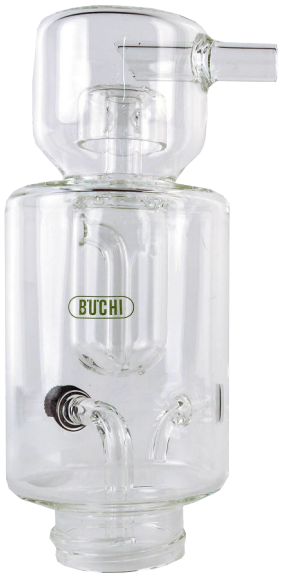
Application Note
No. 310/2018

Nitrogen determination in compound fertilizer according to Devarda

KjelFlex K-360 with Devarda Splash Protector, Metrohm Titrino 877



1. Introduction

Nitrogen is the most needed nutrient by crops, it is mainly absorbed by plants in the form of ammonium nitrogen and nitrate/nitrite nitrogen. The application of nitrogen fertilizer not only improves the yield but also the quality of the crop. From this aspect, the nitrogen content is a significant factor that affects the quality of the fertilizer.
In this Application Note, the total nitrogen content and nitrate/nitrite nitrogen content in a fertilizer sample were determined by Devarda distillation. The nitrate/nitrite is reduced to ammonium with Devarda's alloy, distilled by steam, absorbed by boric acid and titrated by sulfuric acid. To ensure the accuracy of the results, sodium nitrate was also tested as a reference for recovery. Due to formation of hydrogen gas during the reaction between alkali and Devarda's alloy, the samples foam a lot with a strong reaction. With the introduction of steam, the gas stream into the condenser is very fast and sodium hydroxide aerosols can pass into the condenser which would falsify the results for nitrogen. Here, the specific Devarda Splash Protector (Figure 1) was necessarily used to prevent that: it operates like a scrubber where all possible sodium hydroxide aerosols are scrubbed-off the gas stream.

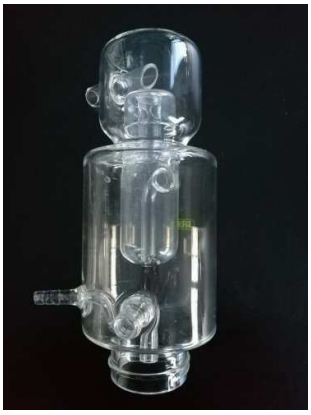


Figure 1: The BUCHI Devarda Splash Protector.

An overview of the determination methods for various nitrogen groups is shown in Table 1.

Table 1: Possible determination methods for various nitrogen groups in fertilizers [1].

Test method	Application range
Direct distillation	Ammonium nitrogen
Devarda's alloy reduction	Nitrate + nitrite + ammonium nitrogen
Sulfuric acid hydrolysis	Amide + ammonium nitrogen
Kjeldahl method	Organic + amide + ammonium nitrogen
Chromium powder reduction+ sulfuric acid hydrolysis	Nitrate + amide + ammonium nitrogen
Comprehensive hydrolysis catalytic reduction method	Nitrate + amide + organic + ammonium nitrogen

2. Equipment

- KjelFlex K-360 with Devarda Splash Protector
- Metrohm Titrino 877 (with pH-electrode)
- Analytical balance (accuracy ± 0.1 mg)

3. Chemicals and materials

Chemicals:

- Sodium hydroxide 32 %, nitrogen free, Sinopharm Chemical Reagent (10019762)
- Boric acid 2 %, 100 g boric acid, Sinopharm Chemical Reagent (100014808) diluted to 5 L with deionized water, pH adjusted to 4.65
- Sulfuric acid 0.25 mol/L, Fluka (35357)
- Sodium nitrate, Sinopharm Chemical Reagent (10019918), ⩾99%
- Devarda's alloy, Alfa Aesar (45526)

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

Samples:

- Compound fertilizer, Norway Yara International Co.,Ltd, declared nitrogen content 15% (nitrate/nitrite nitrogen 6.5%, ammonium nitrogen 8.5%), phosphorus 15% and potassium 15%, respectively. Except for the nutrient elements, medium trace elements like magnesium and boron are also contained.

