Metrohm

Application Bulletin 133/3 e

Determination of ammonia with the ion-selective electrode

Tips and tricks for a reliable determination according to common standards

Branch

General analytical laboratories; water, waste water, environmental protection; fertilizers

Keywords

Titration; ion measurement; potentiometric titration; ammonium; standard addition; mineral water; tap water; direct measurement; waste water; liquid fertilizers; soil; NH_3-selective gas membrane electrode; combined electrode; EPA 350.2; EPA 350.3; ASTM D1426; ISO 6778; branch 1; branch 2; branch 11; branch 16; 6.0506.100; 6.0506.150; agriculture

Summary

Although the known photometric methods for the determination of ammonia/ammonium are accurate, they require a considerable amount of time (Nessler method 30 min, indophenol method 90 min reaction time). A further disadvantage of these methods is that only clear solutions can be measured. Opaque solutions must first be clarified by time-consuming procedures.

These problems do not exist with the ion-selective ammonia electrode. Measurements can be easily performed in waste water, liquid fertilizer, and urine as well as in soil extracts.

Especially for fresh water and waste water samples several standards, such as ISO 6778, EPA 350.2, EPA 305.3 and ASTM D1426, describe the analysis of ammonium by ion measurement. In this Application Bulletin, the determination according to these standards is described besides the determination of other samples as well as some general tips and tricks on how to handle the ammonia ion selective electrode.

Determination of ammonia in ammonium salts, of the nitric acid content in nitrates, and of the nitrogen content of organic compounds with the ion-selective ammonia electrode is based on the principle that the ammonium ion is released as ammonia gas upon addition of excess caustic soda:

$NH_4^+ + OH^- = NH_3 + H_2O$

The outer membrane of the electrode allows the ammonia to diffuse through. The change in the pH value of the inner electrolyte solution is monitored by a combined glass electrode.

If the substance to be measured is not present in the form of an ammonium salt, it must first be converted into one. Organic nitrogen compounds, especially amino compounds are digested according to Kjeldahl by heating with concentrated sulfuric acid. The carbon is oxidized to carbon dioxide in the process while the organic nitrogen is transformed quantitatively into ammonium sulfate.

Instruments

- Titrator with ‘STDADD’ and ‘MEAS Conc’ mode
- 10 mL buret (for standard addition)
- Stirrer

Electrode

NH_3-selective electrode (for low concentration)	6.0506.100
NH_3-selective electrode (for high concentration)	6.0506.150

General hints

Handling of the electrode

To achieve optimal measurements, observe the following points:

- Before the first use or after a longer storage in the dry state, the inner glass electrode must be soaked for 6 to 12 hours in an ammonia - free pH = 4 buffer solution. Rinse with distilled water afterwards and dry by dabbing with a soft paper towel.
- Both electrodes should be mounted with the membrane as described in the manual (8.109.8031). 2.5 mL of outer electrolyte solution is added. After it is mounted together, the electrode should be shaken carefully to remove any air bubbles from the membrane. Then the electrode is placed for approximately 10 min in distilled water.
- The membrane of the electrodes should never be touched with your fingers or any kind of objects, as this would reduce the water-repellant effect of the membrane.
- Rinse the electrode after each measurement with distilled water and remove any adhering water droplets by dabbing with a soft paper towel. Before each new measurement, the electrode should be conditioned in distilled water for at least 10 min. For determining concentrations under 1 mg/L, the electrolyte must be diluted 1:9 with deionized water and the electrode must be conditioned for approximately 30 min. For storage times of 1 to 5 days the electrode is placed in c(NH_4Cl) = 0.1 mol/L. For longer periods, take the electrode apart, clean the outer shaft with deionized water and store the inner part (pH electrode) in KCl sat.
- A too large slope in a standard addition is usually due to too short conditioning times or to an error in the preparation of the electrode. However, slopes that are not more than 3 mV above the theoretical value can be tolerated.
- The measurements should be performed using a constant stirring speed and at a constant temperature. Stirring should be continuous because bubbles can form on the membrane during an interruption in stirring, which can cause false readings. Make sure that the stirrer is switched on and that a stirring bar is in the measuring vessel. If additions are made without stirring, erroneous results are obtained!
- If more than 5 to 6 minutes are required to obtain a stable reading, the membrane and inner electrolyte must be replaced.
- If samples with greatly varying ammonia concentrations are measured frequently, the time required to reach a stable reading becomes longer for the samples with lower ammonia concentrations.
- Refer to the hints given in the manual (8.109.8031) for NH_3-selective electrodes.

