Metrohm

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Determination of ammonium or Kjeldahl Nitrogen

Branch

General analytical chemistry; food, stimulants, beverages, flavours; water, wastewater, air, environmental protection; fertilizers, base materials, explosives

Keywords

Kjeldahl; nitrogen determination; ammonium; titration; photometric titration; potentiometric titration; coulometric determination; Optrode; Unitrode; separate double Pt-sheet electrode; branch 1; branch 2; branch 7; branch 11; 6.1115.000; 6.0259.100; 6.0309.100

Summary

The potentiometric titration of Kjeldahl nitrogen is one of the most widely employed analytical methods. Many of the standard procedures in the food and animal feed industry, in waste water and refuse analysis as well as in agriculture and the fertilizer industry are based on this method. Extensive test series (interlaboratory tests) have been carried out to determine and optimize the recovery rates and digestion conditions. The knowledge derived from these tests has been integrated in the corresponding standards. Normally, the samples are digested with concentrated sulfuric acid using a catalyst as admixture. The formed ammonium sulfate is distilled off as ammonia in alkaline solution, collected in an absorption solution and then titrated. The first part of this bulletin describes in detail the determination of nitrogen after distillation of the digestion solution using either potentiometric or photometric indication. The second part indicates the possibilities of the coulometric titration (without distillation).

Method 1 – Potentiometric determination

Instruments

- Titrator with SET modus
- 20 mL buret
- Kjeldahl digestion and distillation apparatus

Electrodes

Unitrode with Pt 1000 (head U)	6.0258.600

Reagents

- Sulfuric acid, puriss p.a., 96%
- Sodium hydroxide, puriss p.a., NaOH
- Broic acid, puriss p.a., H_3BO_3
- Hydrochloric acid, c(HCl) = 0.1 mol/L
- Catalyst (Kjeldahl tablets, Hg and Se free)

Solutions

Titrant	c(HCl) = 0.1 mol/L If possible this solution should be bought from a supplier.
$c(H_3BO_3)$ = 0.1 mol/L	200 g boric acid is weighed into a 5 L volumetric flask and dissolved in dist. water. The solution is then filled up to the mark with dist. water.
w(NaOH) = 40 %	2 kg NaOH is slowly dissolved in approx. 5 L dist. water.

Sample preparation

Digestion

In a digestion flask an appropriate amount of sample containing no more than 25 mg N is mixed with 10 – 20 mL conc. H_2SO_4 and two Kjeldahl tablets. The digestion flask is tilted back and forth to make sure that the sample is completely moistened with H_2SO_4. Then it is heated up, until a distinct reaction occurs and continued boiling slightly until the brown color and all carbon particles have disappeared.

The solution should now appear clear and greenish. Upon completion of the digestion, the mixture is allowed to cool down.

Distillation

The Kjeldahl flask containing the digested sample is placed into the Kjeldahl distillation apparatus and approx. 50 mL water and as much w(NaOH) = 40% as needed are added to get a blue to brownish solution. The formed ammonia is then distilled off by steam distillation and retained in the form of ammonium in a sample beaker containing 50 mL of $w(H_3BO_3)$ = 2%.

Analysis

Calibration

The electrode is initially calibrated by a two point calibration with buffer pH 4 and 7.

Titer

100 - 150 mg TRIS is weighed into a titration beaker, dissolved in approx. 70 mL dist. water and titrated to until after the equivalence point.

Blank

For the blank determination, a digestion and distillation is performed the same way as described under sample preparation omitting the sample.

Sample

For determining the nitrogen content, the obtained solution is titrated with c(HCl) = 0.1 mol/L to a pH of 4.6.

