an original 2.2% urea nitrogen was converted. Values for ammoniacal nitrogen were generally high with urea present, giving low apparent organic nitrogen. The error can be held down by not prolonging distillation. Consideration of a low temperature procedure for ammoniacal nitrogen is suggested.

represented actual conversion of organic nitrogen to mineral nitrogen.

In this work urea was tested in the presence of two natural organics regularly sold to fertilizer manufacturers—leather tankage and activated sewage sludge. Simulated fertilizers were prepared and were analyzed in this laboratory and by a commercial analytical firm. Mixtures of the natural organics and ammoniated superphosphate, with and without urea, were also prepared. They were analyzed shortly after their preparation and also after standing for a month or more. Finally, two sets of 8-6-4 and 10-6-4 fertilizers were prepared in the laboratory. Every set included four fertilizers, each of the natural organics being used with and without urea. All of these were analyzed when fresh. One set was analyzed again 5 weeks later.

The results of the analyses made it clear that the standard procedures for the analysis of fertilizers tend to give low results for organic nitrogen and water-soluble organic nitrogen when applied to products of the type under consideration. Even more significantly, direct determinations of urea showed that it was retained practically unchanged, except in samples of fertilizer kept at 50° C. (122° F.) for 5 weeks. Even in these samples, the urea nitrogen decreased by only 0.3 to 0.4%, out of an original 2.2%, and this nitrogen was not actually lost, as it was still present in ammoniacal form.

Sources of Nitrogen

A substantial part of the nitrogen in mixed fertilizers is commonly supplied as anhydrous or aqua ammonia, or as ammoniating solutions, which contain ammonia along with ammonium nitrate, urea, or both. The remaining nitrogen is added in the form of solids, such as ammonium sulfate, ammonium nitrate, urea, and natural organics.

Although not included in this work, urea-formaldehyde products are becoming increasingly important in specialty fertilizers. They may be either formed *in situ* or manufactured separately and later mixed with the other ingredients. The nitrogen in them is mostly organic, partly water-insoluble and partly water-soluble. The water-soluble organic nitrogen represents both free urea and condensation products of low molecular weight, such as methylenediurea. When these products were first introduced to the fertilizer industry they were valued mainly for the water-insoluble nitrogen that they contained. Now, however, it is realized that the water-soluble reaction products are valuable, because they supply readily available nitrogen, yet have very little tendency to burn grass.

Analytical Procedures

Interest was mainly in the official procedures for determining nitrogen (*1*), and these procedures describe a set of four determinations: total nitrogen by a Kjeldahl procedure (*A*); water-insoluble nitrogen, assumed to be organic (*B*); ammoniacal nitrogen, by distillation from a slurry of magnesium oxide (*C*); and nonnitrate, water-soluble nitrogen (*D*) by a procedure involving the removal of nitrate nitrogen by reaction with ferrous sulfate. If *A*, *B*, *C*, and *D* represent the results of the respective determinations,

$$\text{Water-soluble organic nitrogen} = D - C$$

$$\text{Organic nitrogen} = B + D - C$$

If the value for ammoniacal nitrogen is high, while the others are correct, the calculated organic nitrogen and water-soluble organic nitrogen will be low.

In the Nitrogen Division laboratory, determinations were made by both the official and alternative methods. In the latter, an aliquot part of the filtrate containing all of the water-soluble nitrogen is passed through an anion exchange resin column which retains the anions, including the nitrate. The nonnitrate, water-soluble nitrogen in the effluent is determined by Kjeldahl digestion and distillation. The nitrate ions are washed from the column by a solution of sodium chloride and determined by the Devarda method.

Urea nitrogen was determined by a modified form of the procedure developed by Fox and Geldard (*4*). In this modification, a dilute solution of sodium hydroxide is added to the suspension of the weighed sample in water to adjust the pH to 8, as measured by indicator paper. The mixture is filtered, and the insolubles are rinsed thoroughly to get all of the urea into the filtrate. The solution of urea obtained in this manner is nearly free from calcium and phosphate ions, which would interfere with the determination.