Possible interferences

- Volatile amines:
  - Simulate an elevated concentration of ammonia. Ethylene amine gives almost the same difference in potential as ammonia. Longer C chains cause less interference.
- Hydrazine:
  - Causes the same interference as described above for volatile amines.
- Complexing ions:
  - Ag, Hg, Cu, and Ni among others simulate a lower ammonia concentration. The interference caused by 20 ppm Hg can be eliminated by using a solution with an additional 0.46 g NaI per 100 mL NaOH instead of the mentioned NaOH solution.
- Concentration:
  - Should not exceed 1 mol/L. At higher concentrations, the sample must be diluted with distilled water. However, in lower concentration ranges, the electrode becomes less sensitive and requires a longer time to reach a stable reading (up to 15 min).
- Proteins:
  - A high protein concentration (1 g/L) simulates higher ammonia concentrations. The calibration curve becomes linear only above 10 mg/L of ammonium.

Sample preparation and handling

- After the addition of NaOH, the pH value must be at least 12. Acidic samples must be neutralized before the addition of NaOH. After addition of NaOH, the measurement must take place immediately. Otherwise, the ammonia evaporates leading to too low results.
- Alkali samples must be measured immediately. The ammonia loss in a stirred alkali sample of 100 mL is approx. 50% within six hours.
- For purpose of storage, the sample must be acidulated with hydrochloric acid to approx. pH 6 (approx. 0.5 mL

c(HCl) = 1 mol/L per liter of sample) and stored in well-sealed vessels.

- Do not add the sodium hydroxide solution until just before the measurement.
- If a standard or sample solution is measured repeatedly, then it must be stored in a sealed or covered vessel between the measurements. This ensures that ammonia will not escape. For best practice, it is recommended that the standard be prepared right before the measurement directly in the beaker.
- Ammonia dissipates very rapidly out of solution when ammonia concentrations are > 1 mol/L. These kinds of samples must therefore be diluted.
- All measurements should be performed at a constant temperature (for example, at 25 °C). Standard and sample solutions must always be measured at the same stirring speed and at the same temperature. A difference in temperature of 1 °C results in a deviation of approx. 2%.
- If possible, use narrow, high measuring vessels (minimum ratio of surface to volume).

Choice of procedure

- Standard addition is a quick and reliable method especially for **undefined sample matrices**.
- Direct measurement is preferred, when several measurements of the same solutions are to be carried out in a defined and **unproblematic sample matrix**.

Choice of standard concentrations

- In order to ensure an accurate evaluation of the standard addition, the standard concentrations (c_{std}) for the different buret volumes (V_{buret} / mL) must be chosen as a function of the sample concentration (c_{smp1}) according to the table below

V_{buret} / mL	c_{std}/ c_{smpl}
5	40:1
10	20:1
20	10:1
50	5:1

If the sample has been substantially diluted with ISA or TISAB, this ratio must be considered.

Example:

Sample concentration (c_{smpl})	5	mg/L
Buret volume (V_{buret})	10	mL
Sample size	10	mL
ISA/TISAB	10	mL
Total volume (V_{total})	20	mL
Factor from table (c_{std} : c_{smpl})	20	

The result is a sample concentration of 2.5 mg/L in the initial solution. The optimal concentration of the standard is therefore 2.5 mg/L x 20 = 50 mg/L.

- Note, however, that this is only a general guide for the standard concentration. Exact measurements are also possible if the above recommendations are not strictly followed.
- The standard solutions must have the same ionic background as the sample solutions.
- Low ammonia concentrations:
  The adjustment time becomes distinctly longer. The blank values of the chemicals are to be taken into account.

Direct measurement

Direct measurement is a simple and rapid method for testing numerous samples with similar sample matrices across a wide range of concentrations.

Observe the following notes when performing direct measurements:

- Select the concentrations of the standard solutions (e.g,. NH_4Cl solutions) in such a way that the anticipated ammonia concentration of the sample solution falls in the middle of the calibration range.
- Make sure that the temperatures of all standard and sample solutions are identical.
- The diffusion of ammonia through the membrane is slowed down considerably in the presence of ammonia concentrations < 6 – 10^{-5} mol/L. The response time of the electrode is prolonged accordingly. A special measurement technique is required for this concentration range.

Calibration of high ammonia concentrations and analysis of waste water samples

Determination according to ISO 6778 is described in this section.

