

DUKE POWER COMPANY
PROCEDURE PREPARATION
PROCESS RECORD

(1) ID No: CP/O/B/8100/20
Change(s) 0 to
0 Incorporated

- (2) STATION: Catawba
- (3) PROCEDURE TITLE: Chemistry Procedure for the Determination of Ammonia
- (4) PREPARED BY: C. Bolin DATE: 9-29-83
- (5) REVIEWED BY: TD Bane DATE: 10-5-83
- Cross-Disciplinary Review By: N/P: DE
- (6) TEMPORARY APPROVAL (IF NECESSARY):
- By: _____ (SRO) Date: _____
- By: _____ Date: _____
- (7) APPROVED BY: M.S. Tuckman / RHC Date: 10-6-83
- (8) MISCELLANEOUS:
- Reviewed/Approved By: _____ Date: _____
- Reviewed/Approved By: _____ Date: _____

MASTER FILE

DUKE POWER COMPANY
NUCLEAR SAFETY EVALUATION CHECK LIST

(1) STATION: Catawba UNIT: 1 2 3
OTHER: Shared
(2) CHECK LIST APPLICABLE TO: CP/O/B/8100/20

(3) SAFETY EVALUATION - PART A

The item to which this evaluation is applicable represents:

Yes No ✓ A change to the station or procedures as described in the FS.
or a test or experiment not described in the FSAR?

If the answer to the above is "Yes", attach a detailed description of the item being evaluated and an identification of the affected section(s) of the FSAR.

(4) SAFETY EVALUATION - PART B

Yes No ✓ Will this item require a change to the station Technical Specifications?

If the answer to the above is "Yes," identify the specification(s) affected and/or attach the applicable pages(s) with the change(s) indicated.

(5) SAFETY EVALUATION - PART C

As a result of the item to which this evaluation is applicable:

Yes No ✓ Will the probability of an accident previously evaluated in the FSAR be increased?
Yes No ✓ Will the consequences of an accident previously evaluated in the FSAR be increased?
Yes No ✓ May the possibility of an accident which is different than any already evaluated in the FSAR be created?
Yes No ✓ Will the probability of a malfunction of equipment important to safety previously evaluated in the FSAR be increased?
Yes No ✓ Will the consequences of a malfunction of equipment important to safety previously evaluated in the FSAR be increased?
Yes No ✓ May the possibility of malfunction of equipment important to safety different than any already evaluated in the FSAR be created?
Yes No ✓ Will the margin of safety as defined in the bases to any Technical Specification be reduced?

If the answer to any of the preceding is "Yes", an unreviewed safety question is involved. Justify the conclusion that an unreviewed safety question is or is not involved. Attach additional pages as necessary.

(6) PREPARED BY: CW Balin DATE: 9-29-83

(7) REVIEWED BY: FD Evans DATE: 10-5-83

(8) Page 1 of 1

DUKE POWER COMPANY
ALARA EVALUATION CHECKLIST

- (1) Station Catawba Unit: 1 2 3
Other: Shared
- (2) Checklist Applicable to: CP/O/B/8100/20
- (3) ALARA Evaluation

Check those items below which were considered applicable during the preparation and review of this document.

- Flushing and draining were used to minimize source - strength and contamination levels prior to performing an operation.
- Permanent and/or movable shielding was specified for reduction of levels.
- Use of permanent or temporary local exhaust ventilation systems was used for control of airborne contamination.
- Operation was designed to be completed with the least practicable time spent in the radiation field.
- Appropriate tools and equipment were specified for the operation to be performed.
- The operation was designed considering the minimum number of people necessary for safe job completion.
- Remote handling equipment and other special tools were specified to reduce external dose.
- Contamination control techniques were specified.
- The operation was designed to be conducted in areas of as low an exposure as practicable.
- Additional ALARA considerations were:

✓ ALARA Principles were not considered since the procedure did not involve work in a radiation area.

- (5) Prepared by: CW Bolin Date 9-29-83
- (6) Reviewed by: TD Egan Date 10-5-83

DUKE POWER COMPANY
CATAWBA NUCLEAR STATION
CHEMISTRY PROCEDURE FOR THE
DETERMINATION OF AMMONIA

1.0 DISCUSSION

1.1 Scope

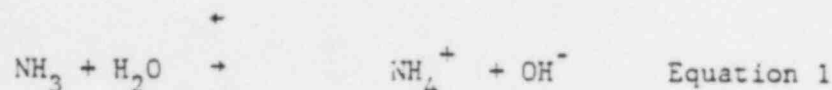
This procedure describes the two methods (gas diffusion electrode and direct Nesslerization) for the determination of ammonia.