Phosphorus pentoxide was determined colorimetrically, as described by Barton (*2*), except that a mixture of nitric and hydrochloric acids was used for digestion. Because phosphorus pentoxide was not of interest in this work, citrate-insoluble phosphorus pentoxide was not determined.

Moisture was determined in two ways, as loss in weight when 5-gram samples were kept in an oven at 100° C. for 5 hours, and when 4-gram samples were kept in a vacuum desiccator at room temperature over Drierite, for approximately 17 hours.

The pH was determined by mixing thoroughly a sample with twice its weight of water and using a glass electrode pH meter.

Materials

Two samples of activated sewage sludge and two of leather tankage were used in this work, both samples of each material being from the same supplier. Analyses of the samples are shown in Table I.

Analyses of some of these samples indicated 0.1 to 0.2% of ammoniacal nitrogen. It was not established in this work whether the natural organics con-

Table I. Data on Natural Organics

	Activated Sludge		Leather Tankage	
	A	*B*	*C*	*D*
Total N, %	5.24	4.91	9.05	8.65
Water-insoluble N, %	4.83	4.40	7.74	7.86
Total P_2O_5, %	6.33	6.86	0.34	0.27
Citrate-insoluble P_2O_5, %	0.88	..	0.20	..
Available P_2O_5, %	5.45	..	0.14	..
Moisture,[a] %	3.22	3.99	8.10	6.16

[a] Loss in weight in 5 hours at 100° C.

tained small amounts of ammonium salts or whether the ammoniacal nitrogen came from the partial hydrolysis of organic compounds during the analytical distillation. It was decided to follow the accepted practice of considering all of the nitrogen in these materials as organic. The small indicated amounts of ammoniacal nitrogen were, therefore, ignored in calculating the theoretical compositions of the various mixtures.

Analysis of the particular lot of pelleted urea used in the first set of samples showed 46.26% total nitrogen, which was completely accounted for as 45.40% urea nitrogen and 0.91% biuret nitrogen. When the analytical distillation, from a slurry of magnesium oxide, indicated the presence of 2.17% ammoniacal nitrogen in the urea, it was misleading, because it did not represent ammonium salts in the urea as supplied, but hydrolysis of part of the urea during the analysis.

The ammoniated superphosphate used in the second part of this work was made by treating normal superphosphate with anhydrous ammonia. Nevertheless, the analysis indicated 0.18% water-insoluble nitrogen, including in the 4.55% total nitrogen, the remaining 4.37% being water-soluble, presumably ammoniacal. Distillation with magnesium oxide yielded 4.12% ammoniacal nitrogen, and distillation with sodium hydroxide yielded 4.24%. In computing the theoretical values shown in Tables III and IV, the ammoniated superphosphate was taken to contain 0.18% water-insoluble nitrogen, which would be counted as organic nitrogen, whatever its actual form of combination, and 4.37% ammoniacal nitrogen.

Comparative Analyses

Two simulated fertilizers were prepared, one containing leather tankage, the other with no natural organic. In order to avoid possible errors at this point due to faulty sample splitting, two batches of each kind were made separately, one being sent to a commercial analytical firm, and the other analyzed in this laboratory. The compositions are given in Table II, along with the theoretical results and those actually found in the two laboratories. The commercial firm did not determine urea nitrogen. Moreover, it did not report water-soluble nitrate nitrogen. The values given in Table II were calculated by subtracting the sum of the reported nitrate and water-insoluble nitrogen from the total nitrogen.

Ammoniacal nitrogen was high in every case, and the percentages of organic nitrogen and water-soluble organic nitrogen found were substantially lower than calculated. On the other hand, the values found for urea nitrogen were close to the theoretical ones.