Reagents

- Metrohm measuring electrolyte (50 mL); 6.2316.030
- Sodium hydroxide
- Ammonium chloride
- Disodium ethylenediaminetetraacetate, EDTA

Solutions

ISA solution	c(NaOH) = 1 mol/L and c(EDTA) = 0.1 mol/L 40 g NaOH and 37.2 g EDTA are weighed into a 1 L volumetric flask containing approx. 800 mL distilled water. After dissolving and reaching room temperature, the solution is filled up to the mark with deionized water.

Standard solutions

10'000 mg/L ammonium	29.7 g ammonium chloride is weighed into a 1 L volumetric flask, dissolved in deionized water and filled up to the mark with deionized water.
10 mg/L ammonium	1 mL $\beta(NH_4)$ = 10'000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.
50 mg/L ammonium	5 mL $\beta(NH_4)$ = 10'000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.
90 mg/L ammonium	9 mL $\beta(NH_4)$ = 10'000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.
130 mg/L ammonium	13 mL $\beta(NH_4)$ = 10'000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.
170 mg/L ammonium	17 mL $\beta(NH_4)$ = 10'000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.

Calibration

For each standard concentration, 50 mL of standard is pipetted into a plastic beaker and 5 mL ISA solution is added. The standards are measured in ascending order, depending on the concentration. Before the measurement of the first standard and in-between measurements of the different standards, the sensor is rinsed with distilled water and conditioned in distilled water for exactly 10 min.

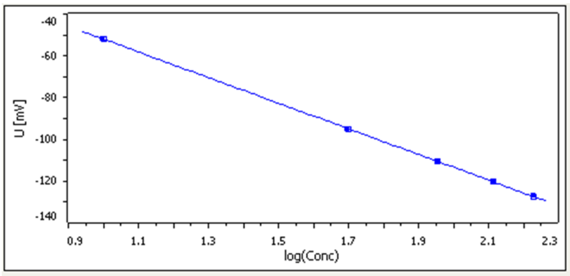
Analysis

50 mL of waste water is pipetted into a plastic beaker, 5 mL ISA solution is added, and the measurement is started. Between measurements, the sensor is rinsed with distilled water and then conditioned in distilled water for exactly 10 min.

Parameters (calibration and analysis)

Number of standards	5
Unit Conc.	ppm
Conc. standard 1	10
Conc. standard 2	50
Conc. standard 3	90
Conc. standard 4	130
Conc. standard 5	170
Stirring rate	8
Signal drift	0.50 mV/min
Min. waiting time	10 s
Max. waiting time	600 s
Measuring interval	2.0 s

Example calibration curve

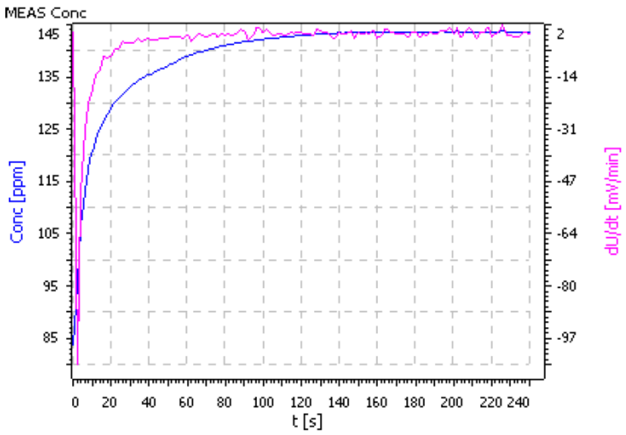


	Conc [ppm]	U [mV]	T [°C]	t [s]
Standard 1	10.000	-51.9	25.0	145
Standard 2	50.000	-95.0	25.0	140
Standard 3	90.000	-110.5	25.0	142
Standard 4	130.000	-120.2	25.0	137
Standard 5	170.000	-127.2	25.0	138

Slope	-61.3	mV
E(0)	9.3	mV
c (blank)	0.00	ppm
Variance	0.045	

Fig. 1: Calibration curve for NH_3 selective electrode

Example sample curve



Comments

- Condition the electrode prior to measurement in an ammonia – free pH 4 buffer solution.
- Use as large a sample volume as possible so that the ratio of surface to volume is as low as possible. This will minimize the absorption of ammonia from ambient air.

Calibration of low ammonia concentration and analysis of tap water

The determination described here is based on EPA 350.3 and ASTM D1426. Compared to the two standards, the volume of sample was reduced.

