Use of Ammonia Selective Ion Electrodes

An Ammonia Ion Selective Electrode, such as or Orion 9512BN, was used to test the performance of the meter and electrode, and to determine optimal operating conditions for the ammonia electrode.

Two different sets of standards were prepared by serial dilution from a 1000 mg/L NH3 standard in Class A volumetric glassware. Standards prepared and used were 100, 10.0, 1.00, and 0.100 mg/L as NH3. A total of six calibrations were run on two different ammonia electrodes to look at reproducibility between electrodes and calibrations.

Standardization Procedure

1. Standards were prepared by serial dilution from a 1000 mg/L standard
2. Measure 50.0 mL of standard, add to a plastic 100 mL beaker
3. Add a magnetic stirbar, place on a stirrer, and begin stirring at a moderate rate
4. Add 0.50 mL of ammonia ISA, 10M NaOH
5. Place the electrode in the standard
6. Seal the beaker by wrapping a piece of Parafilm stretch plastic around the top of the beaker sealing around the electrode
7. Put the meter in mV mode, and monitor the electrode's signal
8. When the electrode signal is stable to your requirement for accuracy, switch to ion mode [if available] and enter the standard value
9. Remove electrode from standard, rinse with DI water, blot dry, place in next standard
10. Repeat for all standards

Standardization Data

Typical standardization:

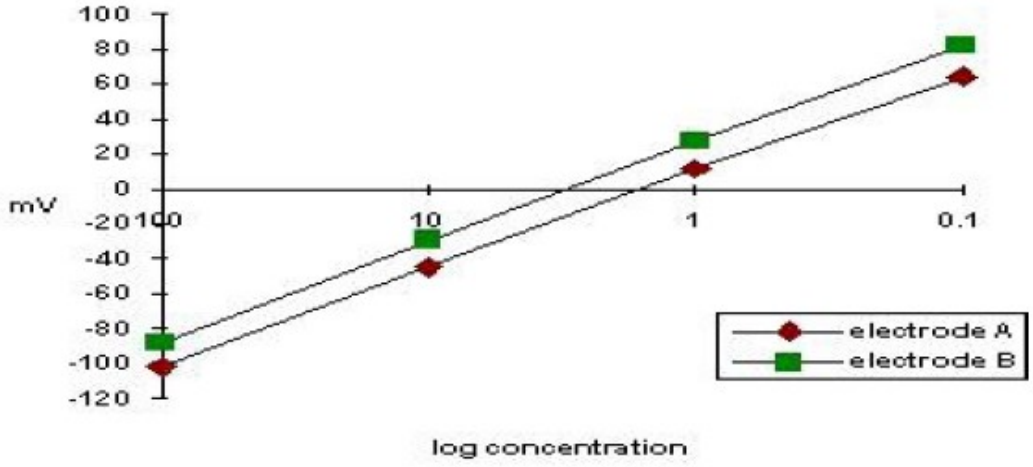
standard	electrode A	electrode B
100 mg/L	-101.8 mV	-88.0 mV
10.0	-44.5	-29.1
1.00	11.7	27.4
0.100	64.2	81.8

This calibration data indicates the electrodes' slopes were:

range	slope for A	slope for B
100 - 10 mg/L	57.3 mV/decade	58.9 mV/decade
10 - 1	56.2	56.5
1 - 0.1	52.5	54.4

These slopes indicate the ammonia electrodes were performing properly, and were well within the normal specified response slope of 59 ± 4 mV/decade at higher ammonia concentrations.