Table II. Comparative Analyses of Simulated Fertilizers

	A Leather Tankage 12-9-5		B No Organic Material 15-17-10	
	Grams per Batch	%	Grams per Batch	%
Composition				
Pelleted urea (ground)	20	9.09	20	16.67
Dicalcium phosphate, reagent	40	18.18	40	33.33
Ammonium sulfate, reagent	30	13.64	30	25.00
Ammonium nitrate, reagent	10	4.55	10	8.33
Potassium chloride, reagent	20	9.09	20	16.67
Leather tankage, sample C	100	45.45	None	...
Total	220	100.00	120	100.00

	Analytical Values					
	Theoretical	Commercial Laboratory	Nitrogen Division	Theoretical	Commercial Laboratory	Nitragen Division
AOAC determinations						
Total N, %	12.78	12.60	12.63	15.89	15.54	15.56
Water-insoluble N, %	3.52	3.51	3.46	None	0.02	...
Ammoniacal N, %	3.67	4.03	3.78	6.72	7.05	6.88
Water-soluble, non-nitrate N, %	8.47	8.59	8.37	14.44	14.33	14.42
Derived values						
Water-soluble N, %	9.26	9.09	9.17	15.89	15.52	15.56
Nitrate N, %	0.79	0.50	0.80	1.45	1.19	1.14
Mineral N, %	4.46	4.53	4.58	8.17	8.24	8.02
Organic N, %	8.32	8.07	8.05	7.72	7.30	7.54
Water-soluble organic N, %	4.80	4.56	4.59	7.72	7.28	7.54
Unofficial determinations						
Urea N, %	4.13	...	4.15	7.57	...	7.60
Nitrate N (by ion exchange resin method), %	0.79	...	0.75	1.45	...	1.40

Table III. Mixtures of Ammoniated Superphosphate and Natural Organics

	Composition by Weight					
Ammoniated superphosphate, %	75	50	25	75	50	25
Activated sewage sludge, sample A, %	25	50	75	...	...	...
Leather tankage, sample C, %	...	...	...	25	50	75
Total N %						
Theoretical	4.72	4.90	5.07	5.68	6.80	7.92
1 day	4.90	5.00	5.18	5.77	6.91	8.06
1 month[a]	4.79	4.95	5.13	5.78	6.91	8.02
Water-insoluble N, %						
Theoretical	1.34	2.51	3.67	2.07	3.96	5.85
1 day	1.35	2.47	3.67	2.14	4.06	5.99
1 month[a]	1.41	2.38	3.79	2.17	4.10	6.03
Ammoniacal N, %						
Theoretical	3.28	2.18	1.09	3.28	2.18	1.09
7 weeks[a]	3.20	2.20	1.15	3.32	2.30	1.24

[a] At room temperature.

Mixtures with Ammoniated Superphosphate

The ammoniated superphosphate described above was used in the following sets of mixtures:

75-25, 50-50, and 25-75 mixtures with activated sewage sludge (Sample A) and leather tankage (Sample C).

50-25-25, 33.34-33.33-33.33, and 25-37.5-37.5 mixtures with crystal urea and one or the other of the above organic by-products. The results are discussed below.

Data on the mixtures without urea are in Table III, and those on mixtures with urea are in Table IV.

Percentages of total nitrogen found in the mixtures without urea (Table III) were slightly high. Those in the mixtures containing urea (Table IV) were substantially higher than the theoretical values, especially at one month. The reason for this is unknown. The percentages of water-insoluble nitrogen in both groups of mixtures were close to the theoretical values.

For the mixtures without urea, percentages of ammoniacal nitrogen found were close to the theoretical ones. The picture is different for the mixtures containing urea, in which considerably more than the theoretical percentages of ammoniacal nitrogen were found. Because this was not true of the mixtures without urea, it is assumed that most of the excess ammoniacal nitrogen resulted from hydrolysis of the urea during the

analysis. The theoretical percentages of urea nitrogen were found by the urease method; hence it was evident that urea had not been converted before the analyses. Even after storage for a month at room temperature, the average percentage of urea nitrogen dropped by only 0.13%. The urea in the mixtures was stable.

Analysis of Laboratory-Made Fertilizers

As a closer approach to industrial practice, two sets of fertilizers, called *P* and *Q*, were made for analysis. Each set comprised four fertilizers, according to the formulations in Table V. There were two 8-6-4 samples, one containing activated sludge, the other containing leather tankage. These were without urea. The remaining two fertilizers contained the same natural organics, but they were 10-6-4 with over 2% nitrogen supplied as urea.

Because preliminary experiments had shown the possibility of sampling errors when coarse ingredients were used, the ingredients of these batches were all made at least fine enough to pass through a 14-mesh (Tyler) sieve, and the completed fertilizers were passed through the same sieve.