Reagents

- Metrohm measuring electrolyte (50 mL); 6.2316.030
- Sodium hydroxide
- Ammonium chloride

Solutions

ISA solution	*c*(NaOH) = 10 mol/L 200 g ice made from distilled water and 400 mL distilled water are placed into a plastic beaker and 400 g NaOH is added. After dissolving and reaching room temperature, the solution is transferred into a 1 L volumetric flask and filled up to the mark with deionized water.
Diluted electrolyte	The Metrohm measuring electrolyte 6.2316.030 is diluted 1:9 with deionized water.

Standard solutions

1’000 mg/L ammonium	2.97 g ammonium chloride is weighed into a 1 L volumetric flask, dissolved in deionized water and filled up to the mark with deionized water.
0.1 mg/L ammonium	0.1 mL β(NH_4) = 1’000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.
0.5 mg/L ammonium	0.5 mL β(NH_4) = 1’000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.
0.9 mg/L ammonium	0.9 mL β(NH_4) = 1’000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.
1.3 mg/L ammonium	1.3 mL β(NH_4) = 1’000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.
1.7 mg/L ammonium	1.7 mL β(NH_4) = 1’000 mg/L is pipetted into a 1 L volumetric flask and filled up to the mark with deionized water.

Calibration

For each standard concentration, 20 mL of standard is pipetted into a plastic beaker and 1 mL ISA solution is added. The standards are measured in ascending order, depending on the concentration. Before the measurement of the first standard and between the measurement of the different standards, the sensor is rinsed with distilled water and conditioned in distilled water for exactly 10 min.

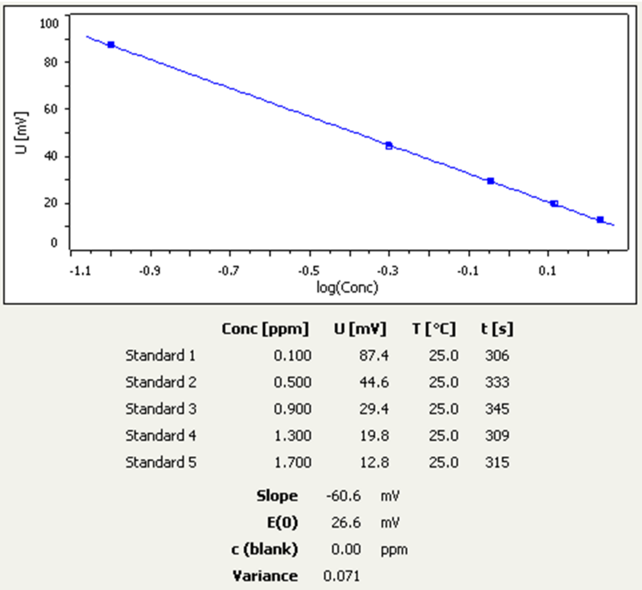
Analysis

20 mL of tap water is pipetted into a plastic beaker, 1 mL ISA solution is added, and the measurement is started. Between measurements, the sensor is rinsed with distilled water and then conditioned in distilled water for exactly 10 min.

Parameters (calibration and analysis)

Number of standards	5
Unit Conc.	ppm
Conc. standard 1	0.1
Conc. standard 2	0.5
Conc. standard 3	0.9
Conc. standard 4	1.3
Conc. standard 5	1.7
Stirring rate	8
Signal drift	0.50 mV/min
Min. waiting time	10 s
Max. waiting time	600 s
Measuring interval	2.0 s

Example calibration curve



	Conc [ppm]	U [mV]	T [°C]	t [s]
Standard 1	0.100	87.4	25.0	306
Standard 2	0.500	44.6	25.0	333
Standard 3	0.900	29.4	25.0	345
Standard 4	1.300	19.8	25.0	309
Standard 5	1.700	12.8	25.0	315

Slope	-60.6	mV
E(0)	26.6	mV
c (blank)	0.00	ppm
Variance	0.071	

Fig. 2: Calibration curve for NH_3 selective electrode in the low calibration range

