

Determination of Kjeldahl Nitrogen in Fertilizers by AOAC Official MethodSM 978.02: Effect of Copper Sulfate as a Catalyst

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In AOAC Official MethodSM 955.04, Nitrogen (Total) in Fertilizers, Kjeldahl Method, fertilizer materials are analyzed using mercuric oxide or metallic mercury (HgO or Hg) as a catalyst. AOAC Official MethodSM 970.02, Nitrogen (Total) in Fertilizers is a comprehensive total nitrogen (including nitrate nitrogen) method adding chromium metal. AOAC Official MethodSM 978.02, Nitrogen (Total) in Fertilizers is a modified comprehensive nitrogen method used to measure total nitrogen in fertilizers with two types of catalysts. In this method, either copper sulfate or chromium metal is added to analyze for total Kjeldahl nitrogen. In this study, the part of AOAC Official MethodSM 978.02 that is for nitrate-free fertilizer products was modified. The objective was to examine the necessity of copper sulfate as a catalyst for the nitrate-free fertilizer products. Copper salts are not environmentally friendly and are considered pollutants. Products such as ammonium sulfate, diammonium phosphate, monoammonium phosphate, urea-containing fertilizers such as isobutylene diurea (IBDU), and urea-triazone fertilizer solutions were examined. The first part of the study was to measure Kjeldahl nitrogen as recommended by AOAC Official MethodSM 978.02. The second part of the study was to exclude the addition of copper sulfate from AOAC Official MethodSM 978.02 to examine the necessity of copper sulfate as a catalyst in nitrate-free fertilizers, which was the primary objective. Our findings indicate that copper sulfate can be eliminated from the method with no significant difference in the results for the nitrogen content of the fertilizer products.

The Kjeldahl method was developed in 1883 (1). It is used for the quantitative determination of nitrogen in various chemical substances. It involves the digestion of the nitrogen-containing compounds with sulfuric acid using heat and conversion of the nitrogen to ammonium ions. Potassium sulfate is added to increase the boiling point of the acid solution. The solution is then distilled with caustic soda (NaOH) to liberate ammonia gas, which is absorbed in a sulfuric acid solution. Part of the sulfuric acid solution is neutralized by the

evolved ammonia gas, and the excess acid is back-titrated with sodium hydroxide.

There are several AOAC Official MethodsSM regarding the Kjeldahl digestion (2). AOAC Official MethodSM 955.04 for total nitrogen in fertilizers includes the use of catalysts such as mercuric oxide or metallic mercury, zinc granules, and zinc dust. Parts C and D of AOAC 955.04 are improved approaches for nitrate-free fertilizer materials and nitrate-containing fertilizer materials, respectively. AOAC Official MethodSM 970.02 for determination of total nitrogen in fertilizers includes the use of catalysts such as chromium metal and alundum. Alundum is mixture of aluminum oxide, silicate, ferric oxide, potassium oxide, and sodium oxide. AOAC Official MethodSM 970.03 is applicable to all fertilizers except nitric phosphate compounds and uses Raney nickel powder as a catalyst. AOAC Official MethodSM 920.03 (magnesium oxide method) and AOAC Official MethodSM 920.04 (formaldehyde titration method) are used for ammoniacal nitrogen determination in fertilizers.

AOAC Official MethodSM 978.02 is for the determination of nitrogen (total) in fertilizers (Kjeldahl method) and is a modified comprehensive nitrogen method (Final Action 1984). In this method, there are two ways to measure total nitrogen: one is to add copper sulfate to analyze for total Kjeldahl nitrogen, and the second is to proceed by adding chromium metal to analyze for total nitrogen, including nitrate nitrogen.

The first approach involves the use of anhydrous copper sulfate or copper sulfate pentahydrate catalyst and alundum for the nitrogen determination. Both copper and fused-aluminum oxide are environmentally hazardous materials. The second option is to proceed by adding chromium metal to analyze for total nitrogen, including nitrate nitrogen. Chromium is also an environmentally hazardous substance.