These fertilizers were made in a laboratory ammoniator, 13 inches in inside diameter and 4 inches long, the same one, except for changes in the solution handling equipment, as was described by Datin, Worthington, and Poudrier (*3*).

Each batch was divided into 2 parts, which were stored in tightly closed bottles, one at 30° C. (86° F.), the other at 50° C. (122° F.). Samples taken at the indicated times were ground for analysis. The values found for each fertilizer were reduced to a common basis—namely, the theoretical moisture content by the oven method, based on the moisture contents of the ingredients and the water released when hydrated monocalcium phosphate is ammoniated. The adjusted data range from 96.3 to 101.5% of those actually found.

Considering the 1-day analyses of the fertilizers in set *P*, as shown in Table VI, the percentages of ammoniacal nitrogen found ran higher than the theoretical ones, in the fertilizers without urea, and considerably higher than the theoretical ones in the fertilizers containing urea. The percentages of urea nitrogen found by direct determination are close to the theoretical ones.

The 5-week analyses gave a similar picture, although differences between experimental and theoretical values were larger. There is one striking difference. Direct determinations of urea nitrogen in the samples of the 10-6-4 fertilizers stored at 30° C. still showed very close to the theoretical 2.20% urea nitrogen, but in the samples stored at 50° C. the urea nitrogen had fallen off to 1.80% in one case and 1.85% in the other. There were corresponding increases in ammoniacal nitrogen. The change is not great, but it indicates that at this temperature there was actually some conversion of urea nitrogen to ammoniacal nitrogen over 5 weeks.

The last set of fertilizers, *Q*, was made about 3 months after set *P*. The same kinds of natural organics were used as before, but each was represented by a new sample.

Table VII gives the analyses, which were made only after the 1-day storage period. Except for the urea determinations, all nitrogen analyses were done by AOAC procedures. The distillations were not prolonged in the determination of ammoniacal nitrogen.

The analytical values found are close to those calculated. In particular, the percentages of ammoniacal nitrogen, organic nitrogen, and water soluble organic nitrogen average close to the theoretical ones. The percentages of urea nitrogen are 0.07% below the theoretical ones, a difference that can scarcely be considered significant.

Table IV. Mixtures of Ammoniated Superphosphate, Urea, and Natural Organics

	Composition by Weight					
Ammoniated superphosphate, %	50	33.34	25	50	33.34	25
Urea (crystal), %	25	33.33	37.5	25	33.33	37.5
Activated sewage sludge, sample A, %	25	33.33	37.5	...	...	...
Leather tankage, sample C, %	...	...	...	25	33.33	37.5
Total N, %						
Theoretical	15.16	18.70	20.46	16.11	19.96	21.89
1 day	15.43	18.73	20.68	16.12	20.21	22.04
1 month[a]	15.58	19.32	20.96	16.55	20.45	22.33
Water-insoluble N, %						
Theoretical	1.30	1.67	1.86	2.02	2.64	2.95
1 day	1.34	1.75	1.80	2.06	2.75	2.98
1 month[a]	1.24	1.69	1.87	1.97	2.62	2.94
Ammoniacal N, %						
Theoretical	2.18	1.46	1.09	2.18	1.46	1.09
1 day	2.81	2.35	2.09	2.85	2.42	2.24
1 month[a]	2.62	2.08	1.81	2.63	2.01	1.76
Urea N, %						
Theoretical	11.58	15.43	17.36	11.58	15.43	17.36
1 day	11.69	15.87	17.42	11.79	15.50	17.45
1 month[a]	11.61	15.58	17.21	11.64	15.53	17.38

[a] At room temperature.

Table V. Formulations of Fertilizers

	8-6-4 Activated Sludge	8-6-4 Leather Tankage	10-6-4 Activated Sludge	10-6-4 Leather Tankage
	Urea			
	None	None	Present	Present
Ingredients, lb./ton				
Natural organic[a]	830	521	861	541
Urea[b]	...	...	95	95
Ammonium sulfate	387	289	380	277
Ammoniating solution[c]	92	143	90	143
Normal superphosphate	403	628	395	628
Potassium chloride	142	142	142	142
Dolomite	50	50	37	50
Clay	96	227	...	124

[a] Table I. A and C used in set *P*, B and D used in set *Q*.
[b] Crystal urea (46.3% N) used in set *P*; pelleted urea (46.47% total N, 45.32% urea N) used in set *Q*.
[c] Ammoniating solution. 22.2% NH_3, 65.0% NH_4NO_3, 12.8% H_2O, 41.0% total N.

