Determination of Urea in Agricultural Nitrogen Solutions

DELORA K. GULLSTROM and P. A. DEMKOVICH

Research Department, Standard Oil Co. (Indiana), Whiting, Ind.

Existing methods for the determination of urea in solutions of ammonia and ammonium nitrate were slow and unreliable. A rapid and accurate method was therefore developed. Urea is decomposed with nitrous acid, the evolved carbon dioxide is absorbed in barium hydroxide, and the excess base is titrated. The method is in routine use and exhibits repeatability of about ±2.0% of the urea present.

UREA IS GAINING INCREASING IMPORTANCE as an ingredient in nitrogen solutions when a base for long-lasting nitrogen fertilizers is desired. Although analytical procedures for ammonium nitrate and free ammonia in aqueous nitrogen solutions are well established, a rapid and accurate method for determining urea in these solutions is not available. To control both blending and shipping operations, urea is determined over a wide range of concentrations in nitrogen solutions and base stocks.

Classical methods for determining urea are neither fast nor accurate enough for routine control. The free ammonia is generally determined by titration with acid. Ammonium nitrate is determined by titrating with sodium hydroxide the nitric acid released in the presence of formaldehyde. Urea can be determined indirectly by a Kjeldahl analysis for total nitrogen; the difference between total nitrogen and that obtained from the ammonia and the ammonium nitrate represents urea. But a Kjeldahl analysis requires 5 to 6 hours and therefore is not useful for blending control. Moreover, cumulative errors in the three analyses can cause the urea determination to become unreliable.

Several direct methods that have been used for the determination of urea were tried. A ureometer method (*4, 5*) similar to that used in clinical analysis, in which sodium hypobromite decomposes urea to evolve nitrogen, lacked precision. A potentiometric titration with chloramine T (*6*) gave no detectable end point in nitrogen solutions, because of the high ionic strength of these solutions. General colorimetric determinations using potassium nitroprusside (*7*), diacetyl, benzoylacetyl (*3*), diazosulfanilic acid (*9*), and *p*-dimethylaminobenzaldehyde (*2*) gave poor sensitivity or precision and were discarded.

Two analytical methods in common use are the urease hydrolysis of urea (*11*) to ammonia and carbon dioxide, and the Van Slyke method (*10*) in which primary amines are decomposed with nitrous acid to carbon dioxide and nitrogen. The ammonia is titrated in the urease method; the volume of nitrogen is measured in the Van Slyke method. The first of these methods was discarded, because precision was poor and the elapsed time required—although shorter than that for a Kjeldahl—was still longer than the desired goal of 1 hour. A recently published paper, however, indicates that the urease hydrolysis method has been adapted to the determination of urea in nitrogen solutions (*8*). The Van Slyke nitrogen determination is also time-consuming, and the large concentrations of ammonia and ammonium nitrate could cause interference by releasing nitrogen.

Because urea is the only carbon compound in nitrogen solutions, measurement of the carbon dioxide evolved by its reaction with nitrous acid should be completely free of interference. A trial on a sample of known urea concentration showed that the evolution of carbon dioxide is quantitative. A trial on a solution of ammonia and ammonium nitrate without urea proved the absence of interferences. Indications were that the elapsed time for a test would be about 1 hour. These studies led to the development of a satisfactory direct method for determination of urea.

Apparatus and Reagents

Glassware as shown in Figure 1.

Sulfuric acid, 1 to 4.

Potassium permanganate, 0.5*N*, with 30 ml. of concentrated sulfuric acid added per liter.

Barium hydroxide–barium chloride solution, 16 grams of barium hydroxide and 32 grams of barium chloride in 1 liter of water.

Sodium nitrite, 5% solution. Prepared fresh every 2 days.

Hydrochloric acid, 0.1*N*, standardized.