Parameters

Calibration

Mode	CAL MEAS pH
Signal drift	2 mV/min
Min. waiting time	10 s
Max. waiting time	110 s

Titer

Mode	MET pH
Stirring rate	5
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.1 mL
Stop volume	20 mL
EP criterion	30 mV
EP recognition	greatest

Blank/Sample

EP1 at pH	4.6
Dynamics	3
Max. rate	5 mL/min
Min. rate	10 µL/min
Stop criterion	Drift
Stop drift	10 µL/min
Stop volume	20 mV
EP1 at pH	4.6

Calculation

Titer

$$f = \frac{m_{Std}}{V_{EP1} \times c_{HCl} \times M_{Std}}$$

f:	Titer of the selected titrant
m_{Std}:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{HCl}:	Concentration of the selected titrant in mol/L; here c(HCl) = 0.1 mol/L
M_{Std}:	Molecular weight of the standard (TRIS); 121.17 g/mol

Sample

$$m_N = (V_{EP1} - Blank) \times c_{HCl} \times f \times M_N$$

$$w_N = \frac{m_N \times 100}{m_S}$$

m_N:	Mass of nitrogen in the sample in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{HCl}:	Concentration of the selected titrant in mol/L; here c(HCl) = 0.1 mol/L
f:	Titer of the selected titrant
M_N:	Molecular weight of nitrogen in g/mol; 14.007 g/mol
w_N:	Mass fraction of Nitrogen in %
100:	Conversion factor
m_S:	Sample weight in mg

Example determination

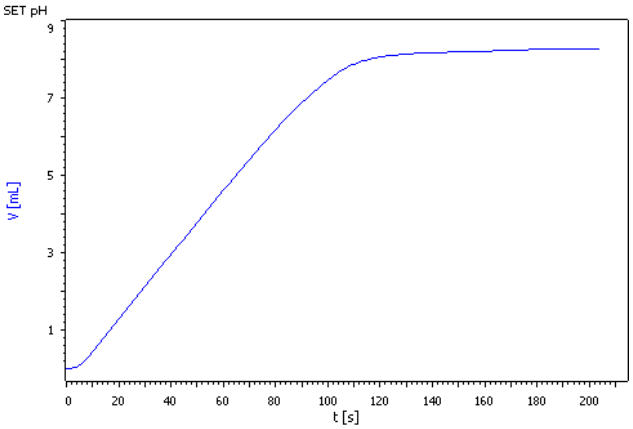

Fig. 1: Potentiometric Kjeldahl nitrogen determination in SET modus

Method 2 – Photometric determination

Instruments

- Titrator with MET and/or DET modus
- 20 mL buret
- Kjeldahl digestion and distillation apparatus

Electrodes

Optrode	6.1115.000

Reagents

- Sulfuric acid, puriss p.a., 96%
- Sodium hydroxide, puriss p.a., NaOH
- Boric acid, puriss p.a., H_3BO_3
- Hydrochloric acid, c(HCl) = 0.1 mol/L
- Sher indicator
- Catalyst (Kjeldahl tablets, Hg and Se free)

Solutions

Titrant	c(HCl) = 0.1 mol/L If possible this solution should be bought from a supplier.
c(H_3BO_3) = 0.1 mol/L	200 g boric acid is weighed into a 5 L volumetric flask and dissolved in dist. water. The solution is then filled up to the mark with dist. water.
w(NaOH) = 40 %	2 kg NaOH is slowly dissolved in approx. 5 L dist. water.

Sample preparation

Digestion

In a digestion flask, an appropriate amount of sample containing no more than 25 mg N is mixed with 10–20 mL conc. H_2SO_4 and two Kjeldahl tablets. The digestion flask is tilted back and forth to make sure that the sample is completely moistened with H_2SO_4. Then it is heated up, until a distinct reaction occurs and continued boiling slightly until the brown color and all carbon particles have disappeared. The solution should now appear clear and greenish. Upon completion of the digestion, the mixture is allowed to cool down.

Distillation

The Kjeldahl flask containing the digested sample is placed into the Kjeldahl distillation apparatus and approx. 50 mL water and as much w(NaOH) = 40% as needed are added to get a blue to brownish solution. The formed ammonia is then distilled off by steam distillation and retained in the form of ammonium in a sample beaker containing 50 mL of $w(H_3BO_3)$ = 2%.

Analysis

Titer

100–150 mg TRIS is weighed into a titration beaker and dissolved in approx. 70 mL dist. water. Five drops Sher indicator are added and the solution is titrated to until after the equivalence point.

Blank

For the blank determination, a digestion and distillation is performed the same way as described under sample preparation omitting the sample.