Discussion

In general, direct determination of urea in the mixtures, using a modified Fox and Geldard (*4*) procedure, showed that all of the urea put into the mixtures was actually present even after a month. Even in mixtures of ammoniated superphosphate, natural organic, and urea, with the urea nitrogen at the unusually high levels of 11 to 17%, the apparent losses of urea nitrogen averaged only 0.13% in 1 month at room temperature.

The preceding paragraph does not apply to samples kept at 50° C. for 5 weeks. In these cases, about 0.3 to 0.4% out of an original 2.2% of urea nitrogen was converted to ammoniacal nitrogen. This suggests that if it is

Table VI. Analyses of Fertilizers—Set P

	8-6-4 No Urea Activated Sludge A			8-6-4 No Urea Leather Tankage C			10-6-4 Urea Present Activated Sludge A			10-6-4 Urea Present Leather Tankage C		
	Theoretical	Found at Storage Temperature 30° C.	50° C.	Theoretical	Found at Storage Temperature 30° C.	50° C.	Theoretical	Found at Storage Temperature 30° C.	50° C.	Theoretical	Found at Storage Temperature 30° C.	50° C.
One-day analyses												
Total N (ion exchange), %	8.19	8.18	8.28	8.41	8.48	8.46	10.36	10.49	10.42	10.57	10.62	10.64
Water-insoluble N, %	2.05	2.20	2.14	2.08	2.19	2.16	2.12	2.34	2.13	2.16	2.27	2.20
Ammoniacal N, %	5.45	5.41	5.47	5.17	5.27	5.22	5.35	5.60	5.69	5.05	5.26	5.31
Water-soluble nonnitrate N (ion exchange), %	5.62	5.50	5.67	5.52	5.55	5.52	7.73	7.66	7.84	7.60	7.60	7.67
Nitrate N (ion exchange), %	0.52	0.48	0.47	0.81	0.74	0.78	0.51	0.49	0.45	0.81	0.75	0.77
Urea N, %	...	...	...	...	...	...	2.20	2.25	2.13	2.20	2.25	2.25
Mineral N, %	5.97	5.89	5.94	5.98	6.01	6.00	5.86	6 09	6.14	5.86	6.01	6.08
Organic N, %	2.22	2.29	2.34	2.43	2.47	2.46	4.50	4.40	4.28	4.71	4.61	4.56
Water-soluble organic N, %	0.17	0.09	0.20	0.35	0.28	0.30	2.38	2.06	2.15	2.55	2.34	2.36
Total P_2O_5, %	6.92	7.11	7.14	6.77	7.02	6.79	6.93	7.12	7.13	6.77	6.96	6.96
Oven moisture, %	3.99	3.99	3.99	6.28	6.28	6.28	3.94	3.94	3.94	6.31	6.31	6.31
Five-week analyses												
Total N (ion exchange), %	8.19	8.53	8.47	8.41	8.48	8.51	10.36	10.86	10.53	10.57	10.58	10.61
Water-insoluble N, %	2.05	2.13	2.04	2.08	1.87	2.08	2.12	2.18	2.18	2.16	2.20	1.98
Ammoniacal N, %	5.45	5.61	5.68	5.17	5.29	5.19	5.35	5.51	5.72	5.05	5.17	5.40
Water-soluble nonnitrate N (ion exchange), %	5.62	5.89	5.93	5.52	5.85	5.59	7.73	8.19	7.86	7.60	7.69	7.91
Nitrate N (ion exchange), %	0.52	0.51	0.50	0.81	0.76	0.84	0.51	0.51	0.49	0.81	0.69	0.72
Urea N, %	...	...	...	...	...	...	2.20	2.26	1.80	2.20	2.17	1.85
Mineral N, %	5.97	6.13	6.18	5.98	6.05	6.03	5.86	6.02	6.21	5.86	5.86	6.12
Organic N, %	2.22	2.41	2.29	2.43	2.43	2.48	4.50	4.84	4.32	4.71	4.72	4.49
Water-soluble organic N, %	0.17	0.28	0.25	0.35	0.56	0.40	2.38	2.68	2.14	1.55	2.52	2.51
Total N (AOAC method), %	8.19	8.44	8.39	8.41	8.60	8.58	10.36	10.57	10.65	10.57	10.68	10.77
Water-soluble nonnitrate N ($FeSO_4$), %	5.62	5.79	5.71	5.52	5.45	5.42	7.73	7.87	...	7.60	7.56	...
Nitrate N (by difference), %	0.52	0.52	0.64	0.81	1.28	1.08	0.51	0.54	...	0.81	0.92	...
Mineral N, %	5.97	6.13	6.32	5.98	6.57	6.27	5.86	6.05	...	5.86	6.09	...
Oven moisture	3.99	3.99	3.99	6.28	6.28	6.28	3.94	3.94	3.94	6.31	6.31	6.31