Procedure

Weigh about 100 grams of the sample solution into a 500-ml. volumetric flask that contains about 200 ml. of water, and dilute to the mark. Pipet an aliquot of the diluted sample into the reaction flask. The aliquot should contain between 0.1 and 0.2 gram of urea. Add 20 ml. of sulfuric acid, 1 to 4. Bubble nitrogen through this solution for 5 minutes at 0.5 liter per minute. Attach two gas-absorption bottles to the reaction flask with Tygon or rubber tubing. Place 100 ml. of the acid permanganate in the first bottle. Into the second bottle, pipet 100 ml. of the barium hydroxide–barium chloride solution and add 50 ml. of carbon dioxide–free water. Add 10 ml.

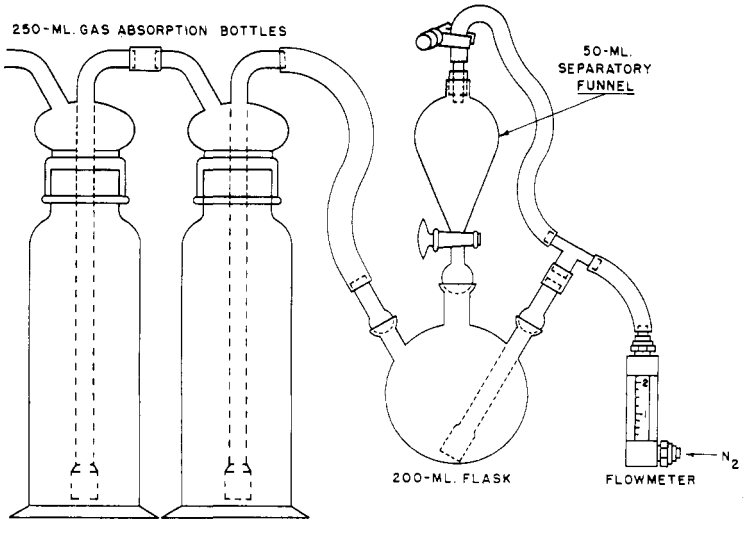

Figure 1. Apparatus for determination of urea

Table I. Precision and Accuracy

Urea Present, %	Urea Found, % Analyst I	Analyst II	Analyst III	ASTM Standard Deviation	ASTM Repeatability[a]
6.00	6.04	6.01	6.09		
	6.05	5.96	6.05		
	6.16	5.98	6.01		
	5.98	5.90	6.17	0.07	0.22
40.0	41.0	40.3	42.3[b]		
	40.9	40.9	40.8		
	40.8	40.3	40.0		
	40.7	39.7	39.2	0.05	1.6
70.0	71.0	70.1	70.9		
	71.0	69.9	69.9		
	68.0	69.9	70.4		
	70.5	69.9	69.1	0.7	2.2

[a] At 95% probability level.
[b] Statistically deviant; not used in calculations.

Table II. Duplicate Urea Determinations on Production Samples

Urea, % Low concn.	High concn.
5.92	51.4
6.08	52.1
5.76	49.5
5.81	51.3
6.05	45.8
5.85	44.6
4.21	70.0
4.17	71.4
s 0.09	0.8
ASTM repeatability 0.28	2.6

of 5% sodium nitrite to the reaction flask through the separatory funnel, equalizing the pressure with either air or nitrogen. Allow nitrogen to bubble through the solution in the reaction flask for 20 minutes. Remove the bottle containing the barium hydroxide and titrate with 0.1N hydrochloric acid to a phenolphthalein end point. In the same manner, titrate another 100-ml. aliquot of the barium hydroxide–barium chloride solution as a blank.

Calculate the concentration of urea in the sample by the relationship:

$$\% \text{ urea} = \frac{(B - S) \times N \times 3.0 \times V}{W \times A}$$

where B is the titration for the blank, ml.; S is the titration for the sample, ml.; N is the normality of the hydrochloric acid; V is the volume to which the sample is diluted, ml.; W is the sample weight, grams; and A is the aliquot used in the analysis, ml.

