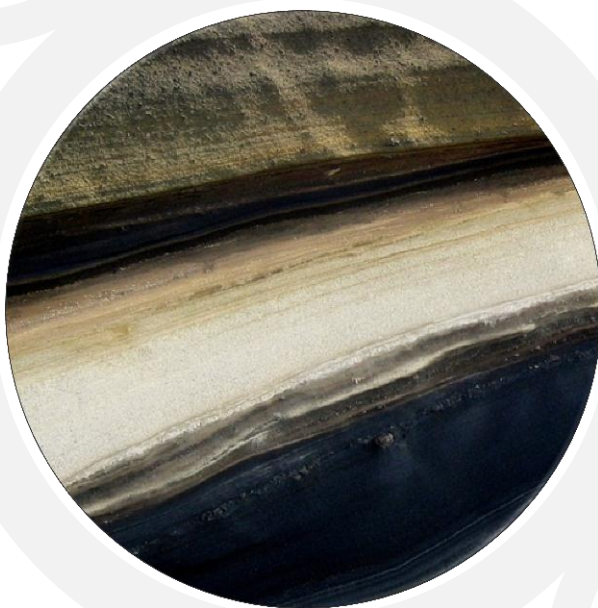




Application Note No. 124/2013

Nitrogen determination in soil

KjelDigester K-449, KjelMaster K-375 with KjelSampler K-376:
Nitrogen determination in soil according to the Kjeldahl method



1 Introduction

An easy and reliable method for the determination of nitrogen in soil, according to EN 13342 and DIN ISO 11261, is introduced below. The samples are digested using the KjelDigester K-449. The distillation and boric acid titration are performed with the KjelMaster K-375 with KjelSampler K-376. The combination of the new KjelDigester and the KjelMaster system K-375/K-376 increases the sample throughput.

2 Equipment

- KjelDigester K-449 (the parameters used are also valid for K-446)
- Scrubber K-415 TripleScrub^{ECO}
- KjelMaster K-375 with KjelSampler K-376
- Analytical balance (accuracy ± 0.1 mg)

NOTE: To protect the valves of the K-375 it is recommended, to have as little solid particles as possible left in the sample tube after digestion.

3 Chemicals and Materials

Chemicals:

- Sulfuric acid conc 98 %, Merck (1007482500)
- Titanium, BUCHI Kjeldahl Tablet (11057980)
- Sodium hydroxide 32 %, Brenntag (81980-452)
- Boric acid 2 % containing potassium chloride (3 g/L), 200 g boric acid, Brenntag (80948-155) diluted to 10 L with deionized water, pH adjusted to 4.65
- Sulfuric acid 0.01 mol/L, 100 mL of sulfuric acid 0.1 mol/L Fluka (35357) diluted to 1 L with deionized water
- Neutralization solution for the Scrubber: 600 g sodium carbonate, calcined, technical, Synopharm (0179420) about 2 mL ethanol and a spatula tip of bromthymol blue, Fluka (18460) diluted to 3 L with distilled water
- Urea, assay 99.5 %, Merck (108487)
- Boiling aids, e.g. digestion rods (043087)

For a safe handling please pay attention to all corresponding MSDS!

Samples:

- Urea stock solution, 1.0560 g Urea/L \rightarrow 0.4925 mg N/mL
- Soil 1 (CRM from University of Wageningen (NL)), nitrogen content declared as "Acid extractable (So-called Totals)" 2.04 g/kg
- Soil 2 (CRM from University of Wageningen (NL)), nitrogen content declared as "Acid extractable (So-called Totals)" 1.57 g/kg

The ready-made soil samples from WEPAL (Wageningen Evaluation Programs for Analytical Laboratories) were dried at 40°C and milled to pass a 0.5 mm sieve.

4 Procedure

The determination of nitrogen in soil includes the following steps:

- Pretreatment of the samples according to e.g. DIN ISO 11464 and 11465 or EN 12880 and EN ISO 5667-13
- Digestion of the sample, using K-449 (K-446 respectively)
- Distillation and titration of the sample, using KjelMaster system K-375/K-376

4.1 Digestion method – urea stock solution (verification of the method)

1. Start the KjelDigester K-449 according to the parameters listed in Table 1
2. Place 3 mL of the urea stock solution in a 300 mL sample tube
3. Add 1 Titanium tablet and 8 mL of sulfuric acid (conc. 98 %)
4. Prepare additional blanks, chemicals without sample
5. Connect the Scrubber K-415 to the K-449 for absorbing the acid fumes created during digestion
6. Insert the rack with the samples into the cooling position and mount the suction module onto the tubes, immediately start the digestion according to the parameters listed in Table 1.
7. Let the samples cool down when the digestion is completed.