Formulations are in Table V. Actual analyses have been adjusted to the bases of the respective theoretical moisture contents.

Table VII. Analyses of Fertilizers—Set Q

	8-6-4 No Urea Activated Sludge B			8-6-4 No Urea Leather Tankage D			10-6-4 Urea Present Activated Sludge B			10-6-4 Urea Present Leather Tankage D		
	Theoretical	Found at Storage Temperature 30° C.	50° C.	Theoretical	Found at Storage Temperature 30° C.	50° C.	Theoretical	Found at Storage Temperature 30° C.	50° C.	Theoretical	Found at Storage Temperature 30° C.	50° C.
One-day analyses												
Total N (AOAC method), %	8.01	7.93	7.89	8.24	8.18	8.13	10.18	10.19	10.18	10.41	10.33	10.25
Water-insoluble N, %	1.83	1.93	1.89	2.05	2.11	2.12	1.89	2.00	1.89	2.13	2.20	2.19
Ammoniacal N, %	5.45	5.33	5.33	5.17	5.09	5.13	5.35	5.29	5.38	5.05	5.05	5.07
Water-soluble, nonnitrate N ($FeSO_4$) %	5.66	5.39	5.61	5.38	5.32	5.30	7.78	7.61	7.77	7.47	7.53	7.37
Nitrate N (by difference), %	0.52	0.61	0.39	0.81	0.75	0.71	0.51	0.58	0.52	0.81	0.60	0.69
Urea N (Urease method), %	...	...	...	...	...	...	2.15	2.06	2.11	2.15	2.10	2.06
Mineral N, %	5.97	5.94	5.72	5.98	5.84	5.84	5.86	5.87	5.90	5.86	5.65	5.76
Organic N, %	2.04	1.99	2.17	2.26	2.34	2.29	4.32	4.32	4.28	4.55	4.68	4.49
Water-soluble organic N, %	0.21	0.06	0.28	0.21	0.23	0.17	2.43	2.32	2.39	2.42	2.48	2.30
Total P_2O_5, %	7.07	6.83	6.99	6.65	6.74	6.51	7.09	7.26	7.01	6.65	6.85	6.77
Oven moisture, %	4.20	4.20	4.20	5.62	5.62	5.62	4.17	4.17	4.17	5.62	5.62	5.62
Vacuum moisture, %	...	2.19	1.96	...	2.89	2.90	...	2.60	2.56	...	3.58	3.43
pH	...	5.75	5.20	...	5.50	4.75	...	5.60	5.10	...	5.30	4.85

Formulations are in Table V. Actual analyses have been adjusted to the bases of the respective theoretical moisture contents, except that actual values of vacuum moisture are given.

important to retain the urea unchanged, fertilizers containing it should be at the lowest practical temperature when sent to storage.

