

Application Bulletin

Of interest to: General analytical laboratories; Food
Environmental protection; Fertilizers

A D 1, 2, 3, 4, 7, 8, 11

Determination of ammonium or Kjeldahl nitrogen

Summary

The potentiometric titration of Kjeldahl nitrogen is one of the most widely employed analytical methods. Many of the standard procedures used 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 ammonium sulfate formed 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 potentiometric determination of nitrogen after distillation of the digestion solution. The second part indicates the possibilities of the coulometric titration (without distillation).

Digestion of the sample

A catalyst (usually in tablet form) is added to the sulfuric acid to achieve a faster and complete digestion of the organic sample components. The following «catalyst» tablets (Kjeldahl tablets) are, for example, available from Merck:

- no. 16469 (5 g): 0.3% CuSO_4 / 48.8% Na_2SO_4 / 48.9% K_2SO_4
- no. 15348 (5 g): 2.8% TiO_2 / 1.8% CuSO_4 / 47.7% Na_2SO_4 / 47.7% K_2SO_4
- no. 10958 (5 g): 1.5% CuSO_4 / 2.0% Se / 96.5% Na_2SO_4
- no. 05561 (2.5 g): 0.06% CuSO_4 / 80% Na_2SO_4 / 19.94% $\text{K}_2\text{S}_2\text{O}_8$

Na_2SO_4 and K_2SO_4 are used to raise the boiling point in the digestion mixture. For environmental protection reasons, one should refrain from using catalysts containing Hg and/or Se.

In a digestion flask, mix 0.15 ... 2 g sample containing no more than 25 mg N with 10 ... 20 mL conc. H_2SO_4 and one Kjeldahl tablet. Tilt back and forth to make sure that the sample is completely moistened with H_2SO_4 . Then heat up until a distinct reaction occurs and continue boiling slightly until the brown color and all carbon particles have disappeared. The solution should now appear clear and nearly colorless. Upon completion of the digestion, allow the mixture to cool down, then carefully dilute with a five-fold amount of water. If the determination of nitrogen is to

be carried out potentiometrically, transfer the mixture quantitatively into the distillation apparatus with dist. water. For the determination by coulometric titration transfer the digestion solution into a 100 mL volumetric flask and fill to the mark with dist. water.

1. Potentiometric titration

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 719 SET Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.213 Exchange Unit 10 mL or 6.3014.223 Exchange Unit 20 mL
- 6.0239.100 combined pH glass electrode with 6.2104.020 electrode cable

Reagents

There are various ways to titrate the obtained distillate. All the reagents used, including those for the digestion, should be as free as possible from blanks.

- Distilled or demineralized water
- Aqueous boric acid solution $w(\text{H}_3\text{BO}_3) = 2\%$
- Hydrochloric acid $c(\text{HCl}) = 0.1 \text{ mol/L}$ or 0.01 mol/L or 0.0714 mol/L
- Sodium hydroxide $c(\text{NaOH}) = 0.1 \text{ mol/L}$ or 0.01 mol/L or 0.0714 mol/L

Analysis

The initial solution* is connected to the distillation apparatus and alkali added to the digestion solution, then the distillation and titrator are started. Titration is performed in the SET pH mode using the following parameter settings:

Parameter	Method A	Method B	Method C
EP at pH**	5.70	4.50	4.70
dynamics	10	6	3
max.rate	2 mL/min	2 mL/min	2 mL/min
min.rate	0.5 $\mu\text{L}/\text{min}$	0.25 $\mu\text{L}/\text{min}$	0.25 $\mu\text{L}/\text{min}$
titr.direction:	auto	auto	auto

* As far as the initial solution and titrant are concerned, there are three possibilities:

Method A: Dist. water as initial solution and titration with HCl.

Method B: Boric acid as initial solution and titration with HCl.

Method C: E.g. 25 mL HCl and 25 mL dist. water as initial solution and back-titration with NaOH.