Ammonia is monitored in the Condensate System because it leads to the corrosion of copper metal. At high temperatures and in the presence of oxygen, ammonia has the ability to dissolve copper. The moisture separators will be an area subject to attack due to its 90-10 Copper-Nickel piping.

1.2 Principle

1.2.1 Gas Diffusion Electrode

The ammonia electrode consists of a silver-silver chloride reference electrode and a glass pH electrode immersed in a filling solution of ammonium chloride. The electrodes and filling solution are separated from the sample solution by a hydrophobic gas-permeable membrane. Dissolved ammonia in the sample solution can diffuse through the membrane until the partial pressure of ammonia is the same on both sides in any given sample. The partial pressure of ammonia will be proportional to its concentration. Ammonia diffusing through the membrane dissolves in the internal filling solution where it reacts reversibly with water in the filling solution:



The relationship between the concentrations of ammonia, ammonium and hydroxide is given by the following equation:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \text{constant} \quad \text{Equation 2}$$

$$\text{or} \quad \frac{\text{constant} [\text{NH}_3]}{[\text{NH}_4^+]} = [\text{OH}^-] \quad \text{Equation 3}$$

The internal filling solution contains ammonium chloride
+
at a sufficiently high level so that the $[\text{NH}_4^+]$ can be
considered constant. This allows Equation 3 to be
simplified as follows:

$$[\text{OH}^-] = [\text{NH}_3] \cdot \text{constant} \quad \text{Equation 4}$$

Equation 4 shows that the $[\text{OH}^-]$ in the filling solution is
directly related to the $[\text{NH}_3]$ in the sample. Thus, when
the electrode is immersed in an alkaline test solution,
ammonia can diffuse through the membrane, changing the
 $[\text{NH}_3]$ in the filling solution.

This in turn changes the $[\text{OH}^-]$ in the filling solution
which is monitored by the glass electrode, i.e. pH.

The potential of the glass electrode (with respect to the
reference electrode) varies in a Nernstian manner with
changes in the hydroxide level:

$$E = E_0 - S \log [\text{OH}^-]$$

Where:

S = the electrode slope (Enclosure 6.1). Substitution in
the above equation shows that the electrode response to
ammonia is Nernstian:

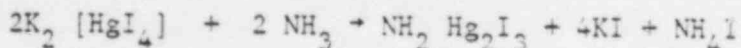
$$E = E_1 - S \log [\text{NH}_3]$$

1.2.2 Direct Nesslerization

Ammonia can be determined in high purity water by direct
Nesslerization. Direct Nesslerization is only applicable
to condensate and demineralized water. In some cases
drinking water and highly purified wastewater may be used
if errors 1 to 2 mg/L are acceptable.

Pretreatment before direct Nesslerization with zinc
sulfate and alkali precipitates calcium, iron, magnesium
and sulfide, which form turbidity when treated with
Nessler reagent. The floc also removes suspended matter
and sometimes colored matter.

Nessler's reagent consists of an alkaline solution of
mercuric iodide in potassium iodide. It reacts with
ammonia according to the following equation:



The ammonia reacts fairly rapidly, but not instantaneously, to form an orange-brown product which remains in colloidal suspension, but flocculates on long standing. A colorimetric analysis is made before flocculation occurs.

Rochelle salt solution is added to inhibit the precipitation of residual calcium and magnesium in the presence of the Nessler reagent and for buffering action to maintain pH.

1.3 Precisions and Interferences

1.3.1 Ammonia Probe

The accuracy and precision of this procedure will be determined by Q-Sum data. Volatile amines (derivatives of ammonia) may interfere with the electrode selectivity. Hydrazine up to 20 ppm does not interfere; however, > 50 ppm hydrazine shows a slight positive interference. During S/G or Condensate System wet layup, the hydrazine level is > 75 ppm. Therefore, these samples must be diluted with Super Q Water to bring the hydrazine concentration below the interference level. For solutions with a boric acid concentration of 13,500 ppm or greater, it becomes necessary to dilute the sample (1:1) with Super Q Water to achieve a pH of 11 to 13 with the addition of 1.0 ml of alkaline reagent.

1.3.2 Nesslerization

The accuracy and precision of this procedure will be determined by Q-Sum data.

