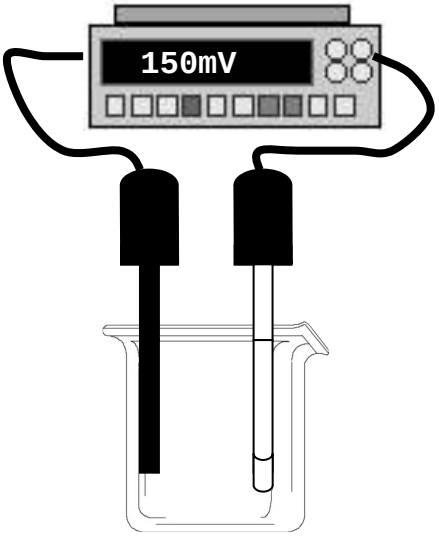
SENTEK

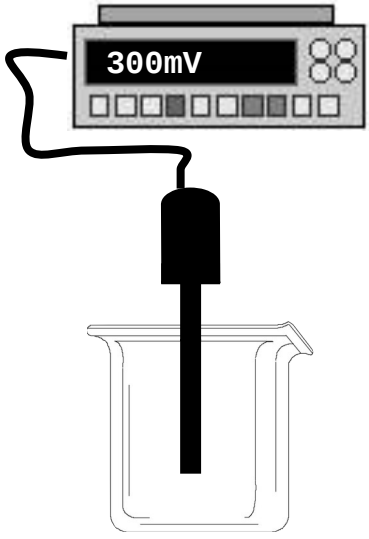
Ion Selective Electrode

OPERATING INSTRUCTIONS

AMMONIUM



Mono/Reference



Combination

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Operating Instructions
Ammonium Ion Selective Electrode

This Document includes operating instructions for two types of Ion Selective Electrode. A single sensing Half Cell Ammonium Electrode which requires a separate Reference Electrode, and a Combination Ammonium Electrode which has the Reference built into the outer shaft.

For extremely low leveL work the Half Cell plus Reference Electrode should be used. For general applications the Combination is more convenient.

Depending on the type of ISE chosen you will need to disregard some information for instance if you have the Combination Electrode then disregard any comments about reference electrodes.

A quick guide is included with a more involved section following.

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Quick Guide for Ammonium Combination ISE

Introduction

The Ammonium ion selective electrode is a combination sensor which does not require a separate reference electrode.
The electrode is designed for the detection and analysis of ammonium ions in aqueous solutions and is ideal for both field and laboratory use.

Installation

1. Remove the black protective cap and keep in a safe place.
2. Connect the electrode to a suitable pH, millivolt or ion meter.
3. Immerse the electrode in the weakest calibration standard to be used for 10 minutes.
4. Rinse the electrode tip with distilled or de-ionised water prior to all measurements.

Operation

1. Start calibration from the lowest calibration standard.
2. Rinse electrode tip with distilled water between readings.
3. Ensure the slope is 56mV $\pm$ 3mV @ 20^{o}C.
4. The electrode need not be immersed in more than 1 cm for an accurate result, but it may be completely immersed if required e.g. when field monitoring from boats, banks or bridges.
5. Avoid strongly acidic or alkaline solutions, detergents or PVC solvents.
6. To prolong the life of the electrode ensure that it is not left in sample solutions for longer than is necessary after a result is obtained.

Storage

Place the black electrode protection cap over the membrane. If appropriate, the electrode can be stored in its box.

Note: The electrode once used can be left dry. Upon re-use the electrode tip must be immersed in a 100ppm ammonium standard.

Specification

Slope:	56mV/dec
Range:	0.09 - 9000ppm
pH Range:	1-8.5
Reproducibility:	2%
Potential Drift:	1mV/8 Hrs
Selectivity coefficients: (max. level for a 10% error at 0.001M Ammonium)	Potassium 9 x 10^{-4} ml Sodium 2.2 x 10^{-2} ml

Operating Instructions for Ammonium ISE
Specifications

Range: The Ammonium Electrode responds to uncomplexed ion activity over the range 1 x 10-1M to 1 x 10-6M.
Linear detection limit is about 10-5M

Interference's: Selectivity ratios for interfering ions are given below.

Interference	Selectivity Ratio
K^+	1.2 x 10-1
Na^+	2.0 x 10-3
Rb^+	4.3 x 10-2
Cs^+	4.8 x 10-3
Li^+	4.2 x 10-3
$Mg^{2}+$	2.0 x 10-4

pH Range: The Ammonium Electrode can be used in the pH range 5-8.

Response Time: The Ammonium Electrode will respond to a step change in the ammonium ion activity in solution in less then 60s. When, however, the electrode is removed from one solution and placed in another of different ammonium concentration, it may take up to 3 minutes to equilibrate.

Temperature
Range: 0 = 50 Deg C.

Stability: The long term drift in E0 1-2mV/day.

