Water-Insoluble & Water-Soluble Nitrogen in Fertilizer using micro-Kjeldahl

1. **Scope**:

   This method is used to determine the amount of water-insoluble nitrogen in fertilizer. It is not applicable to encapsulated products or urea-formaldehyde samples.

2. **Principle**:

   Leaching the sample with water removes the water-soluble portion of the organic material and most of the inorganic nitrogen salts. Samples are prepared and stored according to RA-SP-SMPL-PREP.

3. **Safety**:

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

   Gloves, eye protection, and a lab coat shall be worn when handling hazardous materials and corrosive reagents.

   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).

4. **Equipment and Supplies**:

   4.1 Analytical Balance capable of measuring to 0.0001g
   4.2 Buchi Kjeldahl Digestion / Distillation Unit: KjelMaster K-375 with KjelSampler K-376, KjelDigester K-449 with Scrubber K-415
   4.3 Kjeldahl Sample Tube, 300 mL
   4.4 Erlenmeyer Flask, 500 mL
   4.5 Whatman #2 Filter Paper, 15 cm
   4.6 Glass wool (Buchi Cat# 033701)

5. **Reagents**:

5.1 Sulfuric Acid, Concentrated (95-98%)
5.2 Standardized Sulfuric Acid, 0.100N or 0.500 N
5.3 Kjeldahl Tablets Titanium (Buchi Cat# 11057980 or equivalent). Each tablet contains 3.5 g K_2SO_4, 0.105 g $CuSO_4 \cdot 5H_2O$, 0.105 g TiO_2
5.4 Kjeldahl Tablets Antifoam (Buchi #Cat# 11057984 or equivalent). Each tablet contains 0.97 g Na_2SO_4, 0.03 g silicone antifoam
5.5 Methanol
5.6 Sodium Hydroxide Solution (32%) or sodium hydroxide pellets
5.7 Activated Charcoal, DARCO® (4 - 12 Mesh, Decolorizing, CAS No. 7440 - 44 - 0), Acros Organics or equivalent
5.8 Boric Acid, 2% Solution with sher indicator (Buchi Cat# 11064972)
5.9 Bromothymol blue (Merck Cat# Merck 3026)
5.10 pH 4 buffer solution
5.11 pH 7 buffer solution

6. **Instrument calibration**:

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

7. **Analysis**:

7.1 Mix sample thoroughly and weigh 1.0g for samples with nitrogen content > 1% and 1.4g for samples with nitrogen content < 1%. Record weight, place sample into the folded filter paper in a funnel and place the funnel over a 500 ml Erlenmeyer flask. Wash the sample with 250mL H_2O. Carefully transfer the residue/filter paper into a Kjeldahl flask and discard the filtrate.

7.2 Add two Kjeldahl Tablets Titanium and 27.5mL concentrated sulfuric acid to the Kjeldahl flask. Place the flask in the rack and transfer the rack in KjelDigester K-449. Turn on the chiller, KjelDigester K-449, and Scrubber K-415. Press “start” on KjelDigester K-449, select the appropriate digestion method (see Table 1), then press “start” again to initiate the digestion programming that digests the sample at 420°C for 2 hours.

7.3 Allow the solution to cool to room temperature then transfer the rack with flasks to the KjelSampler K-376.

7.4 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 including one Magruder check sample, and cleaning. Select the correct method and distill and titrate the samples according to the parameters listed in Table 2.

8. QA/QC

8.1 A QC sample shall be run with each set and should be a similar matrix to the samples. It is extracted and 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.

8.2 Any analyte found in the MB shall be less than the method detection limit.

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

8.4 Reporting limit (RL) is 0.06% of nitrogen.

9. Calculations

Water-soluble nitrogen is determined by calculating the difference between total nitrogen and water-insoluble-nitrogen (WIN) as determined by this method.

Water Soluble Nitrogen = Total Nitrogen – Water-Insoluble Nitrogen

10. Maintenance

10.1 Daily when in use maintenance

10.1.1 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.

10.1.2 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.

10.2 Monthly maintenance

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

10.2.2 Check the distillate amount according to the parameters listed in Table 3. 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.

10.3 Half-yearly maintenance

10.3.1 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 not exceeding 2000 distillations.

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

10.3.3 Replace the glass splash protector before 5000 distillations. The plastic splash protector needs to be replaced before 8000 distillations.

10.4 Yearly maintenance

10.4.1 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.

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

11. **References**:

11.1 AOAC Official Methods of Analysis, Method #945.01 (Chapter 2.4.14), 19th Edition, 2012.

11.2 AOAC Official Methods of Analysis, Method #955.04 (Chapter 2.4.03), 19th Edition, 2012.

11.3 Operation Manual K-375/K-376/K-377, Operation Manual K-415, Operation Manual K-446/K-449

Table 1: Temperature profile for digestion with the K-449.

Step	Temperature [°C]	Time [min]
Preheat	350	0
1	420	120
Cooling	-	30

Table 2: Parameters for distillation and titration with the KjelMaster K-375.

H_2O volume	**50 mL**		**Titration solution**	**H_2SO_4 0.5 N**
NaOH volume	125 mL		Sensor type	Potentiometric
Reaction time	5 s		Titration mode	Standard
Distillation mode	Fixed time		Determination mode	Standard
Distillation time	300 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.	70 mL		Titration algorithm	Normal

Table 3: 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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