Nitrate Determination by Standard Addition Technique: Fertilizer

The nitrate content in fertilizer was determined by multiple standard addition technique using the excellence titrator (T5, T7 or T9) performing the sample preparation type "Aliquot excl. ISA".

Sample	Fertilizer, 2.0 g
Compound	Nitrate, NO_3^- M = 62.0 g/mol, z=1
Chemicals	ISA solution: 5 mL mixture of 0.9 mol/L aluminium sulfate + 0.01 mol/L silver sulfate
NO_3^--Standard	2000 mg/L Nitrate in 1:10 ISA solution
Indication	ISE DX262-NO_3^- Reference DX200-SC, bridge electrolyte 2 M $MgSO_4$ Temperature sensor DT1000
Chemistry	A small amount of the NO_3^--standard solution is added several times in succession. The resulting differences in potential are used to determine the original sample concentration.
Calculation	Concentration [mg/L] R1 = cRawStd Content [ppm] R2 = (cRawStd*VTOT/VALIQUOT)*(VDILUTION/m)
Waste disposal	-
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Preparation and Procedures

CAUTION

- Use safety glasses, a lab coat and wear gloves.
- Ensure accurate cleaning of sensor is sufficient after each titration series.

Sample handling

- Weigh 2.0 g of fertilizer in a 500 mL volumetric flask, add 300 mL deionized water, sonicate for 10 minutes, and make up to the mark with deionized water.
- Stopper the flask and mix thoroughly.
- Filter it using filter paper and use the filtrate as an aliquot.

Reagents

Nitrate standard: 2000 mg/L nitrate in 1:10 ISA solution:
(more information please find under comments):

- Accurately weigh 3.262 g KNO_3 into a 1000 mL volumetric flask
- Add 90.91 mL of ISA solution
  (ISA:standard =1:10)
- Fill up to the 1000 mL volumetric mark with deionized H_2O
- Enter the actual concentration in mg/L of your final nitrate solution (depending on the corresponding weight of KNO_3)

Remarks

- Since there are different types of fertilizer available from different producers, it may be necessary to slightly adapt the method to your specific sample depending on its nitrate content.
- Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.
- The polymer measurement membrane can be damaged by mechanical impact (e.g. magnetic stirrer, cleaning). Do not touch with bare hands. Remove and cleaning of water drops with a soft paper tissue.

Instruments	- Titration Excellence T5/T7/T9 - 1 x 10 mL DV1010 glass burette (ME-51107501)
Accessories	- Temperature Sensor DT1000 (ME- 51108898) - 100 mL PP Titration beaker (ME- 51109388) - XS205 Balance

Results

Results

R1: 9946.508 ppm
R2: 8927.134 ppm
R3: 9105.524 ppm
R4: 9437.713 ppm
R5: 8924.692 ppm

Statistics

Method-ID	Fertilizer
Samples	5
Mean	9268.314 ppm
s	432.904
srel	4.671 %

Table of measured values

Single Results

E.g. of sample Nr.1:

Sample ID	Fertilizer
Raw Result (R1)	36.296 mg/L
Content (R2)	9946.508 ppm
Sample size	2.00699 g
Volume	4.080 mL
No. of additions	5
dE	8 mV
Termination	30 mL
Slope	59.28 mV/pX
Coefficient of determination (R2)	0.99999984

Raw results

Add. No.	cRawStd [mv]	Meas. value [mV]	dE [mV]	dV [mL]	Slope [mV/pX]	Temperature [°C]
0	NaN	221.4	NaN	0	NaN	23.2
1	NaN	213.5	7.9	0.369	NaN	23.2
2	35.40492	205.5	8.0	0.517	-58.19	23.1
3	35.71322	197.5	8.0	0.7255	-58.59	23.1
4	36.4138	189.4	8.1	1.0225	-59.40	23.1
5	36.29553	181.4	8.0	1.446	-59.28	23.1