In order to determine whether the use of copper sulfate is necessary, a series of measurements were done with and without copper sulfate catalyst. Early on in an internal series of studies, when determining the total nitrogen in a variety of fertilizers, including ammonium sulfate, monoammonium phosphate (MAP), diammonium phosphate (DAP), urea-containing fertilizers such as isobutylene diurea (IBDU), and urea-containing triazone fertilizers, we determined that the presence of the alundum is not necessary, and it was replaced with glass beads.

Study Objectives

In this study, several types of fertilizer compounds were selected, and the total Kjeldahl nitrogen for each fertilizer was measured using two procedures to determine the effect of elimination of the copper sulfate catalyst:

(a) The procedure outlined in AOAC Method 978.02 (16th Ed.) is followed in principle (with modifications for scaling

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Table 1. Summarized total Kjeldahl nitrogen measurements by the digestion method

Compound	Formulation	Cupric sulfate added, 0.4 g		<i>n</i> (x) ^a	Range of bias	
		Yes	No		Yes	No
Ammonium sulfate ^b	21.18% N	21.15 ± 0.05	21.12 ± 0.08	1 (38)	0.039	0.053
TRISERT-K ^c	5-0-20-13S	5.22 ± 0.16	5.21 ± 0.17	4 (8)	0.118	0.128
TRISERT-KS ^c	15-0-12-8S	14.91 ± 0.00	14.92 ± 0.01	1 (4)	0.000	0.005
N-SURE ^c	28-0-0	28.02 ± 0.15	28.03 ± 0.15	20 (38)	0.113	0.115
TRISERT-N ^c	26-0-0	29.93 ± 0.33	29.94 ± 0.25	1 (4)	0.235	0.180
TRISERT-CB ^c	26-0-0-5B	25.86 ± 0.04	25.90 ± 0.08	1 (4)	0.025	0.055
TRISERT-NB ^c	26-0-0	26.11 ± 0.16	26.10 ± 0.19	20 (38)	0.133	0.143
FORMOLENE-PLUS ^c	30-0-0	30.00 ± 0.08	29.97 ± 0.14	8 (10)	0.058	0.120
CR-9 ^c	29.5-0-0	29.37 ± 0.00	29.34 ± 0.00	1 (4)	0.000	0.000
DAP (diammonium phosphate) ^{d,e}	18-46-0	17.66 ± 0.07	17.60 ± 0.07	12 (24)	0.055	0.075
MAP (monoammonium phosphate) ^d	11-52-0	10.93 ± 0.18	10.97 ± 0.33	6 (12)	0.150	0.235
IBDU (1,1'-isobutylene diurea) ^{f,g}	30-0-0	30.47 ± 0.12	30.56 ± 0.02	2 (8)	0.085	0.012

^a Number of materials with number of replicates in parenthesis. Each material was run in duplicate except the ammonium sulfate.

^b Aldrich Chemical Co., Milwaukee, WI, Cat. No. 204501, MW = 132.14 g/mole, purity 99.999%.

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^d CF Industries, Plant City, FL.

^e Mosaic Research and Development, Mosaic Co., Lithia, FL.

^f Nu-Gro, Grand Rapids, MI.

^g Wilbur-Ellis Co., Fresno, CA.

down the amounts of samples and reagents used), and the results of analyses are tabulated in Table 1 under a column identified as “Yes” indicating copper sulfate was used.

(b) The second procedure also follows the scaled down modification of AOAC 978.02 (16th Ed.), except copper sulfate is deleted from the list of reagents added for digestion. Results of analyses for this procedure are also tabulated in Table 1 under the column identified as “No” indicating no copper sulfate was used.

Procedure for Determination of Total Kjeldahl Nitrogen in Fertilizers

(Adopted from AOAC Method 978.02, 16th Ed.)

