Application Note – N°. 875/2025

Nitrogen content in rare earths

Abstract: An easy and reliable method for the determination of the nitrogen content in rare earths using the Devarda method is introduced. The Devarda method determines the nitrogen content as a sum of nitrites, nitrates and ammonia. The distillation is performed with MultiKjel. The obtained results correspond well to the expected values with low relative standard deviations (rsd).

1. Introduction

An easy and reliable method for the determination of the nitrogen content in rare earths is introduced. The nitrogen in rare earths consists of ammonium ions, nitrites and nitrates. The former can be determined directly using steam distillation with the MultiKjel in combination with a Metrohm Eco Titrator. To determine the nitrite and nitrate content they are first converted to ammonia using the Devarda's alloy powder prior to steam distillation and titration.

This application note complies with official methods e.g. AOAC 892.01. [1]

2. Equipment

- MultiKjel with Eco Titrator (potentiometric) and recirculating chiller F-314 (11K36531211).
- 500 mL sample tubes (043982).
- Analytical balance (accuracy ± 0.1 mg).
- Devarda splash protector (11071014).
- Volumetric flask 100 mL.

3. Chemicals and Materials

- Sodium hydroxide 32%, VWR (9913.9010).
- 2% boric acid pH 4.65 with Sher indicator (11064972).
- Sulfuric acid 0.01 mol/L, volumetric solution, titer = 1.0005, Carl Roth (Order No. X872.1).
- Sodium nitrate (Purity ≥ 99.5%) Fluka (31440).
- Devarda's alloy powder, Fluka (31385).

Sodium nitrate solution: 1.5098 g sodium nitrate was weighed into a 100 mL volumetric flask and filled to mark with deionized water.

For safe handling please refer to all the corresponding MSDS!

4. Procedure

The determination of nitrate content includes the following steps:

1. Weigh in 0.7 g of sample in a 500 mL distillation tube.
2. Add 2 g ± 0.0020 g Devarda alloy to the 500 mL distillation tube just before distillation.
3. Direct distillation of the sample to determine the nitrate concentration with the MultiKjel.

Table 1: Parameters for distillation and titration with MultiKjel and Eco Titrator.

Method parameters MultiKjel		Instrument Settings	
Reaction Detection	Off	MaxAccuracy mode	On
H_2O Volume	50 mL	Chiller/Tap water	Chiller F-314
NaOH Volume	60 mL	Chiller temperature	10 °C
Reaction Time	300 s	AutoDist mode	On
Steam Steps	Fixed time		
Steam Power	100%	Automated Titration on Eco Titrator	
Level Detection	Off	Eco Titrator Method	
Distillation Time	200 s	Titrant	H_2SO_4 0.01 M
Stirrer Speed Distillation	5	Sensor type	Potentiometric
Titration Type	Boric acid titration	Method	Nitrogen (N)
H_3BO_3 Volume	60 mL (2%)	Endpoint	pH = 4.65

Stirrer Speed Titration	8
Titration Start Time	200 s
Sample Tube Aspiration	0 s
Reciever Aspiration	20 s

The determination of ammonia content includes the following steps:

1. Weigh in 3 g of sample in a 300 mL distillation tube (500 mL distillation tube can also be used).
2. Direct distillation of the sample to determine the ammonia concentration with the MultiKjel.

Table 2: Parameters for distillation and titration with MultiKjel and Eco Titrator.

Method parameters MultiKjel		Instrument Settings	
Reaction Detection	Off	MaxAccuracy mode	On
H_2O Volume	25 mL	Chiller/Tap water	Chiller F-314
NaOH Volume	35 mL	Chiller temperature	10°C
Reaction Time	5 s	AutoDist mode	On
Steam Steps	Fixed time		
Steam Power	100%	Automated Titration on Eco Titrator	
Level Detection	Off	Eco Titrator Method	
Distillation Time	180 s	Titrant	H_2SO_4 0.01 M
Stirrer Speed Distillation	5	Sensor type	Potentiometric
Titration Type	Boric acid titration	Method	Nitrogen (N)
H_3BO_3 Volume	60 mL (2%)	Endpoint	pH = 4.65
Stirrer Speed Titration	8		
Titration Start Time	180 s		
Sample Tube Aspiration	0 s		
Reciever Aspiration	20 s		

4.1 Calculation

The results are calculated as a percentage of nitrates. 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).

$$w_{N,NH3} = \frac{(V_{Sample} - V_{Blank}) \cdot z \cdot c \cdot f \cdot M_N}{m_{Sample} \cdot 1000} \quad (1)$$

$$w_{N,Dev} = \frac{(V_{Sample} - V_{Blank}) \cdot z \cdot c \cdot f \cdot M_N}{m_{Sample} \cdot 1000} \quad (2)$$

$$w_{NO_3} = w_{N,Dev} - w_{N,NH3} \quad (3)$$

$$\%\mathrm{NO3} = \frac{w_{NO_3} \cdot \mathrm{M_{NO3}}}{M_N} \cdot 100 \quad (4)$$

$$\%N_{NaNO3} = \frac{\mathrm{w_{N,Dev}} \bullet 100}{P} \quad (5)$$

$w_{N,NH3}$: Weight fraction of nitrogen by ammonia determination.
$w_{N,Dev}$: Weight fraction of nitrogen by Devarda method.
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 nitrate (14.007 g/mol).

