NH_3-selective electrodes

Manual

8.109.8031EN / v2 / 2023-07-14

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Technical Communication
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1 Introduction

The NH_3-selective gas membrane electrodes are combined electrodes, i.e. they contain one measuring electrode and one reference electrode.

They enable the rapid, simple, inexpensive and precise determination of dissolved ammonia (NH_3) in aqueous systems, e.g. in natural water, sewage, boiler feed water, beer, etc.

In addition, the NH_3-selective gas membrane electrodes can detect the following substances:

- Ammonium ions (NH_4^+) after their conversion into ammonia
- Organic nitrogen (N) after a Kjeldahl digestion

Discolored or turbid samples do not compromise the measurement, which means that, generally speaking, no pre-distillation is necessary.

The membrane of the NH_3-selective electrode is gas-permeable and water-repellent, i.e. water cannot dampen the membrane and cannot permeate the pores. In the case of samples that contain surface-active substances, or in the case of nonaqueous systems, fluid makes its way into the membrane. This leads to difficulties, e.g. in the case of sewage samples (detergents) or with nylon or dye samples (nonaqueous systems). An ammonia determination of such samples should therefore be carried out by suspending the electrode above the solution instead of immersing it.

2 Accessories

NOTE

Subject to change without notice.

2.1 Scope of delivery

6.0506.100 NH_3-selective electrode

Qty.	Order no.	Description
1	–	Measuring electrode with Metrohm plug-in head G and certificate
3	–	Membrane modules with certificates
1	6.2316.030	Measuring electrolyte (50 mL)
1	8.109.8031ML	Manual for NH_3-selective electrodes, German/English

6.0506.150 NH_3-selective electrode

Qty.	Order no.	Description
1	–	Measuring electrode with Metrohm plug-in head G and certificate
1	–	Package with 20 membranes each
1	–	Membrane module
1	6.2316.030	Measuring electrolyte (50 mL)
1	–	Tweezers
1	–	Pasteur pipette
1	8.109.8031ML	Manual for NH_3-selective electrodes, German/English

2.2 Optional accessories

6.0506.100 NH_3-selective electrode

Order no.	Description
6.1255.000	**Replacement module kit for NH_3-selective electrode 6.0506.100**
Comprised of: 3 replacement membrane modules with certificates, 1 measuring electrolyte (50 mL).	

6.0506.150 NH_3-selective electrode

Order no.	Description
6.1255.050	**Replacement module kit for NH_3-selective electrode 6.0506.150**
Comprised of: 1 replacement membrane module, 1 package of 20 membranes, 1 tweezers.	
8.109.8032ML	**Leaflet for membrane module (mounting instructions)**

3 Mode of operation

Ammonia (NH_3) reacts in water with the formation of ammonium ions (NH_4^+):

$$NH_3 + H_2O \overset{K}{\longleftrightarrow} NH_4^+ + OH^- \quad (1)$$

The equilibrium of this reaction, i.e. the relative proportion of ammonia and ammonium ions, is determined by the pH value of the solution. In acidic solutions, ammonia reacts almost completely to ammonium ions. At a pH value of 9.2, the ratio of ammonia to ammonium ions is approximately 1 : 1. If the pH value of the solution is known, then the ratio of ammonia to ammonium ions can also be calculated directly. The following applies:

$$\log \frac{a(NH_4^+)}{a(NH_3)} = \log K - pH \quad (2)$$

The value of the equilibrium constant K is also dependent on the temperature.

Table 1 Temperature dependency of the ammonia – ammonium ions equilibrium

Temperature in °C	– log(K)
5	4.13
25	4.78
35	5.08

The addition of an excessive amount of a strong base, e.g. concentrated caustic soda (NaOH), causes the ammonium ions to be transformed into ammonia in their entirety. Determination of the ammonium concentration is thus indirectly possible by means of the determination of ammonia. In the case of the NH_3-selective electrode, a gas-permeable, hydrophobic membrane separates the measuring solution from the measuring electrolyte. Ammonia now diffuses through the membrane for as long as the partial pressure on the two sides is identical in size. The partial pressure of ammonia is always proportional to its concentration. The measuring electrolyte is comprised of a sufficiently concentrated ammonium chloride solution, which means that the ammonium concentration can be assumed to be constant.

The potential U of the measuring electrode is proportional to the hydroxide concentration of the measuring electrolyte:

$$U = U_0 - U_N \cdot \log\ a(OH)^- \quad (3)$$

U_N is the Nernst potential (slope) of the electrode. Because of the fact that the hydroxide concentration is proportional to the ammonia concentration (equation 4), the electrode obeys the Nernst equation for the ammonia concentration as well:

$$a(OH^-) = a(NH_3) \cdot Konstante \quad (4)$$

$$U = U'_0 - U_N \cdot \log\ a(NH_3) \quad (5)$$

Using equation 5, either the ammonia concentration or the ammonium concentration can be determined from the measured data. U'_0 is determined essentially by means of the internal reference electrode. This responds to the existing chloride concentration contained in the non-refillable reference electrolyte (gel).