Step 1—Digestion

Add 15 g K₂SO₄ or 12 g anhydrous Na₂SO₄, 0.4 g anhydrous CuSO₄, or 0.6 g CuSO₄·5H₂O, and approximately 0.8 g alundum granules. Add 37 mL diluted sulfuric acid with water H₂SO₄ + H₂O (1+1, v/v) or 20 mL concentrated sulfuric acid if adequate ventilation is available. Add sufficient test portion mass, precisely 0.1000 to 2.800 g for fertilizers with 30 to 5% nitrogen, respectively. Rinse the inner wall with about 10 mL water. Transfer the flasks to a preheated (400°C) Kjeldahl block digester and digest the test portions for 75 min.

AOAC Official MethodSM 955.04 or the subsequent modified versions (970.02 and 978.02) does not specify the temperature. It describes using a preheated block in such a way to bring 250 mL water to boiling in 5 min. This corresponds to 400°C.

Modifications of Step 1 included elimination of copper sulfate and alundum. Because alundum was eliminated, two

glass beads were used to reduce bumping. Also, 7–8 g K₂SO₄ was used instead of 15 g, and 15 mL concentrated H₂SO₄ was used instead of 37 mL (1+1).

The ratio of K₂SO₄ and H₂SO₄ (1+1) is approximately 2.5 (37 mL/15 g = 2.466). The amounts were reduced accordingly, but within the same ratio. As a result, 7.5–8 g K₂SO₄ and 15 mL concentrated H₂SO₄ were used, and the wall of the digestion tubes was washed with 5–10 mL water, so a total of 20–25 mL H₂SO₄ (1+1) was used instead of 37 mL. This maintains the ratio of K₂SO₄ to H₂SO₄ (1+1) as prescribed but uses less reagents.

Step 2—Determination

Remove the flasks from the heating block and upon cooling (the reaction mixture must be near room temperature) wash the inner wall with 20–30 mL water and mix. Prepare the distillate receiving flask (a 300 mL Erlenmeyer flask) by adding 30 mL of 0.25 N standardized sulfuric acid to trap the expected total nitrogen in the test portion. Add 2–3 drops of methyl purple indicator and install the receiver on the outlet tube of the distillation unit, being sure that the distillate outlet tube end is totally immersed in the standardized acid solution. Install the digestion tube on the distillation unit. Initiate steam generation and slowly dispense about 80 mL (30–35%) sodium hydroxide into the flask. Continue steam distillation until about 250 mL or more of steam condensate has been collected in the receiving flask. This usually requires about 6–8 min. If color changes to green, add more 0.25 N H₂SO₄ to bring the color back to purple and record the amount of acid added. Titrate to a grey end point

Table 2. Statistical data for total Kjeldahl nitrogen by the digestion method for different classes of fertilizers

