Short Note No. 191/2015
TKN determination in water and waste water

KjelDigester K-449, KjelMaster K-375 with KjelSampler K-376 using colorimetry:
Determination of TKN (total Kjeldahl nitrogen) in water and waste water according to the Kjeldahl method

The determination of TKN (total Kjeldahl nitrogen) in water and waste water is a routine procedure for quality assurance and inspection. Here, a reliable procedure for the colorimetric TKN determination in water, according to ISO 5663, AOAC 973.48, and EPA 351.3 is introduced [1]. The sample is digested with sulfuric acid and the Kjeldahl Tablet Titanium using the KjelDigester K-449, followed by distillation and titration with the KjelMaster system K-375 / K-376 equipped with the colorimetric sensor using the Sher mixed indicator.

1. Introduction

TKN is one of the key parameters for the evaluation of water and its pollution. The samples require digestion with sulfuric acid such that nitrogen reacts to ammonium sulfate. After conversion to ammonia through the alkalinization with sodium hydroxide, the sample is distilled by steam distillation into a boric acid receiver containing a mixed indicator according to Sher. The nitrogen content is determined by colorimetric titration with sulfuric acid solution.

2. Experimental

Equipment: KjelDigester K-449 / KjelMaster K-375 with KjelSampler K-376

Samples: Urea stock solution 0.499 mg N/mL / surface water of a river (city moat, slightly turbid pond) in Beijing, China.

Determination: The samples were added directly into a sample tube, depending on the nitrogen content as described in Table 1. One Titanium tablet, digestion rods to avoid bumping and 8 mL of sulfuric acid (conc. 98 %) were added.

Table 1: Nitrogen content depending on sample volume

Nitrogen content	Sample volume [mL]	Digestion Time
50 – 100 mg N/L	25	50
20 – 50 mg N/L	50	70
10 - 20 mg N/L	100	90
< 10 mg N/L	200	160

For digestion the parameters listed in Table 2 were applied to the K-449. The total digestion time depends on the sample volume described in Table 1. The method was verified by using an urea stock solution as reference.

Table 2: Temperature profile for digestion with the K-449

Step	Temperature[°C]	Time [min]
1	250	0
2	420	See Table 1
Cooling	---	25

3 Setpoints of the boric acid containing Sher mixed indicator were determined according to Reference [2]. Subsequently, the ammonia of the digested samples (inclusive blank samples) was distilled into a boric acid solution by steam distillation and titrated with sulfuric acid (Table 3) performed by the KjelMaster system K-375 / K-376 equipped with the colorimetric sensor.

Table 3: Method parameters for distillation and titration with the KjelMaster System K-375 / K-376.

H_2O volume	50 mL	Receiving solution	60 mL H_3BO_3 2 %
NaOH volume	60 mL	Titration solution	H_2SO_4 0.01 mol/l
Reaction time	5 s	Sensor type	Colorimetric
Dist. mode	fixed time	Titration mode	Online
Dist. time	180 s	Titration start time	90 s
Stirrer sp. dist	5	Stirrer sp. Titr.	10
Steam output	100%	Titr. algorithm	Optimal

3. Results

The recoveries of the urea stock solution are within the 99 -102 %. The determined TKN results of the urea stock solution and the water sample are well reproducible and with low relative standard deviations. All the results are presented in Table 4 - 5.

Table 4: Determined TKN contents and recoveries of the urea stock solution (rsd in brackets, n=3)

Sample volume	TKN [mg/L]	Recovery [%]
25 mL	61.6	101.1 (1.0)
	100.1	100.2 (0.9)
200 mL	0.497	99.5 (6.1)
	1.01	100.8 (0.6)

Table 5: Results of the TKN determination in surface water of a pond (Beijing, China) with total sample volume of 200 mL

	TKN_{actual} [mg/L]	Rsd [%]
Sample	0.97	5.0

4. Conclusion

The determination of TKN in water and waste water with sulfuric acid and the Kjeldahl Tablet Titanium using the KjelDigester K-449 and KjelMaster system K-375 / K-376 equipped with the colorimetric sensor provides reliable and reproducible results even at very low nitrogen concentrations. The TKN for the water sample mearued was determined 0.97 mg/L. The LOQ of this method was determined to be 0.25 mg N/L.

5. References

[1] ISO 5663, AOAC 973, 48, EPA 351.3
[2] Technical Note 179/2015 “Colorimetric titration procedure using Sher indicator”

For more detailed information and safety considerations please refer to the Application Note no. 191/2015.