Figure 2: Compound fertilizer granulate (left) and after grinding (right).

The samples were purchased at an internet business platform.

4. Procedure

There were both ammonium and nitrate/nitrite nitrogen in the samples as declared in the package. It is recommendable to determine the two forms of nitrogen from two separate samples (once with direct distillation and once with Devarda distillation). Reason: after direct distillation, there is water and alkali remaining in the sample tube. Once the Devarda's alloy is added, hydrogen gas generates immediately before mounting the sample tube back on KjelFlex K-360, which could lead to the loss of reducer and probably bring an incomplete reduction of nitrate/nitrite. Therefore, the total nitrogen was determined by Devarda distillation first. After that, direct distillation was performed with a new weighed sample to determine the ammonium nitrogen content. The nitrate/nitrite nitrogen content was obtained by substracting the result of direct distillation from that of Devarda distillation.

The determination of the nitrogen content in fertilizer includes the following steps:

- Homogenization of the sample by grinding to powder using a mortar
- Approximately weigh 0.25 g sample into a 300mL sample tube, accurate to 0.1 mg
- Add 2.0 g Devarda's alloy
- Let samples react with NaOH and Devarda alloy for two minutes
- Distillation and titration of the sample, using KjelFlex K-360 and Titrino 877

4.1. Detailed reaction process

The composition of Devarda's alloy is 50% Cu, 45% Al, 5% Zn. Al and Zn are both amphoteric metals who react with acid and alkali to release hydrogen.

$$8Al + 3NO_3^- + 5OH^- + 18H_2O = 3NH_3 \uparrow + 8[Al(OH)_4]^-$$

4.2. Distillation and titration

For the Devarda determination of the nitrogen which originates from nitrates, nitrites and ammonium, the samples were distilled according to the parameters listed in Table 2.

Table 2: Parameters for Devarda distillation and titration with the KjelFlex system K-360.

Parameter	Value
H_2O volume	30 mL
NaOH volume	30 mL
Boric acid	60 mL
Reaction time	120 s
Steam power	100%
Distillation time	180 s
Titration start	180 s
Titration type	Boric acid
Aspiration of sample tube	no
Stirrer speed distillation	5
Stirrer speed titration	7

Note: The sample tube must not be aspirated to avoid Devarda' alloy residue blocking the. valves.

To determine only ammonium nitrogen in fertilizer, direct distillation was performaned according to Table 3.

Table 3: Parameters for direct distillation of ammonium nitrogen.

Parameter	Value
H_2O volume	30 mL
NaOH volume	30 mL
Boric acid	60 mL
Reaction time	5 s
Steam power	100%
Distillation time	240 s
Titration start	240 s
Titration type	Boric acid
Aspiration of sample tube	yes
Stirrer speed distillation	5
Stirrer speed titration	7

Note: Sample tube could be aspirated because there was no Devarda's alloy added to the new weighed sample.

Titrate the distillate according to parameters listed in Table 4.

Table 4: Parameters for titration using the Metrohm titrino 877.

Titration solution	H_2SO_4 0.25 mol/L
Sensor type	pH electrode
Measuring mode	Endpoint pH
Endpoint pH	4.65

4.3. Calculation

The results are calculated as a percentage of nitrogen. The following equations (1), (2), (3) and (4) are used to calculate the results. For the reference substance, the purity of the sodium nitrate is considered in equation (3).

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

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

$$\%N_{NaNO3} = \frac{\%N \cdot 100}{P} \quad (3)$$

$$\%N_{nitrate/nitrite} = \%N_{total} - \%N_{ammonium} \quad (4)$$

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 H_2SO_4)
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
$\%NaNO_3$: percentage of weight of nitrogen corrected for the purity of reference substance
P : purity of the reference substance sodium nitrate [%]
$\%N_{nitrate/nitrite}$: percentage of nitrate/nitrite nitrogen in sample
$\%N_{total}$: percentage of total nitrogen in sample
$\%N_{ammonium}$: percentage of ammonium nitrogen in sample

5. Result

5.1. Blank determination

Only Devarda's alloy was weighed into the sample tubes for blank determination as shown in Table 5.