Section 1

Recommended Equipment

Meter — If using a mV meter without direct reading facility ensure it resolves to 0.1mV.

Reference Electrode: — Double Junction with 0.1M LiAc in the outer chamber. For use with Mono ISE

Magnetic Stirrer

Anglepoise Stand

Required Solutions

Reference Electrode Filling Solutions

Outer Chamber LiAc 0.1M

Standard Solutions

0.1M NH_4Cl
1000ppm NH_4Cl

Ionic Strength Adjustment Buffer (ISAB)

4M LiAc

NB: Only highest quality de-ionised water should be used when preparing solutions and standards.

Section 2

Activity Coefficients

The activity coefficient of ammonium ion depends upon the ionic strength of the Solution.
The following table can be used to calculate the approximate activity coefficients at various ionic strengths.

Ionic Strength	0.001	0.005	0.01	0.05	0.1	0.2
Activity Coeff.	0.975	0.945	0.925	0.850	0.805	0.755

The ionic strength of the solution to be tested can be calculated from the formula:

$$\text{Ionic Strength} = \tfrac{1}{2} \sum_{i=1}^{N} c_i z_i^2$$

Where c_i is the concentration of species i, z_i is its charge and all species, cations and anions must be taken into account.

Once the ionic strength is calculated and the activity coefficient found from table above, then the activity of the ion of interest is found from:

$$\text{Activity } (a_i) = \text{Concentration } (c_i) \times \text{Activity Coeff. } (f)$$

If the total ionic strength of all solutions is kept constant by the addition of a solution of high ionic strength that does not react or interfere with standards or samples, then the electrode can be calibrated in concentration units without considering the effects of activity.

Section 3

Setting Up.

The Sensing Electrode

The Ammonium Electrode consists of an inert fluorocarbon body with a solid state PVC membrane unit. The sensitive membrane consists of liquid exchange material immobilised in a poly-(vinyl chloride) matrix. Connection to a millivolt meter is via coaxial cable and BNC plug. As an alternative, other plugs may be specified.

The Reference Electrode

The Reference Electrode should be prepared as indicated in the Reference Electrode instruction manual.

Points to remember:

1. Remove protective teat from the end of the Reference Electrode.
2. The fill hole should be left uncovered during use.

Section 4

Calibration and Making Measurement

General Hints for Accurate Results

a) Temperature
ALWAYS ensure that standards and samples are kept at the same temperature and that the temperature remains constant.

b) **Stirrin**g

It is preferable to stir standards and samples.
Stir such that no vortex is visible.
If using a magnetic stirrer, it is a good policy to place a piece of insulating material between the plate and the beaker to eliminate any temperature effects arising from the stirrer itself. Some samples are impossible to stir consistently. If this is the case it may be better not to stir but remember to treat any standards in the same way.

Calibration and Measurement using a pH/mV Meter.

Set the mode or function switch on meter to mV.

1. Prepare standards and electrodes as described in Section 3. Pipette 100ml of 10-1M standard into a beaker and add (accurately) 2.0ml of Ionic Strength Adjustment Buffer (ISAB). Repeat for each of 10-2, 10-3, and 10-4M standards.

2. Connect the Ammonium and reference electrode to meter and place in the special electrode Holder in a vertical position.

3. Place electrodes in the 10-1M standard. Wait for stable reading and record the mV value.

4. Raise the electrodes from the solution, rinse with de-ionised water, blot with a tissue and place in the 10-2M standard. Wait for a stable reading and record the mV value.

5. Repeat this process sequentially for 10-3M and 10-4M ammonium solutions and plot the calibration curve of mV readings against the corresponding standard solution concentration using semi-log graph paper. (linear scale = mV; log scale = Concentration)

6. Pipette 100ml of sample into a beaker and add (accurately) 2.0ml of ISAB. Rinse the electrodes with de-ionised water, blot with a tissue and place in the sample. Wait for a stable reading, record mV value and read concentration from the graph.

Calibration using a Direct Readout Concentration Meter

Set the mode or function switch on meter to "Concentration"

1. Prepare standards and electrodes as described in Section 3. Select two standards such that their concentrations bracket the expected sample concentration and are a decade apart. For each standard pipette 100ml into a clean beaker and add (accurately) 2.0ml of Ionic Strength Adjustment Buffer (ISAB).

2. Connect the Ammonium and reference electrode to meter and place in the special electrode holder in a vertical position.

3. Lower electrodes into standard of highest concentration. Wait for a stable reading and enter correct value in the concentration units in which you wish to work.

4. Remove electrodes, rinse with de-ionised water, blot with a tissue and place in second standard. Wait for a stable reading and enter the correct value in concentration units.

5. Pipette 100ml of sample into a beaker and add (accurately) 2.0ml of ISAB. Rinse the electrodes with de-ionised water, blot with a tissue and place in the sample. Wait for a stable reading and read the concentration of the sample directly from the display in concentration units.

Checking the Electrode Slope.

This can be done using either of the meter types above.