4 Selecting the electrode

In the following you will find a list of criteria that is intended to make it easier for you to select the correct electrode:

6.0506.100, 6.1255.000	**6.0506.150, 6.1255.050**
$5 \cdot 10^{-6}$…10^{-2} mol/L	10^{-4}…1 mol/L
Clean sample (e.g. drinking water, boiler feed water or mineral water)	Sewage sample
	Long-term measurement, monitoring
More rapid response time close to the detection limit	More rapid regeneration time after high concentrations
Lower detection limit	Better signal stability with higher concentration
Complete membrane modules for simple replacement	Less expensive replacement of contaminated membranes (e.g. oleaginous sewage)
Membrane module individually tested and certified	Replacement membranes without certificate

5 Assembling the electrode

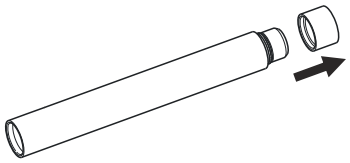
The way that you assemble your electrode depends on the type of the electrode.

- The electrode 6.0506.100 is supplied with complete membrane modules.
- The electrode 6.0506.150 is supplied with a membrane module with separate membranes. The membrane must first be mounted on the membrane module. It can be replaced as needed.

Mounting the membrane on the membrane module

Electrode 6.0506.150

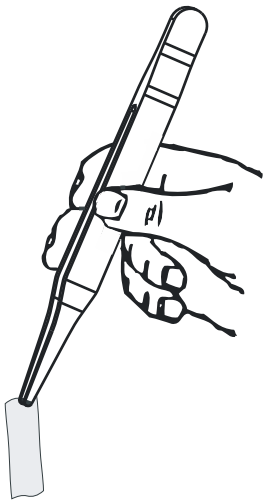
1 Unscrew the cover from the membrane module.



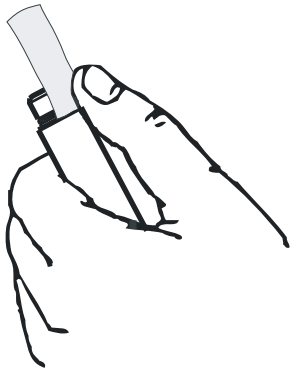
2 Make ready the package with the membranes.

Each membrane is stored between two white paper strips. This prevents the membranes from sticking together.

3 Use the tweezers provided to take out one membrane, holding it on its narrow side.



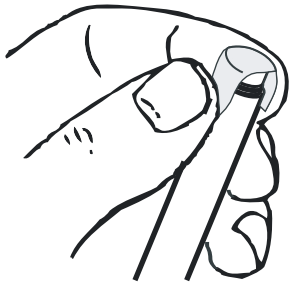
4 Place the membrane on the screw thread of the membrane module and use your thumb to hold it in place.



5 Place the membrane carefully lengthwise over the opening of the screw thread.

NOTE

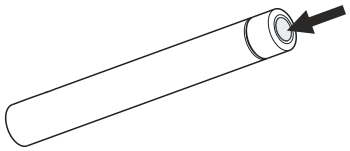
The part of the membrane which lies above the opening of the screw thread may not come into contact with fingers or other objects under any circumstances. The water-repellent effect of the membrane would otherwise be reduced as a result.



6 Pull the membrane slightly at its sides and press it firmly against the screw thread.

The membrane must lie taut and wrinkle-free above the opening.

7 Screw the cover on the membrane module over the taut membrane.



8 Check once again to ensure that the visible part of the membrane lies taut and wrinkle-free above the opening.

Preparing the electrode for use

CAUTION

The membrane of the membrane module may not come into contact with fingers or with other objects under any circumstances. The water-repellent effect of the membrane would otherwise be reduced as a result.

Electrode 6.0506.100 and 6.0506.150

1 Fill the membrane module with 2 mL of the measuring electrolyte (6.2316.030).

2 Remove the measuring electrode from the electrode carrier and rinse with distilled water.

3 Introduce the measuring electrode into the membrane module and screw both parts together.

4 Prior to initial use, shake the assembled NH_3-selective electrode several times as you would a fever thermometer in order to remove any air bubbles from the membrane.

5 Before making the first measurement, condition the electrode for at least 10 minutes in distilled water.

6 Storing the electrode

The type of storage depends on the storage duration. Observe the following notes:

Storage between measurements

- Store electrode in distilled water.