Hydrazine, even at low concentrations, interferes. Iron, magnesium and sulfides can form precipitates that cloud the colorimetric analysis. Pretreatment can usually remove these, but turbidity in the original samples can affect results. Boric Acid \leq 1500 ppm does not interfere.

1.4 Limits and Precautions

1.4.1 Ammonia Probe

The concentration range of this procedure is 0.1 ppm to 2 ppm ammonia. The samples and standards must be adjusted to a pH 11 to 13. The electrode must be held at a 20° angle with respect to the vertical to prevent air bubble entrapment under the electrode.

Avoid touching the electrode membrane during assembly or other times because this can affect its hydrophobic properties. Membrane failure is characterized by a shift in electrode potential, drift and poor response. Failure may also be apparent on visual inspection as dark spots or discoloration of the membrane.

When handling or mixing sodium hydroxide, personnel shall wear a labcoat, eye protection and gloves.

1.4.2 Nesslerization

This method is good on water of high purity only and has a range from 0.02 mg/L to 5 mg/L ammonia nitrogen.

This method is not valid in the presence of more than 1500 ppm boric acid.

The Nessler reagent is poisonous. Gloves should be worn throughout the analysis to insure the reagent is not absorbed.

When handling or mixing sodium hydroxide, personnel shall wear a labcoat, eye protection and gloves.

2.0 APPARATUS

2.1 Ammonia Probe

- 2.1.1 pH/ion meter
- 2.1.2 Orion model 95-10-00 ammonia electrode
- 2.1.3 Electrode holder (electrode must be held at a 20° angle)
- 2.1.4 Multielectrode selector
- 2.1.5 Magnetic stirrer and teflon-coated stirring bars
- 2.1.6 Timer
- 2.1.7 250 ml beaker; one beaker for each standard sample

2.2 Direct Nesslerization

2.2.1 Spectrophotometer

NOTE: Allow to warm up for at least 20 minutes.

- 2.2.2 Two 100mm and two 10mm light path optically matched sample cells.
- 2.2.3 100 ml, 50 ml, 10 ml, 5 ml pipets (Class A)
- 2.2.4 pH meter
- 2.2.5 Automatic pipets with required tips
 - 2.2.5.1 1000µl pipet (1.00 ml)
 - 2.2.5.2 500µl pipet (0.50 ml)

- 2.2.5.3 250ul pipet (0.25 ml)
- 2.2.5.4 100ul pipet (0.10 ml)
- 2.2.6 Millipore filtration assembly
- 2.2.7 Filters, 0.45u

3.0 REAGENTS

3.1 Ammonia Electrode

3.1.1 Orion ammonia electrode filling solution.

3.1.2 Alkaline Reagent (10M NaOH)

In a 100 ml volumetric flask dilute 80.0 ± 1.0 ml of commercially available 50% NaOH to 100 ml with Super Q Water.

3.1.3 Stock Standard Solution (170 ppm as NH_3)

In a 1000 ml volumetric flask, dissolve 0.5349 ± 0.0005 grams of ammonium chloride (NH_4Cl) in Super Q Water and dilute to volume. Prepare fresh monthly. Store in a polyethylene bottle.

3.1.4 Electrode Storage Solution (0.05M NH_3)

In a 1000 ml volumetric flask, dissolve 2.6750 ± 0.0005 grams of ammonium chloride in Super Q Water. Prepare fresh solution every six (6) months.

3.2 Direct Nesslerization

3.2.1 Nessler Reagent

Dissolve $100 \pm 1.0\text{g}$ HgI_2 and $70 \pm 0.5\text{g}$ KI in 200 ml Super Q Water. Add this mixture slowly while stirring to a cool solution of $160 \pm 1\text{g}$ NaOH in 500 ml of Super Q Water. Dilute this solution to 1 liter, then store for one day and filter. Store in pyrex glassware out of sunlight. If a precipitate forms, remake this solution. This solution is stable for one year.

CAUTION: The Nessler reagent is toxic; gloves shall be worn to avoid ingestion.

3.2.2 Rochelle Salt Solution

Dissolve $50 \pm 0.5\text{g}$ of potassium sodium tartrate tetrahydrate, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ in 100 ml Super Q Water. To remove the ammonia usually present in the salt, boil off 30 ml of the solution. After cooling, dilute to 100 ml. This solution is stable 90 days.

3.2.3 Zinc Sulfate Solution, 10%

Dissolve $100 \pm 1.0\text{g}$ $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and dilute to 1 liter. This solution is stable 90 days.