** Depending on the method used the following endpoints are selected:

- Method A: pH = 5.6 ... 5.8
- Method B: pH = 4.4 ... 4.5
- Method C: pH = 4.7

Calculation

- 1 mL c(HCl) = 0.1 mol/L corresponds to 1.4007 mg N
- 1 mL c(HCl) = 0.01 mol/L corresponds to 0.140 mg N
- 1 mL c(HCl) = 0.0714 mol/L corresponds to 1.000 mg N

Remarks

- Due to the fact that a SET titration, i.e. a titration to a preset endpoint, is carried out the electrode has to be calibrated prior to the analysis using, e.g., the buffer solutions pH = 7.00 and pH = 4.00.
- The easiest and safest method is to use 2% aqueous boric acid as the initial solution.

Figures

```
'fr
716 DMS Titrino      0E2/116  716.0021
Datum 1999-03-22    Zeit  14:09   26
pHc(init)          10.76    DET pH  *****
EP1                 4.241 ml    5.66
Stopp V erreicht
=====
```

```
'fr
716 DMS Titrino      0E2/116  716.0021
Datum 1999-03-22    Zeit  14:27   29
pHc(init)           6.78    DET pH  *****
EP1                  4.526 ml    4.46
Stopp V erreicht
=====
```

```
'cu
716 DMS Titrino      0E2/116  716.0021
Datum 1999-03-22    Zeit  14:09   26
Start V             0.000 ml  DET pH  *****
2.0 ml/div          dpH=2.0/div
```

```
'cu
716 DMS Titrino      0E2/116  716.0021
Datum 1999-03-22    Zeit  14:27   29
Start V             0.000 ml  DET pH  *****
2.0 ml/div          dpH=1.0/div
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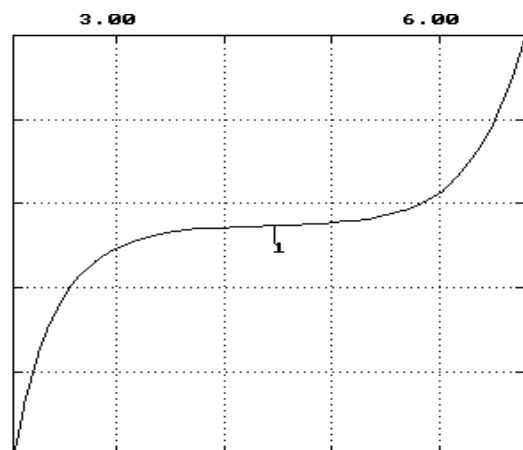
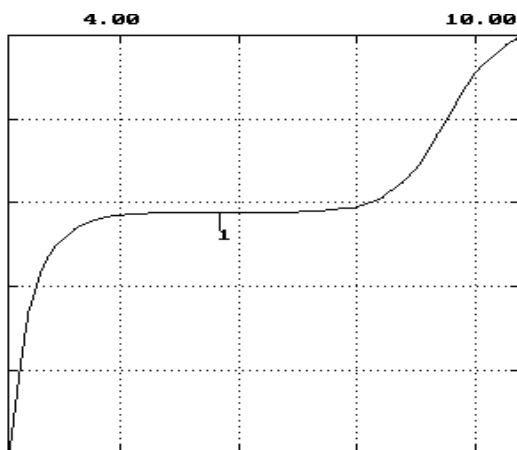


Fig. 1: Method A: dist. water as initial solution, HCl as titrant.

Fig. 2: Method B: boric acid as initial solution, HCl as titrant.

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'fr
716 DMS Titrimo      0E2/116  716.0021
Datum 1999-03-22    Zeit  15:05    32
pHc(init)          1.58      DET pH  *****
EP1                14.853 ml    4.69
Stopp V erreicht
=====
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```
'cu
716 DMS Titrimo      0E2/116  716.0021
Datum 1999-03-22    Zeit  15:05    32
Start V            0.000 ml  DET pH  *****
2.0 ml/div         dpH=2.0/div
```