Example sample curve

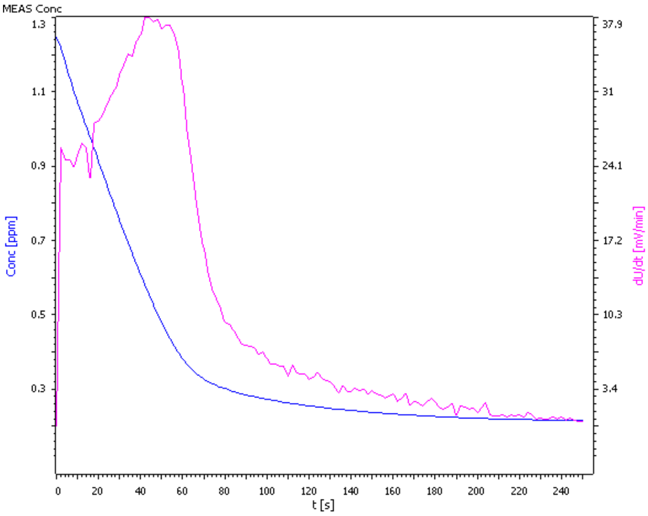


Fig. 3: Analysis of β(NH_4) = 0.25 mg/L

Comments

- If low concentrations of ammonia are measured, the electrolyte of the outer compartment is diluted 1:9 with deionized water.
- Condition the electrode prior to measurement in an ammonia – free pH 4 buffer solution.
- The standards EPA 350.2, EPA 350.3 and ASTM D1426 differ from the here described procedure in such a way that 100 mL sample are used instead of the 20 mL here described.
- At such a low concentration range, it is important to prepare the standards as shortly as possible before measurement. Otherwise the calibration curve will not be linear and the measurement gets faulty.

Standard addition

In principle, there are three types of standard addition:

- **man** (Standard addition with manual addition of standard addition solution.)
- **dos** (Standard addition with addition of standard addition solution by a dosing device.)
- **auto** (Standard addition with automatic addition of standard addition solution from a dosing device in such a way that a constant potential difference results.)

Please consult the manual of your device or ***tiamo***™ for the characteristics of the individual types. The most reliable method is automatic standard addition («auto»). Note, however, that in order to get accurate results the difference in potential ΔU chosen must be at least 12 mV per standard addition and that at least 4 standard additions must be performed (total ΔU at least 30 mV). If exactly defined volumes of the standard additions are required but maximum ease of operation is also desirable, choose «auto dos» and enter the individual standard addition volumes.

Reagents

ISA solution c(NaOH) = 10 mol/L	400 g NaOH is dissolved in approx. 500 mL deionized water containing ice cubes made of deionized water. After dissolution, the solution is transferred into a 1 L volumetric flask and filled up to the mark with deionized water.
EDTA solution c(EDTA) = 1 mol/L	29.22 g EDTA is suspended in 50 mL water and c(NaOH) = 10 mol/L is added dropwise until everything was dissolved. Afterwards the solution is transferred into a 100 mL volumetric flask and filled up to the mark with deionized water

Standard solutions

10'000 mg/L ammonium	29.7 g NH_4Cl is weighed into a 1 L volumetric flask, dissolved and filled up to the mark with deionized water.
1000 mg/L ammonium	2.97 g NH_4Cl is weighed into a 1 L volumetric flask, dissolved and filled up to the mark with deionized water.
Standard $c(NH_4)$ = 0.100 g/L ~ 100 ppm	0.297 g NH_4Cl is weighed into a 1 L volumetric flask, dissolved and filled up to the mark with deionized water.
Standard $c(NH_4)$ = 0.010 g/L ~ 10 ppm	10 mL of $c(NH_4)$ = 1'000 mg/L is transferred into a 1 L volumetric flask and filled up to the mark with deionized water.

Sample preparation

No sample preparation is required for tap water, aquarium water, melted snow, and liquid fertilizer.

Soil

Approx. 30 g dried soil (2 h at 120 °C) is weighed into a 500 mL beaker and 300 mL c(HCl) = 2 mol/L is added. The suspension is boiled for 1 h and allowed to cool down. Afterwards the suspension is filtrated into a 500 mL volumetric flask and filled up to the mark with deionized water.

Analysis

Tap water and melted snow

50 mL sample is pipetted into a 100 mL beaker and 1 mL c(NaOH) = 10 mol/L is added. Immediately afterwards, the standard addition with $\beta(NH_4)$ = 10 mg/L is started.

Aquarium water and mineral water

50 mL sample is pipetted into a 100 mL beaker and 1 mL c(EDTA) = 1 mol/L is added. Immediately afterwards, the standard addition with $\beta(NH_4)$ = 10 mg/L is started.

Fertilizer

0.1 mL fertilizer, 49.9 mL deion water and 1 mL c(EDTA) = 1 mol/L are pipetted into a 100 mL beaker and 1 mL c(NaOH) = 10 mol/L is added. The standard addition with $\beta(NH_4)$ = 10'000 mg/L is started directly after the addition of the c(NaOH) = 10 mol/L.

