Application Note – N°. 830/2024

LOD/LOQ determination in potentiometric titration

Abstract: The limit of detection (LOD) and limit of quantification (LOQ) refer to the minimum signal or quantity, respectively, that can be reliably observed from a given signal, with a satisfactory level of confidence or statistical significance. By using 2% boric acid solution together with 0.02 N of sulfuric acid, the best results were found resulting in an LOD of 0.004 and LOQ of 0.01 mg of N.

1. Introduction

The limit of detection (LOD) and limit of quantification (LOQ) refer to the minimum signal or quantity, respectively, that can be reliably observed from a given signal, with a satisfactory level of confidence or statistical significance. In this application note, the LOD and LOQ of the potentiometric titration using Metrohm Eco Titrator in combination with BUCHI's MultiKjel distillation unit is determined according to DIN 32645.[1]

2. Equipment

- MultiKjel with Eco Titrator and recirculating chiller F-314 (11K36531211).
- Analytical balance (accuracy ± 0.1 mg).

3. Chemicals

- Sodium hydroxide 32%, VWR (9913.9010).
- BUCHI ready to use 2% boric acid pH 4.65 with Sher indicator (11064972).
- BUCHI ready to use 4% boric acid pH 4.65 with Sher indicator (11064973).
- Sulfuric acid 0.01 mol/L, volumetric solution, titer = 0.1002 VWR (95032.1000).
- Sulfuric acid 0.05 mol/L, volumetric solution, titer = 0.04998 Supelco (1.09074.1000).
- Sulfuric acid 0.1 mol/L, volumetric solution, titer = 0.1001 VWR (30145.297).
- Sulfuric acid 0.25 mol/L, volumetric solution, titer = 0.2502 VWR (30143.291).
- Hydrochloric acid 0.1 mol/L, volumetric solution, titer = 0.0999 VWR (31955.293).

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

4. Procedure

To determine the LOD/LOQ, a certain number of blanks are measured the following steps:

- A steam distillation protocol followed by a titration employing MultiKjel coupled with Metrohm Eco Titrator.

4.1 Distillation and titration

Distill and titrate according to the parameters listed below in Table 1. The preparation of the MultiKjel system could be done by just using the tab "PREP" that combines both Preheating and Priming steps with a least one further priming step. By keeping the AutoDist mode activated, further preheating or priming is not required even with intermittent breaks in between the determinations.

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

Method parameters MultiKjel		Instrument Settings	
Reaction detection	Off	MaxAccuracy mode	On
H_2O volume	60 mL	Chiller/Tap water	Chiller F-314
NaOH volume	20 mL	Chiller temperature	10°C
Reaction time	5 s	AutoDist mode	On
Steam steps	No		
Steam power	100%	Automated titration on Eco Titrator	
Level detection	Off	Titrant	0.02 N–0.5 N
Distillation time	180 s	Sensor type	Potentiometric (pH)
Stirrer speed distillation	5	Endpoint	4.65
Titration type	Boric acid titration	Method on Eco Titrator	Blank Nitrogen (N)
H_3BO_3 volume	60 mL (2% / 4%)		
Stirrer speed titration	8		
Titration start time	180 s		
Sample tube aspiration	30 s		
Reciever aspiration	30 s		

5. Result

5.1 Determining Limit of Detection (LOD) and Limit of Quantification (LOQ)

The “blank method” from DIN 32645 was used for the determination of the detection limit (LOD) and the quantification limit (LOQ). [1]

In total, 10 blank values were determined using empty 300 mL sample tubes. The results are presented in Table 4.

Table 2: Results of the blank determination.

Boric acid conc. Titration solution (H_2SO_4) AutoDist mode	4% 0.5 N On	4% 0.2 N On	2% 0.02 N On	2% 0.02 N Off
1	0.1650	0.3990	0.2410	0.3360
2	0.1630	0.3980	0.2330	0.3340
3	0.1640	0.4040	0.2470	0.3400
4	0.1640	0.3990	0.2500	0.3300
5	0.1640	0.3990	0.2580	0.3300
6	0.1650	0.3970	0.2580	0.3300
7	0.1630	0.3990	0.2570	0.3310
8	0.1650	0.4000	0.2650	0.3300
9	0.1640	0.4040	0.2510	0.3250
10	0.1630	0.3970	0.2590	0.3260
Average [mL]	0.1640	0.3996	0.2519	0.3312
Standard deviation [mL]	0.0008	0.0025	0.0096	0.0045
Relative standard deviation (RSD)	0.50%	0.63%	3.81%	1.35%

It is noted that by keeping the AutoDist mode activated, the distillation time is automatically adjusted when using sample tubes at room temperature, resulting in slightly longer distillation time and therefore more distillate. Due to dilution of the boric acid by the addition of distillate, a higher consumption of titrant solution is expected.

The following equation (1) was used to calculate the limit of detection (LOD):

$$LOD = \phi n;\alpha \bullet SD \qquad (1)$$

$\phi n;\alpha$: factor 3.0; depending on the number of blanks (n = 10) and the level of significance (α=0.01).

SD: Standard deviation of the blank determination.

Depending on the LOD, the limit of quantification (LOQ) can be calculated, see equation (2) and the final results in Table 3.

$$LOQ = LOD \bullet k = \phi n;\alpha \bullet SD \bullet k \qquad (2)$$

k : factor 3

Table 3: Results of the measurements of LOD / LOQ.

Boric acid conc. Titration solution (H_2SO_4) AutoDist mode	4% 0.5 N On	4% 0.2 N On	2% 0.02 N On	2% 0.02 N Off
LOD [mg N]	0.0172	0.0210	0.0081	0.0038
LOQ [mg N]	0.0515	0.0631	0.0242	0.0113

6. Conclusion

The presented application note provides insight into the LOD and LOQ determination according to DIN 32645 using Metrohm Eco Titrator in combination with BUCHI's MultiKjel distillation unit. [1]

Hereby, an excellent LOD and LOQ of less than 0.1 mg absolute nitrogen (N) for low nitrogen contents was found. By using 2% boric acid solution together with 0.02 N of sulfuric acid, the best results were found resulting in an LOD of 0.004 and LOQ of 0.01 mg of N. By keeping the AutoDist mode activated, further preheating or priming was not required even with intermittent breaks in between the determinations.

To address high nitrogen levels (> 6.75 mg nitrogen), it is recommended to use 4% boric acid solution. [2] Although this solution leads to higher LOD and LOQ values, the overall impact is reduced due to the increased amount of nitrogen.

7. References

[1] DIN 32 645 Nachweis-, Erfassungs- und Bestimmungsgrenze.
[2] Kjeldahl Knowledge Base.

Kjel Line Operation Manual