Ammoniacal Nitrogen in Fertilizer

1. **Scope**:

This procedure is to be used for the analysis of ammoniacal nitrogen in fertilizer.

2. **Safety**:

All laboratory safety rules for sample preparation and analysis shall be followed. Read the SDS for all materials before use.

Prior to all maintenance work on the device switch off the power supply and remove all sources of flammable vapor (risk of high voltage).

Always wear personal protective equipment such as protective eye goggles, clothing and gloves when maintaining the instrument (risk of chemical burns by corrosives or of intoxication by harmful chemicals).

Always let the device cool down after operation before performing any maintenance work (risk of burns by hot surface).

3. **Equipment and Supplies**:

- Analytical Balance capable of Measuring to 0.0001g
- Buchi KjelMaster K-375 with KjelSampler K-376
- Kjeldahl Sample Tube, 300 mL

4. **Reagents**:

- Standardized Sulfuric Acid, 0.500 N
- Sodium Hydroxide Solution (32%)
- Boric Acid, 2% Solution with sher indicator (Buchi Cat# 11064972)
- Bromothymol blue (Merck Cat# Merck 3026)
- pH 4 buffer solution
- pH 7 buffer solution

5. **Instrument calibration**:

- Buret function should be checked daily.
- Pumps (H_2O, NaOH and H_3BO_3) should be calibrated monthly or as needed.
- pH electrode should be checked daily at the beginning of the analysis.

6. **Analysis**:

6.1 Turn on KjelMaster K-375 and KjelSampler K-376. Setup a sequence that includes preheating, prime (3x), two blanks (one empty tube (not used), one method blank (used in the calculations)), samples (one Magruder check sample and samples), and cleaning.

6.2 Mix sample thoroughly. Weigh 0.5g of sample into a labeled Kjeldahl flask with nitrogen content 5%-15%. For nitrogen content < 5% use proportionally more sample. For nitrogen content >15% use proportionally less sample. Record the weight.

6.3 Select the correct method and distill and titrate the samples according to the parameters listed in Table 1.

7. **QA/QC**

7.1 A QC sample shall be run with each set and should be a similar matrix to the samples. It is analyzed using the same method. Acceptable QC samples may be a NIST reference material or a Magruder test sample with a known mean and standard deviation. NIST results shall be within the certified value. Magruder sample results shall be within 2 standard deviations of the assigned value.

7.2 Any analyte found in the MB shall be less than the MDL.

7.3 Method detection limit (MDL) is 0.03% of ammoniacal nitrogen.

7.4 Reporting limit (RL) is 0.30% of ammoniacal nitrogen.

8. **Calculations**

% Ammoniacal Nitrogen (N) =

$$\frac{[\text{Sulfuric Acid (mL)} - \text{Blank (mL)}] \times (0.5\ \text{N}) \times 1.4007}{\text{Sample Weight (g)}}$$

9. **Maintenance**

9.1 Daily maintenance

9.1.1 Calibrate the pH electrode with fresh buffer solutions pH 4.00 and 7.00 before analyzing samples. The electrode shall pass the following criteria at 25 °C room temperature: slope 95 – 105%, zero-point pH 6.4 – 7.6. If the electrode does not fulfill the criteria, treat the electrode according to the recommendation described in the electrode supplementary sheet. If the treated electrode still does not fulfill the criteria, replace the electrode.

9.1.2 After sample analysis, clean the system. Rinse off the pH electrode with distilled water and gently shake off excess water. Do not touch anything to it to remove droplets. Place the pH electrode into the storage holder containing saturated (4.2 mol/L) KCl solution.

9.2 Monthly maintenance

9.2.1 Calibrate the pumps with the same volume used for each of the methods. An acceptable difference at 50mL is ± 5mL.

9.2.2 Check the distillate amount according to the parameters listed in Table 2. The function test checks the pump's H_2O steam ability. Carry out preheating three times so that the system is warm before performing this test. Run the method with an empty sample tube and empty receiving vessel. The distillate amount with above parameters shall be ≥ 130mL.

9.3 Half-yearly maintenance

9.3.1 Depending on sample throughput and instrument care, an exchange of the rubber seals on the splash protector (connection to the sample tube) and the sealing cap should be performed after around 2000 distillations.

9.3.2 Inspect the sealing cap in the sampler arm (K-376 / K-377 dip tube). Replace when necessary to avoid leakages.

9.4 Yearly maintenance

9.4.1 Inspect wear parts including NaOH pump, boric acid pump, dip tube, pH electrode, wave spring in the sampler arm, and hoses inside the distillation unit (especially the ones that have contact with steam, NaOH and H_3BO_3). Replace when necessary.

9.4.2 Decalcify of the steam generator according to the instruction manual.

10. **Discussion and References**:

- AOACI Official Methods of Analysis, Method #920.03 (Chapter 2.4.07), 19th Edition, 2012.
- AOACI Official Methods of Analysis, Method #955.04 (Chapter 2.4.03), 19th Edition, 2012.
- Operation Manual K-375/K-376/K-377, Operation Manual K-415, Operation Manual K-446/K-449

Table 1: Parameters for distillation and titration with the KjelMaster K-375.

H_2O volume	100 mL	Titration solution	H_2SO_4 0.5 N
NaOH volume	15 mL	Sensor type	Potentiometric
Reaction time	5 s	Titration mode	Standard
Distillation mode	Fixed time	Determination mode	Standard
Distillation time	200 s	Measuring mode	Endpoint pH
Aspiration sample tube	Yes	Normality	0.500
Titer	1.0000	End point pH	4.65
Titration type	Boric acid	Titration start volume	0.000 mL
Receiving solution vol.	60 mL	Titration algorithm	Normal

Table 2: Parameters for checking the distillate amount.

H_2O volume	0 mL	Stirrer speed distillation	5
NaOH volume	0 mL	Steam output	100%
Reaction time	0 s	Titration type	None
Distillation mode	Fixed time	Aspiration sample tube	Yes
Distillation time	300 s	Aspiration receiving vessel	No

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