Soil

0.5 mL prepared soil solution is pipetted into a 100 mL beaker and 49.5 mL water as well as 1 mL c(EDTA) = 1 mol/L is added. After the addition of 1 mL c(NaOH) = 10 mol/L, the standard addition with $\beta(NH_4)$ = 100 mg/L is started immediately.

Parameters

STDADD auto

Stirring rate	6
Number of additions	4
Volume auxiliary solution	1 mL (for tap water, aquarium water) 51.9 mL (for fertilizer) 51.5 mL (for soil)
Stop volume	10 mL
Dosing rate	fast
Delta U	12 mV
Signal drift	0.5 mV/min
Min. waiting time	60 s
Max. waiting time	300 s
Measuring interval	2.0 s
Switch off stirrer during measurement	off

Calculation

No additional calculation is necessary for tap water, aquarium water, mineral water, and melted snow.

Fertilizer

$$w(NH_4^+) = \frac{\text{Result}}{1000 \cdot \rho(\text{Fertilizer}) \cdot 10}$$

$w(NH_4^+)$:	Mass fraction of NH_4^+ in %
Result:	Result obtained from the standard addition in mg/L
1000:	Conversion factor from mg/g to g/g
ρ(fertilizer):	Density of fertilizer in g/mL
10:	Conversion factor from g/g to %

Soil

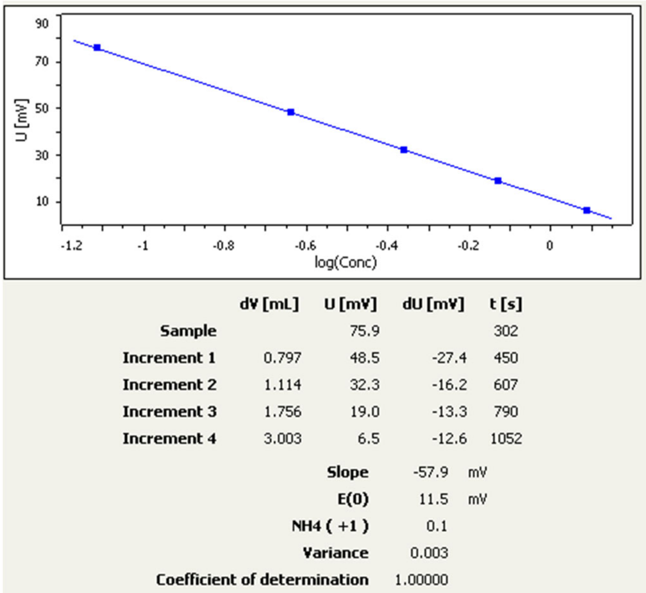
$$w(NH_4^+) = \frac{\text{Result} \cdot V_{VF} \cdot 100}{1000 \cdot m_{soil}}$$

$w(NH_4^+)$:	Mass fraction of NH_4^+ in %
Result:	Result obtained from the standard addition in mg/L
1000:	Conversion factor from mg/L to mg
m_{soil}:	Weight of soil which was used for extraction in mg

V_{VF}: Volume of the volumetric flask, which was used for dilution of the extracted soil (here: 500 mL)
100: Conversion factor to %

Example Curves

Tap water

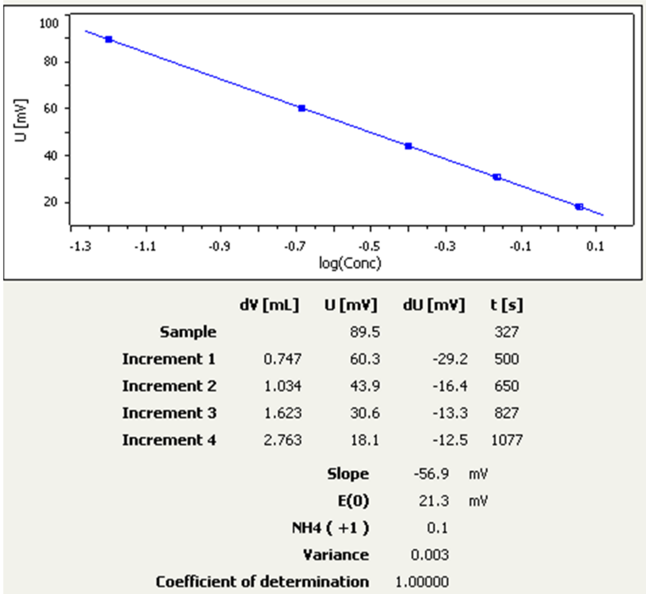


	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		75.9		302
Increment 1	0.797	48.5	-27.4	450
Increment 2	1.114	32.3	-16.2	607
Increment 3	1.756	19.0	-13.3	790
Increment 4	3.003	6.5	-12.6	1052

Slope	-57.9	mV
E(0)	11.5	mV
NH4 (+1)	0.1	
Variance	0.003	
Coefficient of determination	1.00000	

Fig. 4: Graph of the standard addition of ammonia in tap water.

