Application Note – N°. 832/2024

TKN determination in wastewater

Abstract: The determination of both Total Kjeldahl Nitrogen (TKN) and ammonia is of great importance. In this application note, an easy and reliable method for the determination of TKN is introduced, providing reliable and reproducible results with low relative standard deviations (rsd).

1. Introduction

Nitrogen in water and wastewater can be found in several forms, organic and inorganic. A wastewater treatment plant removes different nitrogen sources until the regulatory standards are met. Therefore, the determination of both Total Kjeldahl Nitrogen (TKN) and ammonia is of great importance. In this application note, an easy and reliable method for the determination of TKN is introduced:

Samples are digested with the KjelDigester K-449 using Kjeldahl tablets Titanium. A steam distillation protocol followed by a potentiometric boric acid titration is performed with the KjelMaster K-375 with KjelSampler K-376 / K-377 in accordance with ISO 5663[1], DIN EN 25 663[2] and the methods listed in 40 CFR part 136.3[3].

2. Equipment

- Scrubber K-415 TripleScrub ECO (114152331)
- KjelDigester K-449 with condensate tryp for aqueous samples (1154492000)
- KjelMaster K-375 with KjelSampler K-377 (113751720)
- Sample tubes 300 mL (037377)
- Digestion rods (043087)
- Analytical balance (accuracy ± 0.1 mg)

3. Chemicals and Materials

Chemicals:

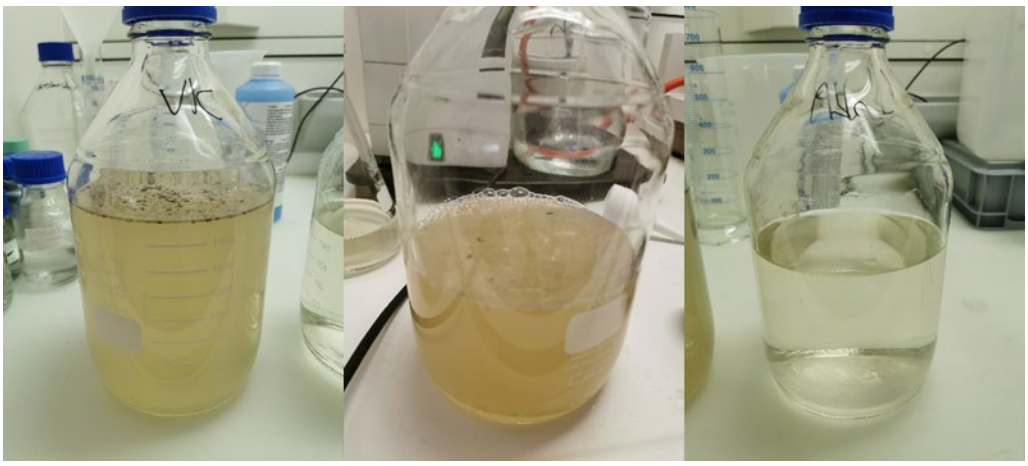
- Sulfuric acid conc 96 %, VWR (85546.320).
- BUCHI Kjeldahl Tablets Titanium (11057980).
- Sodium hydroxide 32 %, VWR (9913.9010).
- 2% boric acid with Sher indicator (11064972).
- Sulfuric acid 0.01 mol/L, VWR (95032.1000), Titer = 0.01001 mol/L
- Neutralization solution for the Scrubber: 600 g sodium carbonate, calcined, technical, Synopharm (0179420) about 2 mL ethanol and a spatula tip of bromothymol blue, Fluka (18460) diluted to 3.0 L with distilled water.
- Urea, assay 99.7 %, Merck (1.08487.000).
- Volumetric pipettes.
- 100-1000 µL micropipette (Eppendorf).
- Deionized water.
- Antifoam tablets (11057984).

For safe handling please refer to all corresponding MSDS!

Samples:

- Urea stock solution 1: ~ 2.5 mg N / mL as a reference solution.
- Raw sewage sample, provided by a wastewater treatment plant in Switzerland.
- Primary effluent sample, provided by a wastewater treatment plant in Switzerland.
- Secondary effluent sample, provided by a wastewater treatment plant in Switzerland.

Samples should be analyzed as quickly as possible for reliable results. If this is not possible, they should be stored at 4 °C and acidified with conc. H_2SO_4.