Cupric sulfate added																
Yes										No						
Group I	Total nitrogen mean	95% confidence interval for mean	SD	High	Low	Median	Absolute deviation from median	Group II	Total nitrogen mean	95% confidence interval for mean	SD	High	Low	Median	Absolute deviation from median	F ^a
A.S. Group A	21.1	21.1	0.051	21.3	21.1	21.1	0.037	A.S. Group B	21.1	21.0	0.079	21.2	20.8	21.1	0.046	0.673
T-K ⁺ Group C	5.2	5.0	0.161	5.5	5.1	5.2	0.105	T-K ⁺ Group D	5.2	5.0	0.171	5.5	5.1	5.1	0.095	0.000
T-KS Group E	14.9	14.7	0.000	14.9	14.9	14.9	0.000	T-KS Group F	14.9	14.7	0.006	14.9	14.9	14.9	0.005	1.000
N-SURE Group G	28.0	27.9	0.153	28.2	27.6	28.1	0.110	N-SURE Group H	28.0	27.9	0.149	28.3	27.8	28.0	0.115	-0.006
T-N ⁺ Group I	29.9	29.7	0.271	30.2	29.7	29.9	0.235	T-N ⁺ Group J	29.9	29.8	0.208	30.1	29.8	29.9	0.180	0.002
T-CB Group K	25.9	25.7	0.029	25.9	25.8	25.9	0.025	T-CB Group L	25.9	25.7	0.064	25.9	25.8	25.9	0.055	0.000
T-NB Group M	26.1	26.0	0.165	26.5	25.9	26.1	0.127	T-NB Group N	26.1	26.0	0.187	26.4	25.7	26.1	0.141	0.001
FOR ⁺ Group O	30.0	29.8	0.085	30.1	29.9	30.0	0.050	FOR ⁺ Group P	30.0	29.8	0.143	30.1	29.8	30.0	0.110	0.031
CR-9 Group Q	29.4	29.2	0.000	29.4	29.4	29.4	0.000	CR-9 Group R	29.3	29.1	0.000	29.3	29.3	29.3	0.000	0.000
DAP Group S	17.6	17.5	0.269	18.1	17.2	17.5	0.184	DAP Group T	17.5	17.4	0.284	18.1	17.3	17.5	0.200	0.013
MAP Group U	10.9	10.8	0.178	11.1	10.7	11.0	0.132	MAP Group V	11.0	10.8	0.327	11.5	10.6	11.0	0.235	0.016
IBDU Group W	30.5	30.3	0.388	30.9	30.1	30.4	0.315	IBDU Group X	30.6	30.4	0.667	31.2	30.0	30.6	0.578	0.019

^a "F" is determined by pairing each subgroup in Group I with its equivalent subgroup in Group II.

(pH 5.7) with 0.25 N standard NaOH. No modifications were made to Step 2.

Step 3—Calculations

The color of the distillate depends upon the amount of total nitrogen in the test portion, which is a function of the amount of ammonia trapped in the receiver flask. A green color indicates that the acid in the trap was neutralized by the ammonia. At this point, add an additional known amount of standardized H_2SO_4 to get to the grey end point. The net volume (in mL) of standardized acid would be equal to the total amount of acid initially added to the receiving flask plus the amount of the acid added, after distillation, to reach to the grey end point. A blue or purple color indicates that there is still acid in the receiving flask, and back titration with NaOH is required. The net volume standardized (std) acid would be equal to the amount of acid in the receiving flask minus the amount of base added, after distillation, to reach to the grey end point.

Weight percent total nitrogen is calculated as follows:

$$\text{Total N, \%} = \frac{(\text{net mL std acid} \times \text{N of std acid}) - (\text{net mL std base} \times \text{N of std base}) \times 1.4008}{\text{sample weight, g}}$$

No modifications were made in Step 3.

Materials

The nitrogen-containing compounds chosen for these studies are listed in Table 2. These materials represent uniform nitrogen-containing compounds both in liquid and in solid forms. These sets of fertilizers represent both inorganic and organic N-containing fertilizers.

Results and Discussion

All materials were analyzed using AOAC *Official Method*SM 978.02 as outlined above with and without copper sulfate.

As illustrated in Table 1, there was no significant difference between the results for total Kjeldahl nitrogen with copper sulfate added or without copper sulfate added to the digestion mixture. The low and high analyses numbers, as well as the range of bias, average, and SD, are provided. The average of the analytical results with catalysts and without catalysts is tabulated. For ammonium sulfate, the average is $21.15 \pm 0.05\%$ with catalysts and $21.12 \pm 0.08\%$ without catalysts. These results and the results for analyses of other products are listed in Table 2.

Conclusions

For a wide variety of ammonium- and urea-containing fertilizer compounds that contain no nitrate nitrogen sources, the results show that AOAC Method 978.02 can be carried out without the addition of environmentally hazardous catalysts with no significant changes in the analytical data. The resulting data were evaluated using a paired test (3). When the paired test was applied to all the data, no significant differences were observed. The results of the pairing tests are shown in Table 2.

References

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- (3) Keeping, E.S. (1995) *Introduction to Statistical Inference* (1995) Dover Publications, Inc., Mineola, NY