Comments

- Multiple standard addition gives three or more measurement points. Thereof, sensor calibration values (slope and intercept) are obtained during the determination and saved as results. Additional calibration is not necessary. Matrix effects are reduced using the multiple standard addition due to the calibration within the sample matrix.
- Before starting a measurement series, sensors must be conditioned. The nitrate content of the conditioning solution should be chosen in the same range as the nitrate concentration of the sample to be measured (e.g. 50 mL of 100 ppm NO_3^- and 5 mL ISA solution). For highly reproducible and accurate results, perform the conditioning in a low nitrate concentration (approx. 20 ppm NO_3^-).
- The sample to be measured should be diluted down to approx. 30 – 100 mg/L (corresponds to R1=cRawStd) in order to get as accurate results as possible.
- To obtain accurate results, the total potential range ΔE_{total} during the standard addition should cover 30 – 100 mV using 5 – 6 additions. Please note that in order to obtain accurate results the no. of additions must be ≥ 3 ($\Delta E_{total} \geq$ 30 mV)
- For good reproducibility, the dispensed amount of nitrate standard solution should not exceed 25 – 35 % of the sample volume used for the titration.
- To improve the results, use the control mode Cautious for the standard addition. The control mode Fast is used for approximate nitrate determination only.
- In case the slope is < 54 mV/log(c), the sensor should be checked and the sample analysis repeated
- The total ion activity of the sample and standard solution must be constant. By adding a constant amount of ionic strength adjustment (ISA) solution to all samples and the standard solution, a constant ionic strength is attained. The ratio of ISA solution to sample and standard is 1:10:
    - ISA : sample=5 mL : 50 mL (V_{tot}=55 mL)
    - ISA : standard solution = 90.9 mL : 909.1 mL (V_{tot}=1000 mL)
- The reference electrode DX200 can also be filled with the bridging electrolyte Aluminium sulfate 0.9 mol/L instead of 2M $MgSO_4$. The solution must be renewed daily. The inner electrolyte (KCl solution 3 mol/L saturated in AgCl) is renewed monthly.
- It is better to filter the sample using suction pump to reduce the filtration time.

Method

001 Title

Type	General titration
Compatible with	T5 / T7 / T9
ID	M720_2015
Title	Nitrate in fertilizer

002 Conditioning (controlled)

Titration stand	Manual stand 1
Speed	30 %
Sensor type	ISE
Sensor	DX262-NO_3^-
Unit	mV
Acquisition	Equilibrium controlled
dE	0.1 mV
dt	60 s
t(min)	120 s
t(max)	240 s
Action	None
Temperature acquisition	No
Temperature	25.0 °C
Condition	No

003 Sample (Standard Addition)

Number of IDs	1
ID 1	Fertilizer
Analysis type	Direct
Sample type	Solid
Entry type	Fixed weight
Weight	2.00699 g
Correction factor	1.0
Temperature	25.0 °C
Sampling	Aliquot excl. ISA
ISA volume	5 mL
Dilution volume	500 mL
Aliquot volume	50 mL
Titrator reader	None

004 Titration stand (Manual stand)

Type	Manual stand
Titration stand	Manual stand 1

005 Stir

Speed	30 %
Duration	60 s
Condition	No

006 Standard Addition[1]

Titrant

Titrant	Nitrate
Concentration	2000.00 mg/L

Sensor

Type	ISE
Sensor	DX262-NO_3^-
Unit	mV
Ion charge	-1

Temperature acquisition

Temperature measurement	Yes
Temperature sensor	DT1000
Unit	°C

Stir

Speed	30 %

Control

Control	Normal
dE (potential difference)	8 mV
Number of additions	5
Show parameters	Yes
Meas. val. acquisition	Equilibrium controlled
dE	0.03 mL
dt	10 s
t(min)	30 s
t (max)	120 s
Show parameters for first addition	Yes
Titrant addition	Dynamic
dE (set value)	0.5 mL
dV (min)	0.02 mL
dV (max)	0.2 mL
Meas. val. acquisition	Equilibrium controlled
dE	0.1 mV
dt	5 s
t (min)	5 s
t (max)	20 s

Termination

At Vmax	30 mL

Condition

Condition	No

007 Calculation R1

Result type	Predefined
Result	Concentration
Result unit	mg/L
Formula	R1=cRawStd
Constant C=	1
M	M[None]
z	z[None]
Decimal places	3
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Write to RFID	None
Condition	No

008 Calculation R2

Result type	Predefined
Result	Content
Result unit	ppm
Formula	R2=(cRawStd*VTOT/VALIQUOT)*(VDILUTION/m)
Constant C=	1
M	M[None]
z	z[None]
Decimal places	3
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Write to RFID	None
Condition	No

009 End of sample

010 Record

Summary	Yes
Results	No
Raw results	No
Resource data	No
Calibration curve	No
Method	No
Series data	No
Condition	No