Discussion

The chemical reaction that represents the decomposition of urea with nitrous acid is:

$$2\,HNO_2 + H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \rightarrow 2\,N_2 + CO_2 + 3\,H_2O$$

If the evolved carbon dioxide is used to measure the urea content, carbon dioxide from other sources must be excluded from the system. In running a sample, therefore, sulfuric acid is added first and nitrogen is bubbled through the solution to remove all the dissolved carbon dioxide.

Because urea hydrolyzes in any acid solution, it was necessary to establish the rate at which it decomposes. No decrease in apparent urea content was observed after 10 minutes of aeration; after 20 minutes a loss of about 3% was noted. Urea decomposition is negligible, because only 5 minutes of aeration were found to be required for removal of dissolved carbon dioxide.

The evolved gases are passed through a solution of acidified potassium permanganate to remove the oxides of nitrogen, which are generated by the excess nitrous acid and would interfere in the analysis by using up barium hydroxide.

The gases then pass into the barium hydroxide–barium chloride solution, where the carbon dioxide reacts to precipitate barium carbonate. Unless the amount of barium hydroxide considerably exceeds that required to react with the carbon dioxide, the results obtained are low. The addition of barium chloride to the barium hydroxide furnishes enough barium ion to absorb the carbon dioxide completely without a large excess of the base. Only one washing bottle is required, and the titration is large enough to give sufficient precision.

The time required for the complete evolution and absorption of carbon dioxide was studied. The nitrogen bubbling rate was maintained at 0.5 liter per minute through the reaction flask. After a reaction time of 10 minutes, 93.4% of the carbon dioxide was recovered. Twenty minutes gave 99.4% recovery, and 30 minutes did not increase it. On the basis of these data, the reaction time for the analysis was set at 20 minutes.

Precision and Accuracy

To establish the precision and accuracy of the method, three synthetic nitrogen solutions containing known concentrations of urea were analyzed by three analysts on different days (Table I). There are no assignable differences among the results obtained by the three analysts. ASTM standard deviation and repeatability (*1*) show that the greatest difference between duplicate results at the 95% probability level should not exceed about 2% of the amount of urea present. Comparison of the analytical results with the known values by means of the t test indicates no significant differences at the 95% probability level.

Table II shows typical data obtained on routine production samples. The standard deviations and the repeatabilities are in good agreement with those obtained on the synthetic samples.

Conclusion

The method is rapid and precise for determination of urea in the presence of high concentrations of ammonia and ammonium nitrate. It can also be used to analyze aqueous urea concentrates. It has been in routine control use for over 4 months and has given satisfactory results when performed by nontechnical personnel. Elapsed time per test is about 1 hour.

Literature Cited

(1) ASTM Standards on Petroleum Products and Lubricants, Committee D-2, November 1956.
(2) Cline, R. E., Fink, R. M., *Anal. Chem.* **28,** 47 (1956).
(3) Dickenmann, R. C., Crafts, B., Zak, B., *Am. J. Clin. Pathol.* **24,** 981 (1954).
(4) Fenton, H. J. H., *J. Chem. Soc.* **33,** 300 (1878).
(5) Knop, *Z. anal. Chem.* **9,** 226 (1870).
(6) Kolthoff and Belcher, "Volumetric Analysis," Vol. III, p. 643, Interscience, New York, 1957.
(7) Pittarelli, E., *Arch. Farmacol. sper.* **45,** 173 (1928).
(8) Smith, J. A., Dock, D. G., Rich, R. W., J. Agr. Food Chem. **6,** 587 (1958).
(9) Snell, F. D., Snell, C. T., "Colorimetric Methods of Analysis," 3rd ed., Vol. IV, p. 323, Van Nostrand, New York, 1954.
(10) Van Slyke, D. D., *J. Biol. Chem.* **73,** 449 (1927).
(11) Van Slyke, D. D., Cullen, G. E., *J. Am. Med. Assoc.* **62,** 1558 (1914).

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