Sample

To the obtained solution, five drops of Sher indicator are added and the solution is titrated until after the first equivalence point with c(HCl) = 0.1 mol/L. Thereby, the solution turns from initially greenish over blue to orange.

Parameters

Titer

Mode	MET pH
Stirring rate	5
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.1 mL
Stop volume	20 mL
EP criterion	30 mV
EP recognition	greatest

Blank/Sample in MET modus

Mode	MET pH
Stirring rate	5
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.1 mL
Stop volume	20 mL
EP criterion	30 mV
EP recognition	greatest

Blank/Sample in DET modus

Mode	DET pH
Stirring rate	5
Signal drift	20 mV/min
Meas. point density	2
Min. increment	10 µL
Max. waiting time	38 s
Stop volume	20 mL
EP criterion	5
EP recognition	greatest

Calculation

Titer

$$f = \frac{m_{Std}}{V_{EP1} \times c_{HCl} \times M_{Std}}$$

f:	Titer of the selected titrant
m_{Std}:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{HCl}:	Concentration of the selected titrant in mol/L; here c(HCl) = 0.1 mol/L
M_{Std}:	Molecular weight of the standard (TRIS); 121.17 g/mol

Sample

$m_N = (V_{EP1} - Blank) \times c_{HCl} \times f \times M_N$

$$w_N = \frac{m_N \times 100}{m_S}$$

m_N:	Mass of nitrogen in the sample in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{HCl}:	Concentration of the selected titrant in mol/L; here c(HCl) = 0.1 mol/L
f:	Titer of the selected titrant
M_N:	Molecular weight of nitrogen in g/mol; 14.007 g/mol
w_N:	Mass fraction of Nitrogen in %
100:	Conversion factor
m_S:	Sample weight in mg

Example determination

Titration in MET modus

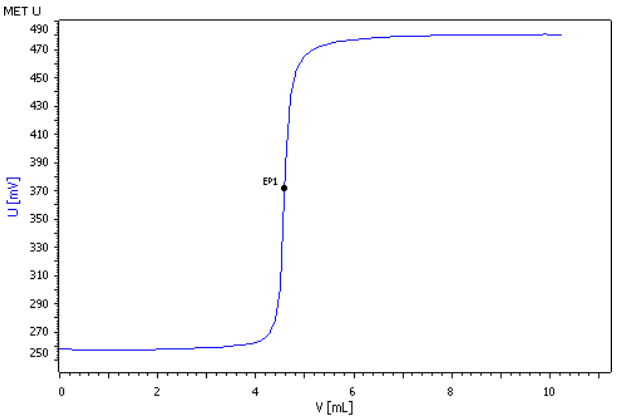

Fig. 2: Photometric Kjeldahl nitrogen determination in MET modus

Titration in DET modus

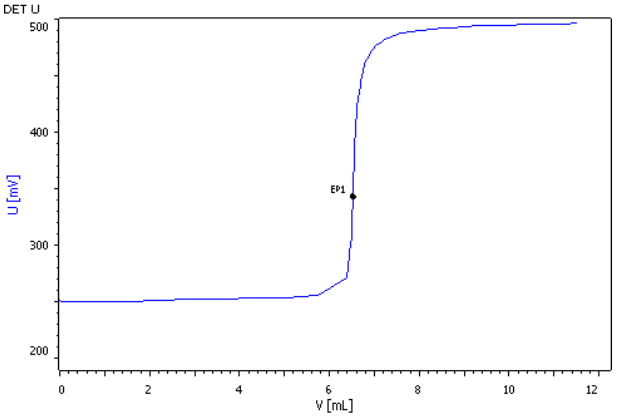

Fig. 3: Photometric Kjeldahl nitrogen determination in DET modus

Method 3 – Coulometric determination

Instruments

- Titrator with BRC modus
- 20 mL Buret
- Kjeldahl digestion apparatus

Electrodes

Separate double Pt-sheet electrode	6.0309.100
Generator electrode with diaphragm	6.0344.100

Reagents

- Sulfuric acid, puriss p.a., 96%
- Potassium bromide, KBr, p.a.
- Sodium tetraborate decahydrate (Borax), p.a.
- Hydrochloric acid, HCl, conc, >=37 %

Solutions

Electrolyte	100 g KBr and 60 g borax are dissolved in approx. 700 mL dist. water and the pH is adjusted to 8.6 with conc. HCl
w(NaOH) = 40 %	400 g NaOH is slowly dissolved in approx. 1 L dist. water.