It is concluded that erroneously high values for ammoniacal nitrogen are a likely cause of apparent losses of organic nitrogen in fertilizers of the type being considered. The high values for ammoniacal nitrogen are caused by hydrolysis of part of the urea in the determination, even in distillation from a slurry of magnesium oxide. This error can be minimized by strictly limiting the amount of distillate to that required by the AOAC "Official Methods of Analysis"; it is doubtful however, if this will suffice, when a large amount of urea is

present. It is suggested that a low temperature procedure, such as the one proposed by Yee and Davis (*5*) be considered.

The natural organics contribute significantly to the apparent ammoniacal nitrogen. It is not known whether ammoniacal nitrogen actually exists in these products or is liberated during the analytical distillation. The above error is partially offset by the tendency for part of the ammoniacal nitrogen in ammoniated superphosphates not to appear as such.

Inspection of all the results shows that, because of errors in preparation, sampling, or analysis, results for any particular form of nitrogen will frequently differ from the calculated ones by 0.2% and more.

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BIOCHEMICAL CHANGES IN PLANT DISEASE

Effect of *Fusarium Oxysporum f. Lycopersici* and Its Metabolites on Leaf Constituents of Susceptible and Resistant Tomatoes

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Extracts from leaves of inoculated and uninoculated tomato plants of varieties susceptible or resistant to Fusarium wilt and of cuttings from plants treated with pectic enzymes, fusaric acid, and lycomarasmin solutions were examined by paper chromatography and compared as to relative amounts of free amino acids, sugars, some acidic components, and phenols present. Healthy plants of both varieties were very similar in respect to these constituents. Following infection, a great number of components changed in concentration in plants of the susceptible variety; little or no change was observed in resistant plants. Many changes were nonspecific and secondary because of dehydration of the tissue by the wilting agents. In contrast, some were specifically induced by the primary action of the parasite or its metabolites. Fusaric acid produced changes characteristic of those in inoculated susceptible plants. An acidic component of the host tissue, obviously an organic phosphate, was affected in a way that suggests it is related to resistance.

Plant diseases are commonly recognized by the characteristic morphological or cytological symptoms associated with them. These symptoms are a reflection of changes in the chemical and biochemical constituents of the plant cells, arising from the interaction of the parasite and the host. This interaction must result in changes in many different cell constituents. Some of these changes cause visible symptoms; other changes must occur which cannot be so readily seen. It is therefore of interest to investigate the biochemical symptoms of infection. The development of paper chromatography has provided a convenient tool for studying such changes in a number of plant constituents and relating these changes to the disease syndrome.

Pectolytic enzymes (*6, 12*), as well as the toxic metabolites fusaric acid (*2*) and lycomarasmin (*4*) produced by *Fusarium oxysporum f. lycopersici* (Sacc.) Snyder and Hansen, play important roles in the development of tomato wilt. The purpose of the present investigation was to determine by paper chromatographic methods changes in leaf constituents of inoculated and uninoculated tomato plants and in cuttings from such plants exposed to the enzyme and toxin preparations.

Materials and Methods

Plants of the susceptible variety Bonny Best and the monogenic resistant variety Jefferson were used. Seeds were sown in vermiculite and at 8 days uniform seedlings were transplanted singly to sand in 4-inch clay pots. At 20 days after transplanting uniform plants of both varieties were inoculated by the root-dipping technique (*13*) with an 8-day still culture of the pathogen grown on modified Richard's medium. Control plants were similarly treated, except that the roots were not dipped in the inoculum. Plants in vermiculite and in sand were watered on alternate days with Hoagland's nutrient solution and distilled water, respectively. The plants were grown during April and May 1957 in a greenhouse at Madison, Wis., which was maintained at approximately 28° C. Water and nutrient solution were allowed to come to this temperature before use. The inoculated, susceptible plants showed severe stunting and distortion of young leaves at 12 days, while the only symptom in resistant plants was a slight stunting.

Cuttings, which included the four uppermost leaves of the plant, were made on the twelfth day after inoculation from certain of the healthy plants of both varieties and were divided into the several treatment groups. Twenty-five plants were used in each treatment group.

Pectinase Treatment (bP, jP). The stems of cuttings were placed in 70% ethanol for 2 minutes and the ends were removed with a sterile razor blade. The cuttings were then placed in Erlenmeyer flasks containing a 0.5% solution of pectolytic enzymes prepared from a culture of the pathogen by S. S. Gothos-

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