Storage duration between 1 and 5 days

- Store the electrode in measuring electrolyte (6.2316.030).

Storage duration of more than 5 days

1 Unscrew membrane module.

2 Rinse the membrane module thoroughly with distilled water inside and outside and place it in dry storage.

3 Store pH glass electrode in c(KCl) = sat. (6.2308.000).

7 Performing measurements

7.1 Measured quantities

Ammonia concentrations are usually specified in one of the following units:

- mol/L
- ppm (NH_3)
- ppm (N)

Table 2 Conversion factors for various concentration specifications

Conc. in mol/L	N content in ppm	NH_3 content in ppm
10^{-4}	1.4	1.7
10^{-3}	14	17
10^{-2}	140	170
10^{-1}	1400	1700
1	14000	17000

7.2 General notes

- The response time of the electrode may take several minutes. It increases with decreasing ammonia concentration.
- 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).
- Immediately prior to the measurement, a sodium hydroxide solution must be added to each measuring solution. The solutions should have a pH value of 11...14 after this addition and the concentration of all dissolved particles should not exceed 1 mol/L.
- Alkali samples must be measured immediately. The ammonia loss in a stirred alkali sample of 100 mL is approx. 50% within six hours.
  For purposes of storage, the samples 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.

- The electrode must be conditioned in distilled water for at least 10 minutes between the measurements. If measurements are being performed at very high concentrations, then the electrode should be conditioned for 30 minutes.
- 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.
- Ammonia dissipates very rapidly out of solution when ammonia concentrations are > 1 mol/L. These kinds of samples must therefore be diluted.
- You will find many additional useful notes on working with the NH_3-selective electrode in Application Bulletin 133.

7.3 Performing direct measurements

Direct measurement is a simple and rapid method for testing numerous samples 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 ammonia concentration of the sample solution to be anticipated 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 $< 6 \cdot 10^{-5}$ mol/L. The response time of the electrode is prolonged accordingly. A special measurement technique is required for this concentration range *(see chapter 7.5, page 14)*.
- Ammonia dissipates very rapidly out of solution when ammonia concentrations are > 1 mol/L. These kinds of samples must therefore be diluted *(see chapter 7.6, page 15)*.

7.4 Performing standard addition

Standard addition is a considerably more convenient method for the measurement of ion concentrations with an ion-selective electrode (ISE). If you need to measure only a few samples, then this method is very simple, because you do not need to incorporate a calibration curve. Furthermore, all matrix effects are eliminated, because the electrode is calibrated in the sample solution.

Observe the following notes when performing standard additions:

- Add defined volumes of a standard solution of the measurement ion to the sample in a series of steps.
  The concentration in the sample solution is calculated on the basis of the resulting change in voltage and the initial voltage prior to the addition of the standard solution. Modern ion meters, such as the 781 pH/Ion Meter or the 867 pH Module, can perform a standard addition automatically when a corresponding dosing device is attached to the instrument.
- In order to guarantee a reliable evaluation of the standard addition, care must be taken to ensure that the buret volume and the concentration of the standard solution are adjusted to the respective measuring conditions. The individual addition volumes must be selected in such a way that the potential difference is at least 15 mV after each additive step. At least four volume additions should be carried out.

Table 3 Recommended concentrations of the standard solution for the standard addition

Buret volume in mL	$c_{Standard\ solution} : c_{Sample}$
5	40 : 1
10	20 : 1
20	10 : 1
50	5 : 1

Example of a standard addition

NOTE

This sample is valid for standard additions with any number of ion-selective electrodes.

Sample concentration	5 mg/L

Buret volume	10 mL
Sample size	10 mL
ISA/TISAB	10 mL
Total volume	20 mL
Factor $c_{Standard\ solution}/c_{Sample}$	20

This results in a sample concentration in the measuring solution of 2.5 mg/L. The optimum concentration of the standard solution is thus 2.5 mg/L · 20 = 50 mg/L. Please note that this is merely to be considered a guideline for standard additions. Even if you deviate from this recommendation, precise measurements will still be possible.

7.5 Performing measurements with very low concentrations

NOTE

The electrode 6.0506.100 or the membrane module 6.1255.000 must be used for measurements with very low concentrations.

The response time of the electrode is relatively long with low ammonia concentrations. The response time decreases with increasing concentration. You can improve the response time of the electrode and the precision of the result for ammonia concentrations < $6 \cdot 10^{-5}$ mol/L with the following measures:

- Condition the NH_3-selective electrode prior to the measurement in an ammonia-free pH 4 buffer solution.
- Dilute the measuring electrolyte 1 : 9 with distilled water.
- Work with sealed measuring vessel.
- 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 the air.