4.2 Digestion method – samples

1. Start the KjelDigester K-449 according to the parameters listed in Table 1
2. Place 0.5 g of each sample in a 300 mL sample tube
3. Add 1 Titanium tablet, 8 mL of sulfuric acid (conc. 98%) and a boiling aid to each tube
4. Prepare additional blanks, chemicals without sample
5. Connect the Scrubber K-415 to the K-449 for absorbing acid fumes created during digestion
6. Insert the rack with the samples into the cooling position and mount the suction module onto the tubes, immediately start the digestion according to the parameters listed in Table 1.

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

Step	Temperature [°C]	Time [min]
1	320	0
2	420	70
Cooling	–	30

NOTE: If the liquid in the sample tube is not clear and blue-green, digest for additional 15 min at 420 °C.

7. Let the samples cool down when the digestion is completed.

4.3 Distillation and titration

Distill the samples according to the parameters listed in Table 2.

Table 2: Distillation and titration with the KjellMaster system K-375/K-376

Method parameters KjellMaster K-375

H ₂ O volume	50 mL	Titration solution	H ₂ SO ₄ 0.01 mol/L
NaOH volume	40 mL	Sensor type	Potentiometric
Reaction time	5 s	Titration mode	Standard
Distillation mode	Fixed time	Measuring mode	Endpoint pH
Distillation time	180 s	Endpoint pH	4.65
Stirrer speed distillation	5	Stirrer speed titration	7
Steam output	100 %	Titration start volume	0 mL
Titration type	Boric acid	Titration algorithm	Optimal
Receiving solution vol.	50 mL	Titration algorithm	Optimal

4.4 Calculation

The results are calculated as a percentage of nitrogen. The following equations (1), (2), and (3) are used to calculate the results.

$$w_N = \frac{(V_{\text{Sample}} - V_{\text{Blank}}) \cdot z \cdot c \cdot f \cdot M_N}{m_{\text{Sample}} \cdot 1000} \quad (1)$$

$$\%N = w_N \cdot 100 \% \quad (2)$$

$$\text{Recovery} = \frac{N_{\text{act}} \cdot 100}{N_{\text{theor}}} \quad (3)$$

w_N : weight fraction of nitrogen

V_{Sample} : amount of titrant for the sample [mL]

V_{Blank} : mean amount of titrant for the blank [mL]

z : molar valence factor (1 for HCl, 2 for H₂SO₄)

c : titrant concentration [mol/L]

f : titrant factor (for commercial solutions normally 1.000)

M_N : molecular weight of nitrogen (14.007 g/mol)

m_{Sample} : sample weight [g]

1000 : conversion factor [mL/L]

$\%N$: percentage of weight of nitrogen

N_{act} : actual value of the nitrogen content in urea stock solution [mg N]

N_{theor} : theoretical value of the nitrogen content in urea stock solution [mg N]

Recovery: Recovery of the nitrogen in urea stock solution [%]

5 Results

5.1. Recovery of urea stock solution

The results of nitrogen determination and recovery for the urea stock solution are presented in Table 3. The theoretical value is 1.4775 mg N/ 3 mL. The recoveries are within the specification of $\geq 98\%$. [1]

Table 3: Results of the recovery of nitrogen in 3 mL urea stock solution

Stock solution	V _{Sample} [mL]	mg N _{theor}	mg N _{act}	Recovery [%]
Sample 1	5.607	1.4775	1.473	99.7
Sample 2	5.599	1.4775	1.471	99.6
Sample 3	5.597	1.4775	1.470	99.5
Sample 4	5.607	1.4775	1.473	99.7
Sample 5	5.636	1.4775	1.481	100.3
Average [%]	–		1.474	99.8
RSD [%]	–		0.3	0.3

The mean blank volume (V_{Blank}) was 0.348 mL (n = 5).

5.2 Nitrogen determination in soil

The results of the determination of nitrogen contents in two certified soil samples are presented in Table 4 – 5.