Set the mode switch on the meter to "mV".

1. Select two standard solutions whose concentrations are one decade apart. For each standard pipette 100ml into a clean beaker and add (accurately) 2.0ml of Ionic Strength Adjustment Buffer (ISAB).

2. Place the Ammonium and reference electrode in the first standard. Wait for a stable reading and record mV value.

3. Remove electrodes, rinse with de-ionised water, blot with a tissue and place in the second standard. Wait for a stable reading and record mV value.

4. The difference between the two recorded mV values should be 56+/-2mV. (If slope is too low see section 5).

The Standard Solutions

10-1M and 1000ppm NH_4Cl solutions are available from Sentek Limited.

To prepare calibration standards (M).

1. Pipette 50ml 10-1M into a 500ml volumetric flask and make up to the mark with de-ionised water.
   = 10-2M

2. Pipette 10ml of 10-2M standard prepared in 1. into 100ml volumetric flask and make up to the mark with de-ionised water.
   =10-3M

3. Pipette 1ml of 10-2M standard prepared in 1. into 100ml volumetric flask and make up to the mark with de-ionised water.
   =10-4M

For standards of 1000;100;10 and 1ppm, follow procedure 1 to 3 above but use the 1000ppm standard as stock solution.

This process of preparation of a series of standards is known as "Serial Dilution".

The Ionic Strength Adjustment Buffer (ISAB)

This is a solution of high ionic strength added to dilute samples and standards before measurement, the purpose of which is to:

1. Ensure that the background ionic strength of all solutions is kept constant.
2. Minimise the differences in ionic strength between samples and standards.
3. Adjust the pH to the correct value for measurement.

The ISAB for the Ammonium Electrode can be supplied by Sentek Limited, or it can be prepared by dissolving 102.02g of Lithium Acetate in a 250ml volumetric flask and making up to the line with de-ionised water.

A Note About Interference's:

An interference is defined as any species (apart from the ion being measured) which affects the measured potential of the sensing electrode/reference electrode pair.
Interference's can be:
1. Species that give a similar response to the ion being measured.
2. Species that interact with the membrane.
3. Species that interact with the ion being measured so decreasing its activity.

Section 5

PROBLEM	POSSIBLE CAUSE(S)	SOLUTION
Wildly erratic readings	Air bubbles trapped on outside surface of membrane.	Check outside o membrane and tap electrode to release bubble.
	Poor connections inside electrode plug	Open plug and check wiring

	Meter or stirrer not grounded properly Excessively violent stirring. Reference electrode junction blocked. Defective Meter.	Ground meter or stirrer Reduce stirrer speed Clean junction (see section 6) Check meter with shorting plug.
Steady continuous drift in on direction	Excessive leakage from reference electrode junction Temperature drift	Replace reference electrode Thermostat all solutions or allow to come to room temp. before measurement.
Electrode slope less than 54mV/Decade	Presence of an interfering ion in a constant concentration, swamping the selected ions. Electrode aged.	Check performance with fresh standards and ISAB. Replace Electrode.
Over range reading	Reference electrode not filled. Defective meter	Fill reference electrode with correct solution. Check meter with shorting plug.

Section 6

Storage and Maintenance.

The Ammonium Mono Electrode and Combination

Storage: Short Term. Rinse the sensing module end of the electrode

with distilled water and clamp electrode in air

Long Term. After rinsing and drying, it should be stored in the Electrode box, away from direct heat.

Maintenance: Check the slope of the electrode on a regular basis.

The Reference Electrode For Use With Mono

General Tips

(Always refer to the reference electrode instruction manual, as this type of electrode design varies).

Storage: Short Term. Overnight the reference can be left soaking in a solution of 0.1M NH4Cl

Long Term: For periods of storage of longer than two days flush out the external chamber and refill with 3M KCl. Replace the electrode storage teat containing 3M KCl and return electrode to Electrode Reference box. (Before using again be sure to flush external chamber and refill with 0.1M LiAC)

Maintenance: To ensure good results the internal filling solution should be replaced at least every six months, if an access aperture is provided. Please note some electrodes have gel filled, zero maintenance, inner chambers. (More often if necessary). The external chamber should be flushed and refilled about every two weeks.

Always ensure that the level of internal filling solution covers the internal element. Top up

the electrode via the side filling hole when needed.

If the external filling solution becomes contaminated by influx of extraneous solutions through the liquid junction: Remove external filling solution using a hypodermic syringe; rinse outer chamber with de-ionised water followed by 0.1M LiAc and then refill with 0.1M LiAc.

If the inner element becomes contaminated the electrode should be discarded.

The major cause of reference electrode failure is junction blockage. The following steps can be taken to unclog a reference junction.

1. Replace filling solution and soak overnight in filling solution.

2. Force filling solution through the junction by applying pressure to the filling hole, or vacuum to the junction.

3. Soak junction for 10 minutes in dilute filling solution heated to 50°C Maximum.