Sample preparation

In a digestion flask, an appropriate amount of sample containing approx. 250 mg N is mixed with 30 – 40 mL conc. H_2SO_4 and two Kjeldahl tablets. The digestion flask is tilted back and forth to make sure that the sample is completely moistened with H_2SO_4. Then it is heat up, until a distinct reaction occurs and continued boiling slightly until the brown color and all carbon particles have disappeared. The solution should now appear clear and greenish. Upon completion of the digestion, the mixture is allowed to cool down.

Approx. 6 g of the digested sample is weight into a 50 mL beaker and 10 g ice is added. As the pH is adjusted to pH 7 with w(NaOH) = 40%, as much dist. water as needed is added to the sample solution to dip in the electrode in the sample solution. After adjusting the pH to pH 7, $Cu(OH)_2$ precipitates, which is removed by filtration with a syringe filter 0.45 µm. The solution is diluted with dist. water to approx. 60 g. The weight of the digestion flask, of the

digested sample, of the used aliquot as well as of the end weight is noted accurately as they are used for the calculation of the sample concentration in g/g.

Analysis

100 mL of the electrolyte is placed into the anodic compartment (coulometric cell) and 5 mL into the cathode compartment. The coulometer is started and conditioned. After conditioning 0.2 – 5 g of the sample solution is added. The sample is titrated by using the BRC mode and the separated double Pt-sheet electrode for indication.

Parameters

Mode	BRC
Stirring rate	6
Dynamics	320 mV
Max. rate	10’000 µg/g
Min rate	100 µg/g
Stop criterion	Drift
Stop drift	50 µg/min
Conditioning	On
Start drift	50 µg/min
Drift correction	Off
Stop time	Off

Calculation

$$m_N = \frac{m_{gen.\,Br_2} \times 2 \times M_N}{M_{Br_2} \times 3 \times 1000}$$

m_N:	Mass of nitrogen in the sample in mg
$m_{gen.\,Br_2}$:	Generated bromine in µg
2:	Stoichiometric factor
M_N:	Molecular weight of nitrogen in g/mol; 14.007 g/mol
M_{Br_2}:	Molecular weight of bromine in g/mol/; 159.808 g/mol
3:	Stoichiometric factor
1000:	Conversion of µg to mg

Example determination

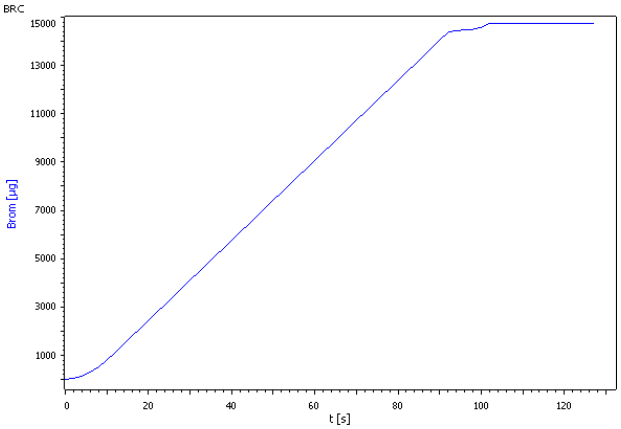

Fig. 4: Coulometric nitrogen determination in BRC modus

Comments

- All weights have to be documented properly as otherwise the sample concentration cannot be calculated.
- The parameter dynamics have to be adjusted in each case individually as the voltage ranges are different for different electrodes.
- The pH of the sample is adjusted to pH 7 because otherwise the pH value of the electrolyte will drop too fast.
- The digestion with a higher amount of sample takes about half an hour longer as for lower amounts of samples.

References

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Author

Competence Center Titration

Metrohm International Headquarters