Aquarium water (sea water)

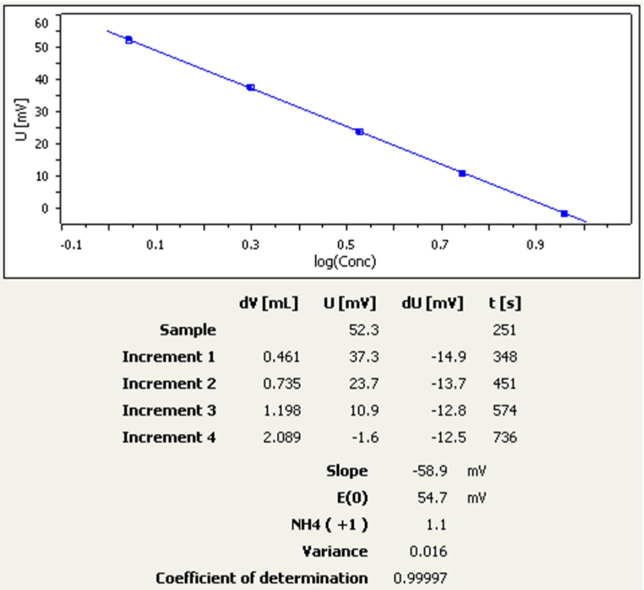


	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		89.5		327
Increment 1	0.747	60.3	-29.2	500
Increment 2	1.034	43.9	-16.4	650
Increment 3	1.623	30.6	-13.3	827
Increment 4	2.763	18.1	-12.5	1077

Slope	-56.9	mV
E(0)	21.3	mV
NH4 (+1)	0.1	
Variance	0.003	
Coefficient of determination	1.00000	

Fig 5: Graph of the standard addition of ammonia in aquarium water (seawater aquarium).

Melted snow

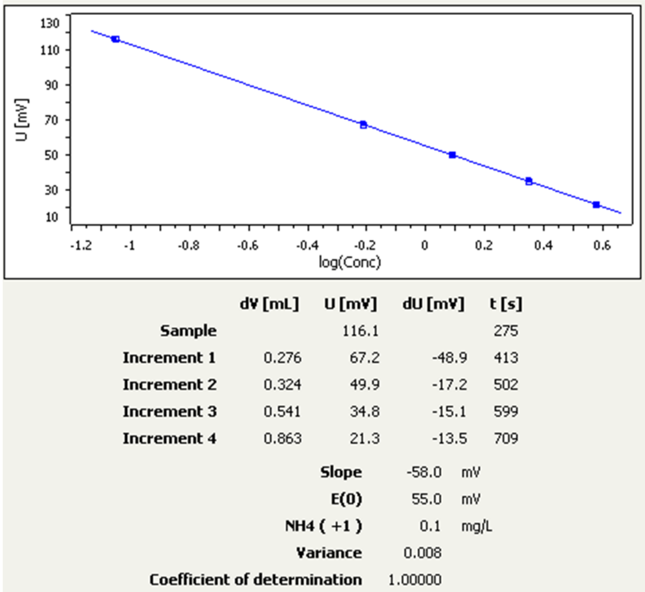


	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		52.3		251
Increment 1	0.461	37.3	-14.9	348
Increment 2	0.735	23.7	-13.7	451
Increment 3	1.198	10.9	-12.8	574
Increment 4	2.089	-1.6	-12.5	736

Slope	-58.9	mV
E(0)	54.7	mV
NH4 (+1)	1.1	
Variance	0.016	
Coefficient of determination	0.99997	