Even when these measures are applied, the response time of the electrode may still be as long as ten minutes, not only for the samples but also when conditioning in pH 4 buffer.

7.6 Influence of dissolved particles on the measurement

Water vapor is a potential interference factor. It can enter through the membrane and change the concentration of ammonium chloride in the measuring electrolyte. This leads to a potential drift. The introduction of water should not be a problem, however, if the following conditions are met:

- The total concentration of the dissolved particles is approx. 0.1 mol/L (osmotic pressure).
- The electrode and the sample solution are maintained at the same temperature.

The addition of the sodium hydroxide solution to samples with small ionic strength results automatically in the correct concentration of particles in solution. Samples with a total ion concentration > 1 mol/L should be diluted prior to the measurement, although the ammonia concentration should not be too close to the detection limit.

Samples with high total ion concentration (i.e. with high osmotic pressure) and with low ammonia concentration can be measured after the osmotic pressure of the measuring electrolyte has been increased. This is increased through the addition of sodium nitrate (2.125 g $NaNO_3$ per 50 mL measuring electrolyte).

8 Troubleshooting

8.1 Problems and their solutions

Problem	Cause	Remedy
The electrode slope is too large (> 62 mV).	*The electrode was insufficiently prepared or conditioned for too short a time in distilled water.*	Refill the electrode and condition for at least 30 minutes in distilled water.
The electrode slope is too small.	*The membrane has a tear.*	Replace the membrane or the membrane module.
	The calibration solutions are contaminated or they have been used too long.	Use fresh calibration solutions.
	Either too little sodium hydroxide solution was added, or none at all.	Add 1 mL sodium hydroxide solution with c(NaOH) = 10 mol/L per 100 mL measuring solution.
	The pH glass electrode (measuring electrode) is possibly defective.	For the test, calibrate the pH glass electrode separately in pH buffer solution or perform an extensive electrode test with 780/781 pH/Ion Meter, 867 pH Module or a Titrando. Replace the measuring electrode if required.
	The measuring electrode was in dry storage.	Soak the measuring electrode for 6 to 12 hours in pH 7 buffer solution.
The measuring range is exceeded.	*The measuring device is possibly defective.*	Check the measuring device.
	The electrode is not connected correctly.	Check the electrode connection.
	The calibration is no longer accurate.	Recalibrate the electrode.
	There is no measuring electrolyte in the membrane module.	Unscrew the membrane module and refill it with 2 mL measuring electrolyte.
	The pH glass electrode (measuring electrode) is possibly defective.	For the test, calibrate the pH glass electrode separately in pH buffer solution or perform an extensive electrode test with 780/781 pH/Ion

Problem	Cause	Remedy
		Meter, 867 pH Module or a Titrando. Replace the measuring electrode if required.
The measuring signal is noisy, the measured values are unstable.	*There is not enough measuring electrolyte in the membrane module.*	Unscrew the membrane module, empty it and refill it with 2 mL measuring electrolyte.
	The pH glass electrode (measuring electrode) is possibly defective.	For the test, calibrate the pH glass electrode separately in pH buffer solution or perform an extensive electrode test with 780/781 pH/Ion Meter, 867 pH Module or a Titrando. Replace the measuring electrode if required.
	The membrane is contaminated (e.g. with oleaginous sample).	Replace the membrane or the membrane module.
A potential drift occurs.	*The membrane is defective (punctured, discolored, dampened); measuring electrolyte runs out.*	Check the membrane module for tears, replace the membrane or the membrane module if necessary.
	The wrong measuring electrolyte is in the membrane module.	Fill the membrane module only with the measuring electrolyte supplied.
	The membrane is severely contaminated: not only gases, but also sample passes through the membrane.	Replace the membrane or the membrane module.
	The total ion concentration of the sample is > 1 mol/L.	Dilute the sample.
	Ammonia escapes too quickly.	Use only closed measuring vessels.
	Temperature fluctuations occur.	Observe uniform tempering of the sample, equipping the measuring vessel with a thermostat if necessary.
	The measuring electrode was in dry storage.	Soak the measuring electrode for 6 to 12 hours in pH 7 buffer solution.

9 Technical specifications

Measuring range	
6.0506.100	$5 \cdot 10^{-6}$…10^{-2} mol/L (NH_3) 0.1…170 ppm (NH_3)
6.0506.150	10^{-4}…1 mol/L (NH_3) 10…17000 ppm (NH_3)
Temperature range	0…50 °C
pH range (measuring electrode)	pH 0…14
Minimum immersion depth	2 mm
Shaft length	133 mm
Shaft diameter	12 mm
Shaft material	PEEK
Module material	
6.0506.100	POM black
6.0506.150	POM black/white
Electrode plug-in head	Metrohm plug-in head G

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