Table 5: Results of blank samples determination.

Blank	$m_{Devarda\ alloy}$ [g]	V_{Blank} [mL]
Blank 1	2.0021	0.062
Blank 2	2.0023	0.076
Blank 3	2.0034	0.058
Average [%]	–	0.065

The mean blank volume (V_{Blank}) was 0.065 mL (n = 3).

5.2. Determination of nitrogen in reference material sodium nitrate for recovery test

The recoveries for the reference sodium nitrate analysis are presented in Table 6. The nominal value of sodium nitrate is 16.32 % nitrogen. The recoveries were within the specification of 98 %-102%.

Table 6: The results of the recovery of nitrogen in reference material sodium nitrate.

Sample	m_{Sample} [g]	V_{Sample} [mL]	%N	Recovery [%]
Sodium nitrate 1	0.2522	5.9600	16.37	99.38
Sodium nitrate 2	0.2501	5.8920	16.32	99.06
Sodium nitrate 3	0.2510	5.9240	16.35	99.25
Sodium nitrate 4	0.2522	5.9440	16.32	99.12
Sodium nitrate 5	0.2518	5.8900	16.20	98.36
Sodium nitrate 6	0.2539	5.9580	16.25	98.67
Sodium nitrate 7	0.2507	6.0440	16.70	101.40
Sodium nitrate 8	0.2516	5.9880	16.49	100.10
Sodium nitrate 9	0.2500	6.0240	16.69	101.35
Sodium nitrate 10	0.2502	5.9100	16.36	99.33
Average [%]	–	–	16.41	99.60

Rsd [%]	–	–	1.04	1.04

The whole Devarda process is shown in Figure 3 below:

Figure 3: The Devarda distillation process of a sample: from the addition of NaOH (left) to the strong foaming during distillation (right). Due to the special design of the Devarda Splash Protector, the alkaline foam cannot pass into the condenser.

The reaction process included the following steps:

1) Alkali and water were added and the reaction started, small bubbles (hydrogen gas) and strong foam formation were visible were.
2) The reaction smoothened and distillation started, a strong foaming was generated and hydrogen gas was consumed at the same time.
3) The foam was hold back by the BUCHI Devarda Splash Protector, thus did not pass into the condenser.

5.3. Determination of nitrogen in compound fertilizer

5.3.1 Determination of total nitrogen

Both, nitrate/nitrite nitrogen and ammonium nitrogen in samples, were determined by the reaction with Devarda's alloy and direct distillation. The expected value of total nitrogen was 15%. The results are given in Table 7.

Table 7: The results of the determination of total nitrogen in fertilizer, expected content 15%.

Compound fertilizer	m_{Sample} [g]	V_{Sample} [mL]	N [%]
Fertilizer 1	0.2508	5.2580	14.50
Fertilizer 2	0.2536	5.3600	14.62
Fertilizer 3	0.2531	5.3880	14.73
Fertilizer 4	0.2534	5.4260	14.82
Fertilizer 5	0.2539	5.3640	14.62
Fertilizer 6	0.2525	5.3720	14.72
Average [%]	–	–	14.67
Rsd [%]	–	–	0.75

The mean blank volume (V_{Blank}) was 0.065 mL (n = 3).

5.3.2 Determination of nitrate/nitrite nitrogen

The content of nitrate/nitrite nitrogen is calculated as the difference of total nitrogen and ammonium nitrogen. The fertilizer used in this application was a balanced compound fertilizer whose nutrient contents were composed of nitrogen : phosphorus : potassium in a ratio of 15%: 15% : 15%. Regarding the total nitrogen, the ammonium nitrogen and nitrate/nitrite nitrogen content are declared to be 8.5% and 6.5%, respectively. The corresponding obtained results are shown in Table 8.

Table 8: The results of the determination of nitrate/nitrite nitrogen, expected content 8.5%.