Picture 1 – 3: Raw sewage (left), primary effluent (middle) and secondary effluent sample (right).

4. Procedure

The determination of nitrogen content in a wastewater sample includes the following steps:

- Homogenization of the sample.
- Filtration if necessary.
- Digestion of the sample.
- Steam distillation followed by titration.

4.1 Homogenization of the sample

Samples with solid particles were homogenized for at least 1 minute using the BUCHI B-400 mixer.

4.2 Filtration of solid particles

Depending on local regulations, solid particles may be filtered out before measurement in order to solely determine the Total Kjeldahl Nitrogen (TKN) content in the solution.

4.3 Digestion method

Kjeldahl Digestion with Kjeldahl tablets Titanium as catalyst:

1. Pipette out the required sample volume (Table 1) in a 300 mL sample tube.
2. Add 2 Kjeldahl tablet Titanium and 15 mL of sulfuric acid (conc. 96 %) and slide in carefully a digestion rod along the sample tube wall in the sample tube as a boiling aid.
3. Prepare additional blanks, chemicals without sample.
4. Connect the Scrubber K-415 to the K-449 for absorbing the acid fumes created during digestion.
5. Mount the suction module onto the sample tubes for standard Kjeldahl digestion with Kjeldahl Tablets Titanium (according to Table 2)
6. Insert the rack with the samples into the cooling position and start preheating step. Once preheating is completed shift the sample rack in the digestion position and immediately start the digestion according to the parameters listed in Table 2.
7. Let the samples cool down in the cooling position when the digestion is completed.

Table 1: Sample amount.

< 10 mg/L	250 mL (in 500 mL sample tube)
10 – 20 mg/L	100 mL
20 – 50 mg/L	50 mL
50 – 100 mg/L	25 mL
Urea stock solution	1 mL

Table 2: Temperature ramp for digestion with the KjelDigester K-449.

Step	Temperature [°C]	Time [min]
Preheating	110	0
1	110	15
2	250	195
3	420	100
Cooling	–	30

NOTE: The digestion time in this Application Note is kept more than required and constant for all concentrations. It could be adjusted according to (AN 118/2013) and on lower recoveries could be further increased. As a first indication the digested sample should be clear and blue green, with acceptable recoveries of a reference substance. Let the samples cool down in the cooling position when the digestion is completed (Table 2).

4.4 Distillation and titration

Distillation and titration was carried out according to the parameters listed below.

Table 4: Parameters for distillation and titration with the KjelMaster system K-375 / K-377.

Method parameters KjelMaster K-375			
H_2O volume	50 mL	Titration solution	H_2SO_4 0.01 mol / L
NaOH volume	60 mL	Sensor type	Potentiometric
Reaction time	5 s	Measuring mode	Endpoint pH
Distillation mode	Fixed time	Endpoint pH	4.65
Distillation time	150 s	Stirrer speed titration	7
Stirrer speed distillation	5	Titration start volume	0 mL
Steam output	100 %	Titration algorithm	Optimal
Titration type	Boric acid		
Receiving solution vol.	50 mL		

4.5 Calculation

The results are calculated as a percentage of nitrogen. The following equations (1) and (2) are used to calculate the results for the reference substance, the purity of the urea is considered in equation (3).

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

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

$$\%N_{Urea} = \frac{\%N \bullet 100}{P} \quad (3)$$

To calculate the results for the Kjeldahl nitrogen concentration, equation (4) is used.

$$\rho_N = \frac{(V_{Sample} - V_{Blank}) \cdot z \cdot c \cdot f \cdot M_N \cdot 1000}{m_{Sample}}$$

w_N : Weight fraction of nitrogen.

ρ_{NH4} : Kjeldahl nitrogen concentration [mg/L]

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 : Titre value (for commercial solutions normally 1.000; refer to the product certificate).

M_N : Molecular weight of nitrogen (14.007 g/mol).

m_{Sample} : Sample weight [g] for Urea or volume [mL] for wastewater samples.

1000 : Conversion factor [mL to L].

%N : Percentage weight of nitrogen.

P : Purity of the reference substance Urea [%] as declared by the manufacturer.

5. Results

The results of total Kjeldahl nitrogen determination in wastewater and recovery for the urea samples are presented in Table 4 and Table 5.