Calibration Graphs

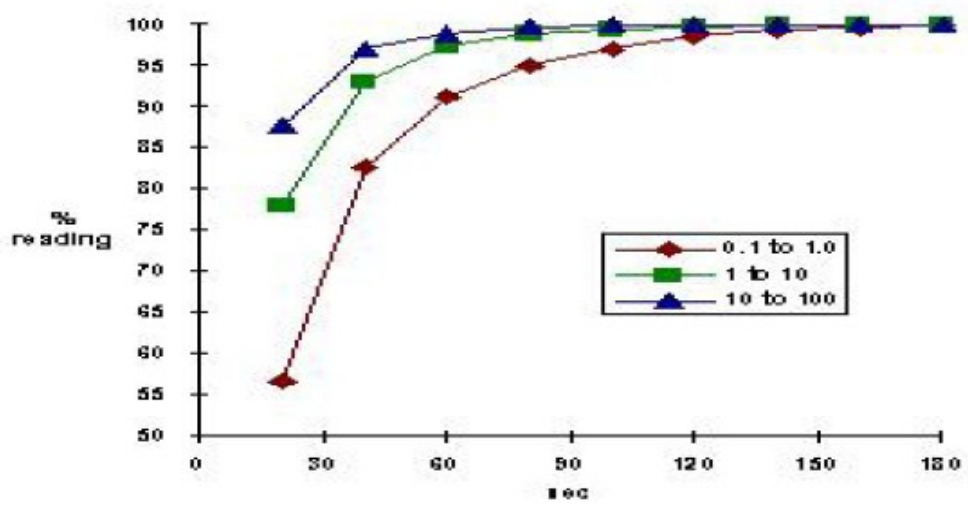


Graphing the electrode potential (in mV) versus the log of concentration (mg/L) gives visual feedback that the electrode response is fairly linear over this concentration range.

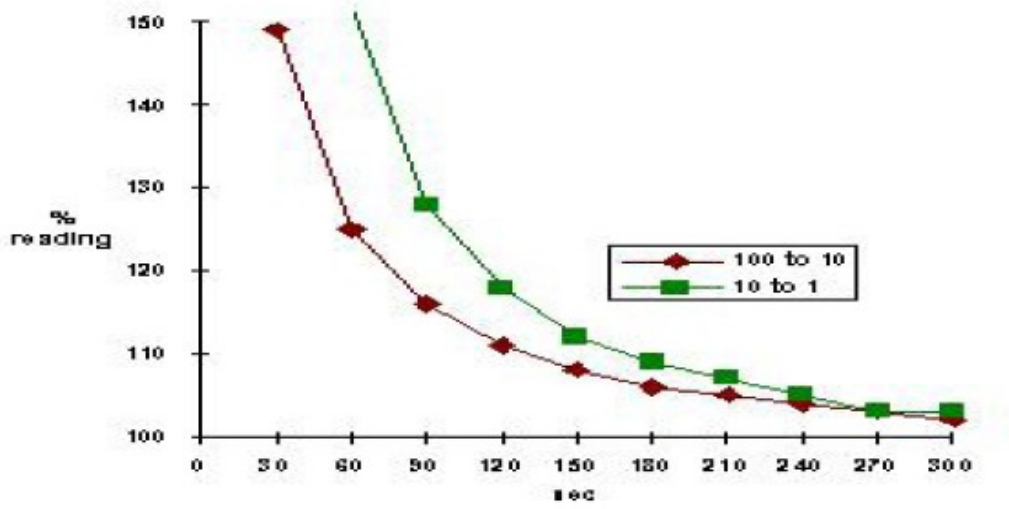
Response time:

The ammonia electrodes' output in mV was followed over time as the electrodes were moved from one standard to another, to examine the speed of response and the time required to reach stable readings.

Response times for going from lower to higher concentration standards:



Response times for going from higher to lower concentrations are even slower.



As the above response time graphs show, upon going from lower to higher concentration the electrode provides a stable signal in about 2 to 3 minutes, with slower response at the lower end of the working range. Upon going from higher to lower concentrations, however, the gas-sensing probe requires considerably more time, on the order of 5 or 6 minutes to reach a stable signal.

The meter was set on slow filter speed, with 3 significant figures of resolution in concentration mode. The electrode signal was observed manually, and only when the electrode appeared to be stable was the standardization procedure begun on the accumet meter (allowing sufficient time for ISEs to reach equilibrium is, or should be, standard practice!). Given this time for the electrode to slowly stabilize, the Denver meter responded correctly to the electrode signal, locking on to the readings at appropriate times.

Conclusion

Slow response appears to be a major problem and source of error with ammonia electrodes. It is difficult to know when the electrode signal stops changing, and the result of taking readings too soon, especially with standards, is apparent drift. Running check standards frequently is critical to verifying accuracy of the electrode measurements.

Analysts report that often the readings appear to slowly drift up and then down. The downward drift can be due to loss of ammonia as gas after the ISA has been added. Use of Parafilm to seal off the beaker reduces this ammonia vaporization and helps obtain more stable readings. Providing steady stirring and allowing the electrode sufficient time to reach equilibrium (steady readings) are helpful technique issues.

Technical information provided by Denver Instrument Co.