Compound fertilizer	m_{Sample} [g]	V_{Sample} [mL]	Ammonium N [%]
Fertilizer 7	0.2518	3.1200	8.52
Fertilizer 8	0.2538	3.1420	8.52
Fertilizer 9	0.2508	3.1020	8.51
Fertilizer 10	0.2519	3.0980	8.46
Fertilizer 11	0.2522	3.1040	8.47
Fertilizer 12	0.2517	3.1120	8.51
Average [%]	–	–	8.50
Rsd [%]	–	–	0.32
Calculated nitrate/nitrite N content [%]		6.17	

The mean blank volume (V_{Blank}) was 0.065 mL (n = 3).

5.3.3 Results discussion

The measured content of the ammonium nitrogen corresponded very well to the declared value of 8.5%. The form of nitrogen was determined easily by direct distillation and also showed a good reproducibility of 0.32% RSD. For total nitrogen determination by Devarda distillation, an average content 14.67% was obtained, which also corresponded well to the declared content of 15.0%.

6. Comparison to other standard methods

This Application Note is based on the standard method AOAC 892.01, while parameters were optimized according to the samples. Several other standard methods are listed in Table 9 for comparison [2, 4, 5]:

Table 9: Comparison to other standard methods.

Parameter	Application note	AOAC 892.01	AOAC 955.04	GBT 3597-2002 (ISO 4176:1981)
Principle	Devarda alloy reduction	Devarda alloy reduction	Salicylic acid reduction	Reaction between Nitrate and nitrogen reagent
	Distillation,	Distillation,	Digestion,	Filtering, washing and drying the precipitation,
	Titration	Back titration	Distillation,	Weighing precipitation
			Back titration	
Nitrogen form	Nitrate, ammonium	Nitrate, ammonium	Nitrate, nitrate-free	Only nitrate
Reaction time	120s	-	About 2h	More than 2h
Reaction temperature	Ambient temperature	Ambient temperature	Heating	Heating
Amount of sample	0.25g	0.35~0.5g	0.7~2.2g	2~5g
Amount of reagent	2.0g Devarda's alloy	3.0g Devarda's alloy, 5ml NaOH solution	2.0g salicylic acid, 2.0g Zn, 0.7g HgO, 15.0g powdered K_2SO_4	10~12mL nitrogen reagent
Receiving solution	2% boric acid, 60ml	Volumetric acid	Volumetric acid	-
Distillate volume	Fixed time	250ml	More than150ml	-
Measurement method	Acid-alkali neutralization	Acid-alkali neutralization	Acid-alkali neutralization	Weighing

7. Conclusion

The determination of total nitrogen and nitrate/nitrite nitrogen in compound fertilizer was performed using Kjelflex K-360 equipped with the BUCHI Devarda Splash Protector, providing reliable and reproducible results which corresponded well to the labeled values. The average total nitrogen content was determined as 14.67% with a good repeatability (RSD = 0.75%), the labeled content was 15.0%. The determined ammonium nitrogen content was 8.50% (labeled value was 8.50%) with a RSD of 0.32% and the nitrate/nitrite content was calculated to be 6.17% (labeled value 6.50%). To ensure the reliability of the results, sodium nitrate was also tested as a reference sample. A good recovery of 99.60% (RSD = 1.04%) was obtained, which was within the specification of 98% -102%.
The presented optimized BUCHI method using the KjelFlex K-360 with Devarda Splash Protector requires a smaller amount of sample, has a shorter reaction time and operates at a higher degree of automation compared to other standard methods.

8. References

[1] GBT 8572-2010 Determination of total nitrogen in compound fertilizer - Titration after distillation (Chinese version).
[2] AOAC 892.01 Nitrogen (Ammoniacal and Nitrate) in Fertilizer-Devarda Method.
[3] Application Note No. 116/2013, Nitrogen determination in sodium nitrate.
[4] AOAC 955.04 Nitrogen (Total) in Fertilizer-Kjeldahl Method.
[5] GBT 3597-2002(ISO 4176:1981) Fertilizers—Determination of nitrate nitrogen content—Nitron gravimetric method(Chinese version).
[6] Operation Manual of KjelFlex K-360.