Fig 6: Graph of the standard addition of ammonia in melted snow

Mineral water

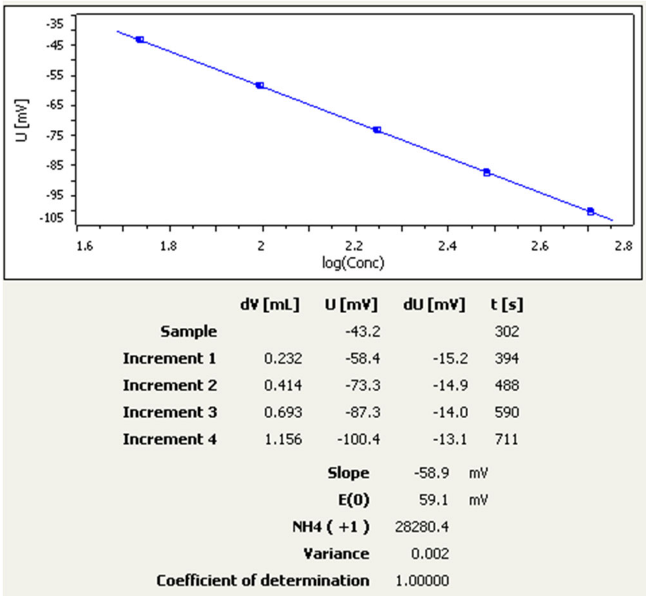


	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		116.1		275
Increment 1	0.276	67.2	-48.9	413
Increment 2	0.324	49.9	-17.2	502
Increment 3	0.541	34.8	-15.1	599
Increment 4	0.863	21.3	-13.5	709

Slope	-58.0	mV
E(0)	55.0	mV
NH4 (+1)	0.1	mg/L
Variance	0.008	
Coefficient of determination	1.00000	

Fig. 7: Graph of the standard addition of ammonia in mineral water

Fertilizer

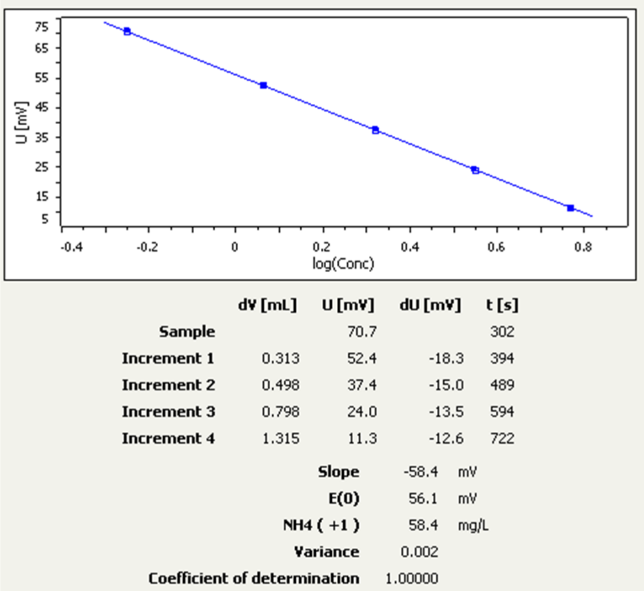


	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		-43.2		302
Increment 1	0.232	-58.4	-15.2	394
Increment 2	0.414	-73.3	-14.9	488
Increment 3	0.693	-87.3	-14.0	590
Increment 4	1.156	-100.4	-13.1	711

Slope	-58.9	mV
E(0)	59.1	mV
NH4 (+1)	28280.4	
Variance	0.002	
Coefficient of determination	1.00000	

Fig. 8: Graph of the standard addition of ammonia in fertilizer

Soil



	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		70.7		302
Increment 1	0.313	52.4	-18.3	394
Increment 2	0.498	37.4	-15.0	489
Increment 3	0.798	24.0	-13.5	594
Increment 4	1.315	11.3	-12.6	722

Slope	-58.4	mV
E(0)	56.1	mV
NH4 (+1)	58.4	mg/L
Variance	0.002	
Coefficient of determination	1.00000	

Fig. 9: Graph of the standard addition of ammonia in soil

Comments

- For low ammonia concentrations the electrolyte is diluted with deionized water 1:9.
- After the addition of c(NaOH) = 10 mol/L the stabilization of the measuring signal takes some time. Therefore, it is necessary to increase the min. waiting time to 60 s.
- The electrode is conditioned for 10 min in ammonia – free buffer pH 4 prior and between measurements.

References

- EPA 350.2
  Nitrogen, ammonia (Colorimetric, titrimetric, potentiometric - distillation procedure)
- EPA 350.3
  Nitrogen, ammonia (Potentiometric, ion selective electrode)
- ASTM D1426
  Standard Test Methods for Ammonia Nitrogen In Water
- ISO 6778
  Water quality - Determination of ammonium. Potentiometric method
- Manual NH3-selective electrodes (8.109.8031)

Date

May 2019

Author

Competence Center Titration

Metrohm International Headquarters