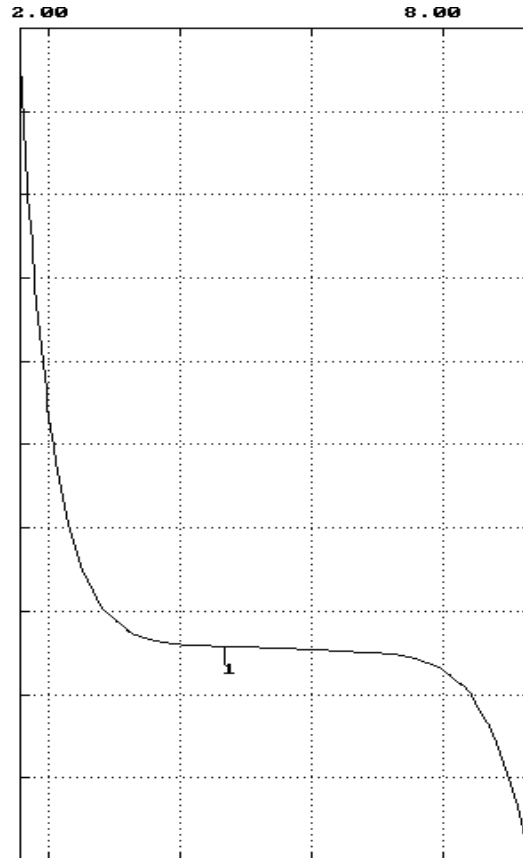


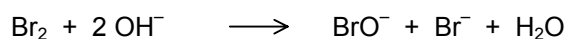
Fig. 3: Method C: HCl/dist. water as initial solution, NaOH as titrant.

2. Coulometric titration

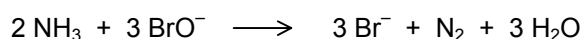
General information

In slightly alkaline solution, ammonia is oxidized to nitrogen with the aid of hypobromite. The following reactions occur in a KBr/borate buffer:

Anode:



The hypobromite formed reacts with ammonia:



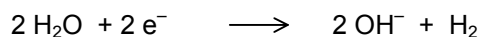
This results in:

$$\text{N:} \quad 14.007 * 1/3 \mu\text{g}/\mu\text{eq} = 4.6689 \mu\text{g}/\mu\text{eq}$$

$$\text{NH}_3: \quad 17.030 * 1/3 \mu\text{g}/\mu\text{eq} = 5.6767 \mu\text{g}/\mu\text{eq}$$

$$\text{NH}_4: \quad 18.038 * 1/3 \mu\text{g}/\mu\text{eq} = 6.0127 \mu\text{g}/\mu\text{eq}$$

Cathode:



Electrolyte solution for coulometry

Dissolve 100 g KBr as well as 60 g borax ($\text{Na}_2\text{B}_4\text{O}_7 * 10 \text{H}_2\text{O}$) in ca. 700 mL distilled water. Adjust the pH value to 8.60 with conc. HCl and make up to 1 L with distilled water.

Instruments and accessories

- Coulometer with titration cell and generator electrode (anode and cathode compartments separated by diaphragm)
- Indicator electrode: double Pt electrode
- Polarization current or polarization voltage source (possibly integrated in the coulometer) for endpoint indication ($I_{\text{pol}} = 10 \mu\text{A} / U_{\text{pol}} = 200 \text{mV}$)

Analysis

100 mL electrolyte solution are placed into the anode compartment and 5 mL into the cathode compartment. Start the coulometer and titrate the blank. Then add 250 μL of the digestion solution and titrate its nitrogen content.

Calculation

1 μeq corresponds to 4.6689 μg N or 5.6767 μg NH_3 or 6.0127 μg NH_4