M_{NO3}: Molecular weight of nitrate (62.005 g/mol).
m_{Sample}: Sample weight [g].
1000: Conversion factor [mL/L].
%NO3: Percentage of weight of nitrates.
$\%N_{NaNO3}$: Percentage of weight of nitrogen corrected for the purity of reference substance sodium nitrate [%].
P: Purity of the reference substance sodium nitrate [%].

5. Result

5.1 Recovery of sodium nitrate

The results of nitrogen determination and recovery for sodium nitrate analysis are presented in Table 3. The nominal value of sodium nitrate is 16.48% nitrogen. The recoveries are within the specification of 99.5–101% for direct distillation.

Table 3: Results of the recovery of nitrogen in sodium nitrate.

$NaNO_3$	m_{Sample} [g]	V_{Sample} [mL]	%N	Recovery [%]
Sample 1	0.015098	9.599	16.44	99.75
Sample 2	0.015098	9.637	16.51	100.18
Sample 3	0.015098	9.684	16.60	100.71
Average [%]	-	-	16.51	100.21
Rsd [%]	-	-	0.48	0.48

The mean blank volume (V_{Blank}) was 0.744 mL (RSD: 2.11%, n = 3).

5.2 Ammonia determination

Table 4: Results of the determination of ammonia-nitrogen.

Sample	m_{Sample} [g]	V_{Sample} [mL]	%N
Cerium carbonate	2.9346	2.923	0.02
Cerium carbonate	3.2755	3.280	0.02
Cerium carbonate	2.9752	3.021	0.02
Average [%]	-	-	0.02
Rsd [%]	-	-	1.40

The mean blank volume (V_{Blank}) was 0.426 mL (RSD: 1.37%, n = 3).

5.3 Nitrate determination using the Devarda method

Table 5: Results of the determination of ammonia-nitrogen. Expected nitrate content: 0.42%.

Sample	m_{Sample} [g]	V_{Sample} [mL]	%N	$\%NO_3^-$
Cerium carbonate	0.6969	4.348	0.14	0.53
Cerium carbonate	0.7053	4.430	0.15	0.54
Cerium carbonate	0.7246	4.585	0.15	0.55
Average [%]	-	-	0.15	0.54
Rsd [%]	-	-	1.24	1.49

The mean blank volume (V_{Blank}) was 0.744 mL (RSD: 2.11%, n = 3).

The Devarda method determines the nitrates, nitrites and ammonia content. The ammonia-nitrogen content was therefore determined in a separate experiment and deducted from the Devarda-nitrogen content. A distinction between nitrate and nitrite is not possible using the Devarda method.

6. Comparison to Standard Methods

This application note is based on the standard method AOAC 892.01 with differences. These differences are shown in Table 6.

Table 6: Differences to AOAC 892.01.

	Application note	AOAC 991.20	Notes / Impact
Sample tube	500 mL	600 - 700 mL	No impact.
Water NaOH Devarda alloy	50 mL 60 mL (32%) 2 g ± 0.0020 g Devarda alloy	300 mL 5 mL (42%) 3 g Devarda alloy	Less Devarda alloy for an economic and ecologic advantage
Distillation time	300 s	3600 s	Great time saving using the MultiKjel system
Receiving solution	60 mL boric acid (2%)	Measured amount of standard acid	Direct titration using boric acid is not reliant on an additional dosing unit for the measured amount of standard acid
Titration solution	Sulfuric acid (0.01 M)	NaOH solution	

7. Conclusion

The determination of both, ammonia-nitrogen and Devarda-nitrogen, using the MultiKjel system provides reliable and reproducible results. The results correspond well to the expected values with low relative standard deviations (rsd). For Cerium carbonate, a nitrate content of 0.54% was determined, which already considers the ammonia-nitrogen.

The recovery rate of sodium nitrate at 100% purity was 100.21% (rsd = 0.48%) which is within the specifications of 99.5–101% for direct distillation.

8. References

[1] AOAC 892.01 Nitrogen (Ammoniacal and nitrate) in fertilizers.

Operation Manual of Kjel Line K-365