Table 4: Results of the determination of nitrogen in soil 1 (Nitrogen content 2.04 g/kg)

Soil 1	m _{Sample} [g]	V _{Sample} [mL]	%N	g N/kg
Sample 1	0.5249	4.065	0.2169	2.17
Sample 2	0.5943	4.251	0.2004	2.00
Sample 3	0.5694	4.291	0.2111	2.11
Sample 4	0.5184	3.806	0.2057	2.06
Sample 5	0.5799	4.414	0.2132	2.13
Average [%]	–	–	0.2095	2.09
RSD [%]	–	–	3.1	3.1

The mean blank volume (V_{Blank}) was 0.348 mL (n = 5).

Table 5: Results of the determination of nitrogen in soil 2 (Nitrogen content 1.57 g/kg)

Soil 2	m _{Sample} [g]	V _{Sample} [mL]	%N	g N/kg
Sample 1	0.5406	3.326	0.1543	1.54
Sample 2	0.5315	3.384	0.1600	1.60
Sample 3	0.5387	3.381	0.1577	1.58
Sample 4	0.5126	3.267	0.1595	1.60
Sample 5	0.5477	3.487	0.1605	1.61
Average [%]	–	–	0.1584	1.58
RSD [%]	–	–	1.6	1.6

The mean blank volume (V_{Blank}) was 0.348 mL (n = 5).

The mean values for the nitrogen determination in soil correspond well to the certified ones. The confidence limits (95 %) for soil 1 are 2.015 - 2.069 g N/kg and 1.550 - 1.591 g N/kg for soil 2. Low deviations between the results are explainable with the different methods of determination. WEPAL calls the method "Acid extractable (So-called totals)", that means that the participants of the evaluation used different methods.

6 Comparison to Standard Methods

The differences between this application and the official methods DIN ISO 11261 and EN 13342 are shown in Table 6.

Table 6: Differences to DIN ISO 11261 and EN 13342

	Application note	DIN ISO 11261	EN 13342	Notes / Impact
Catalyst	3.7 g Tablets Composition: 94.4 % K_2SO_4 2.8 % TiO_2 2.8 % $CuSO_4 \cdot 5H_2O$	1.1 g mixture 200 g K_2SO_4 6 g $CuSO_4 \cdot 5H_2O$ 6 g TiO_2	5 g mixture - 1000 ± 20 g K_2SO_4 - 100 ± 2 g $CuSO_4 \cdot 5 H_2O$	The choice of catalyst does not influence the result.
Sulfuric acid	8 mL	4 mL containing salicylic acid (25 g/L)	10 mL	No impact, same ratio of sulfuric acid/catalyst.
Sodium thiosulfate pentahydrate	no	0.5 g	no	Only necessary, if salicylic acid is used.
Water	50 mL	20 mL	40 mL after digestion, than additional approx. 150 mL before distillation	The K-375 generates steam in a separated vessel; therefore it is not necessary to add such a high amount of water.
Sodium hydroxide	40 mL (Conc. 32 %)	20 mL (Conc. 40 %)	30 mL (Conc. 50 %)	No impact, same ratio of sodium hydroxide/sulfuric acid.
Boric acid	50 mL 2 %	5 mL 2 %	50 mL 4 %	No impact.
Titration	potentiometric	colorimetric or potentiometric	potentiometric or colorimetric	No impact.
Titration solution	0.01 mol/L H_2SO_4	0.01 mol/L H_2SO_4	0.05 mol/L H_2SO_4	No impact.

7 Conclusion

The determination of nitrogen in soil using the KjelDigester K-449 and KjelMaster system K-375/K-376 provides reliable and reproducible results. These results correspond well to the certified values of the different sample with low relative standard deviation (RSD). The recovery with urea stock solution was 99.8 % (RSD = 0.3 %), which was within the specification of ≥ 98 % [1].

With the KjelDigester K-449 the digestion process (including preheating, digestion and cooling) is very fast and is fully automated. Together with the fully-automatic KjelMaster system K-375/K-376, the time to result is significantly reduced and full walk-away convenience is guaranteed.

8 References

- [1] Application Note 100/2013, Nitrogen Determination in Reference Substances – Operational Quality Check Procedure
DIN ISO 11261:1995 Soil quality – Determination of total nitrogen – Modified Kjeldahl Method
EN 13342:2000 Characterization of sludges – Determination of Kjeldahl nitrogen

Kjeldahl Calculator App

Operation Manual of KjelDigester K-446/K-449

Operation Manual of Scrubber K-415

Operation Manual of KjelMaster system K-375/K-376