3.2.4 Stock Ammonium Solution, 1000 ppm $\text{NH}_3 - \text{N}$

Dissolve $3.819 \pm 0.001\text{g}$ of anhydrous NH_4Cl , dried at 105°C for one (1) hour in water and dilute to 1,000 ml. This solution is stable 6 months.

3.2.5 Standard Ammonium Solution, 10 ppm

Dilute 10.00 ml stock solution to 1,000 ml with Super Q Water. This solution is stable for 1 month.

3.2.6 Sodium Hydroxide Solution

Dissolve $240 \pm 1\text{g}$ of NaOH in 1 liter of Super Q Water.

4.0 PROCEDURE

4.1 Ammonia Electrode

4.1.1 Preparation of Standards

NOTE: Two 0.85 ppm standards will be run daily (when in use) for Q-sum.

Prepare a series of standards by diluting suitable volumes of the stock standard solution, Section 3.1.3, to 100 ml with Super Q Water in a volumetric flask.

<u>ul of stock solution</u>	<u>Conc. ppm</u>
100	0.17 (170 ppb)
1000	1.70 (1700 ppb)

NOTE: An alternate standard may be prepared by diluting 500ul of stock solution to 100 ± 1.0 ml with Super Q Water, this is equal to 0.85 ppm NH_3 .

4.1.2 Preparation of the Electrode

When initially placing the electrode into service, it should be assembled as shown in Enclosure 6.2.

NOTE: The internal filling should be diluted 1 part filling solution to 9 parts Super Q Water.

The assembled electrode is to be allowed to stand in 0.05M NH_3 standard for at least one hour (preferably overnight) prior to use. When the electrode is not in use, allow the electrode to stand in 0.05M NH_3 standard. However, before making measurements and between measurements, the probe should stand in pH 4 buffer for 4 - 10 minutes, until the reading has stabilized.

4.1.3 Calibration

Set the pH meter function switch to "MVabs" and the electrode switch to the correct channel. Allow samples and standards to adjust to room temperature.

- 4.1.3.1 Place 50 ml. of the 0.17 ppm NH_3 standard in a 100 ml beaker, with a stirring bar, on a magnetic stirrer. Be sure the bar does not hit the electrode. The electrode must be immersed one inch in the standard or sample.

NOTE: Rinse the electrode carefully with Super Q Water before placing in each solution.

- 4.1.3.2 Check to be sure there is not an air bubble under the membrane. Adjust the stir rate until there is no vortex, then disengage the pH meter "Standby" pushbutton.

- 4.1.3.3 Add 1 ml alkaline reagent to the sample to adjust the pH between 11 and 13. Immediately set the timer for 4 minutes.

- 4.1.3.4 After 4 minutes, set the 0.17 ppm NH_3 solution to read + 104 mv by adjusting the Channel calibration knob.

NOTE: Do not adjust the calibration knob on the pH meter.

Let the probe stand in pH 4 buffer for several minutes before reading 1.7 ppm NH_3 .

- 4.1.3.5 Repeat Sections 4.1.3.1, 4.1.3.2 and 4.1.3.3, substituting the 1.7 ppm NH_3 solution for the 0.17 ppm NH_3 solution.

- 4.1.3.6 After 4 minutes, check the 1.7 ppm NH_3 solution mV reading. The mV reading should be + 45 mV @ 25°C.

NOTE: Enclosure 6.1 shows the change in slope (mV) vs. temperature for a ten-fold change in the ammonia concentration.

If the reading is not + 45 mV, adjust the reading using the correct channel calibration knob of the electrode switch to reduce the error by one half.

<u>EXAMPLES</u>		<u>ERROR</u>
Case 1 -	Actual reading: +49 mV	4mV
	Adjust to read: +47 mV	2mV
Case 2 -	Actual reading: 43 mV	2mV
	Adjust to read: 44 mV	1mV

By doing this, the reading for the 0.17 ppm standard will change as follows:

Case 1: from +104 mV to about +106 mV

Case 2 from +104 mV to about +103 mV

This reduces the error encountered over the concentration range to a minimum.

NOTE: If the mV reading for the 1.7 ppm standard is not between +41 and +49 mV, either the membrane needs replacement or the sensing element needs cleaning (assuming the standard is correct). To clean the sensing element, carefully wipe its surface with a soft tissue.