Table 4: Results of the Kjeldahl nitrogen determination of the urea sample (n=2).

Reference	m_{Sample} [mg]	V_{Sample} [mL]	Recovery [%]	Mean value
Urea	6.1355	10.478	97.16 %	**100.30 %** rsd : 0.24 %
	6.1355	10.512	97.49 %	

The mean blank volume (V_{Blank}) was 0.5627 mL (n = 3, RSD = 2.29 %).

Table 5: Results of the TKN determination. Sample volume: 100 mL (n = 3).

Sample	V_{Sample} [mL]	$N_{measured}$ [mg]	TKN conc. [mg/L]	Filtered
Raw sewage sample	9.6600	2.5510	25.510	Yes
	9.5510	2.5205	25.205	Yes
	11.912	3.1825	31.825	-
Primary effluent sample	11.072	2.9470	29.470	Yes
	10.803	2.8715	28.715	Yes
	12.344	3.3037	33.037	-
Secondary effluent sample	1.986	0.3991	3.991	Yes
	1.945	0.3876	3.876	Yes
	1.764	0.3369	3.369	-

The mean blank volume (V_{Blank}) was 0.5627 mL (n = 3, RSD = 2.29%).

6. Comparison with Regulation and Standard Methods

Table 6: Comparison to ISO 5663 [1], DIN EN 25 663 [2], Standard Methods [5] and PAI-DK01 [4] in 40 CFR Part 136.3 [3].

	Application Note	ISO 5663 DIN EN 25 663 [1,2]	Standard Methods 4500-N_{org} B / 4500-NH_3 C [3,5]	PAI-DK01 [4]	Notes / Impact
Catalyst	3.7 g tablet, of: 94.4 % K_2SO_4 2.8 % $CuSO_4$ 2.8 % TiO_2	5 g mixture of: 99.0 % K_2SO_4 1.0 % Se	7 g mixture of: 95.7 % K_2SO_4 4.3 % $CuSO_4$	5.7 g mixture of: 94.8 % K_2SO_4 5.2 % $CuSO_4$	No use of toxic selenium or mercury in this study. The choice of catalyst does not influence the result. Easy handling using tablets in this study
Sulfuric acid	8 mL	10 mL	6.7 mL	8 mL	Comparable
Water dosed before distillation	50 mL	250 ±50 mL	Dilute to total sample volume of 500 mL	50 mL	-
Base	32 mL NaOH (conc. 32 %)	50 mL NaOH (conc. 36 %)	NaOH until pH 9.5	NaOH (conc. 50%), volume not specified	No impact, same ratio of sodium hydroxide/sulfuric acid
Titration method	Potentiometric	Colorimetric	Colorimetric	Colorimetric	Equal
Indicator		Methyl red / methylene blue	Methyl red / methylene blue	Methyl red / bromocresol green indicator	No impact
Titration solution	H_2SO_4 0.01 mol/L	HCl 0.01 mol/L	H_2SO_4 .01 mol/L	H_2SO_4 0.01 mol/L	No impact

7. Conclusion

The determination of TKN in water and wastewater using the KjelDigester K-449 and KjelMaster system K-375 / K-376 by potentiometric titration provides reliable and reproducible results with low relative standard deviations (rsd).

With the KjelDigester K-449 the digestion process (including preheating, digestion and cooling) is fast and is fully automated. Together with the fully-automatic KjelMaster system K-375 / K-376, the time to result is significantly reduced and it allows unattended operation.

8. References

Kjeldahl Optimizer App

Operation Manual of KjelDigester K-449

Operation Manual of Scrubber K-415

Operation Manual of KjelMaster K-375

[1] ISO 5663, Water quality – Determination of Kjeldahl nitrogen – Method after mineralization with selenium.

[2] DIN EN 25 663, Determination of Kjeldahl Nitrogen in Water.

[3] 40 CFR Part 136.3 table IB, Guidelines Establishing Test Procedures for the Analysis of Pollutants: Total Kjeldahl Nitrogen, https://ecfr.io/Title-40/pt40.25.136, accessed on October 11th, 2023.

[4] ISO 5664, Water quality – Determination of ammonium – Distillation and titration method.

[5] DIN 38 406-E5-2 Bestimmung des Ammonium-Stickstoffs-Massanalytische Bestimmung nach Destillation (Determination of ammonia nitrogen-titration after distillation).