4.1.4 Unknown Concentrations (samples to be analyzed)

Use the same procedure as with the standard, as described in Sections 4.1.3.1 through 4.1.3.3, substituting the sample to be analyzed for the standards. Read the mV response for each sample after 4 minutes have elapsed. Rinse the electrode thoroughly after it has been in any solution. Always place the electrode in pH 4 buffer several minutes before placing in the sample.

4.1.5 Calculations

Record the sample analyzed and the corresponding mV reading for the sample. Compare the mV reading to a graph correlating mV to ppb and record the results in ppb NH_3 .

4.2 Direct Nesslerization

- 4.2.1 Prepare two standard curves by diluting the following amounts of 10 mg/L standard ammonia solution in Section 3.6 in 100 ml volumetric flasks.

NOTE: Generation of a standard curve is not required if this method is in current use; however, four standard (two for the high range and two for the low range) will be run daily.

4.2.1.1 For standards with a concentration of 0.25 mg/L or greater, a 10mm sample cell will be used. The following standards should be used in preparing the high standard graphs.

<u>Amount of 10 mg/L Standard in ml</u>	<u>Final Conc. mg/L NH₃ - N</u>
100.0	10.0
50.0	5.0
10.0	1.0
5.0	0.5

4.2.1.2 For standards with a concentration of < 0.25 mg/L, a 100mm sample cell will be used. The following standards should be used in preparing the low standard graph:

<u>Amount of 10 mg/L Standard in ml</u>	<u>Final Conc. mg/L NH₃ - N</u>
1.0	0.1
0.50	0.05
0.25	0.025
0.10	0.010

4.2.2 For sample blanks and standards with low turbidity, calcium, magnesium and iron; i.e. does not produce turbidity when the Nessler reagent is added, go directly to 4.2.3. Otherwise, pretreat samples, as in 4.2.2.1 through 4.2.2.5.

4.2.2.1 Add 1 ml of the zinc sulfate solution (Section 3.2.3) to 100 ml of the sample.

4.2.2.2 Add 0.4 to 0.5 ml of the NaOH solution (Section 3.2.6) and mix to obtain a pH of 10.5 ± 0.3 as determined with a pH meter.

4.2.2.3 Let the solutions stand three (3) minutes.

4.2.2.4 Filter the sample and collect 50 ± 0.5 ml of the solution.

4.2.2.5 Add 100ul of the Rochelle salt solution (Section 3.2.2) to the samples and mix.

- 4.2.3 Add 1 ml of Nessler Reagent (Section 3.2.1) to 50 ml of untreated samples, blank, and standards or the treated samples from 4.2.2.5 in a 100 ml beaker. Mix well.
- 4.2.4 Let stand for ten minutes.
- 4.2.5 Instrument Calibration
- 4.2.5.1 Adjust spectrophotometer to a wavelength of 420 nm. Allow spectrophotometer to warm up 20 minutes.
- 4.2.5.2 Set the Mode Selector Knob to "Absorbance".
- 4.2.5.3 Pour the blank into a 10mm sample cell, place in spectrophotometer and set zero absorbance. Be sure to clean all cell faces with Kimwipes or bibulous paper.
- 4.2.6 Pour the high standards and/or the unknown samples into the 100mm sample cells. Place in the spectrophotometer in order of increasing concentrations and read the absorbance. Check the zero absorbance with the reagent blank before each sample.
- 4.2.7 Prepare the high standard curve plotting absorbance vs. concentration.
- 4.2.8 Determine the concentration of the unknown sample by comparing the sample absorbance with the standard curve.
- NOTE: If the concentration of the sample is below 0.25 mg/L NH_3 , go to 4.2.9.
- 4.2.9 Pour the low standards and/or the unknown samples containing < 0.25 mg/L NH_3 into a 100mm sample cell. Place in the spectrophotometer in order of increasing concentration and read the absorbance. Check the zero absorbance with the reagent blank before each sample.
- 4.2.7 Prepare the low standard curve plotting absorbance vs. concentration.
- 4.2.8 Determine the concentration of the unknown sample by comparing the sample absorbance with the standard curve.

5.0 REFERENCES

- 5.1 Standard Methods for the Examination of Water and Wastewater 14th ed., 1976
- 5.2 Steam Production Department System Power Chemistry Procedure CP/16
- 5.3 McGuire Nuclear Station Chemistry Procedure CP/O/B/8100/04
- 5.4 Orion Research 1978 Instruction Manual

6.0 ENCLOSURES

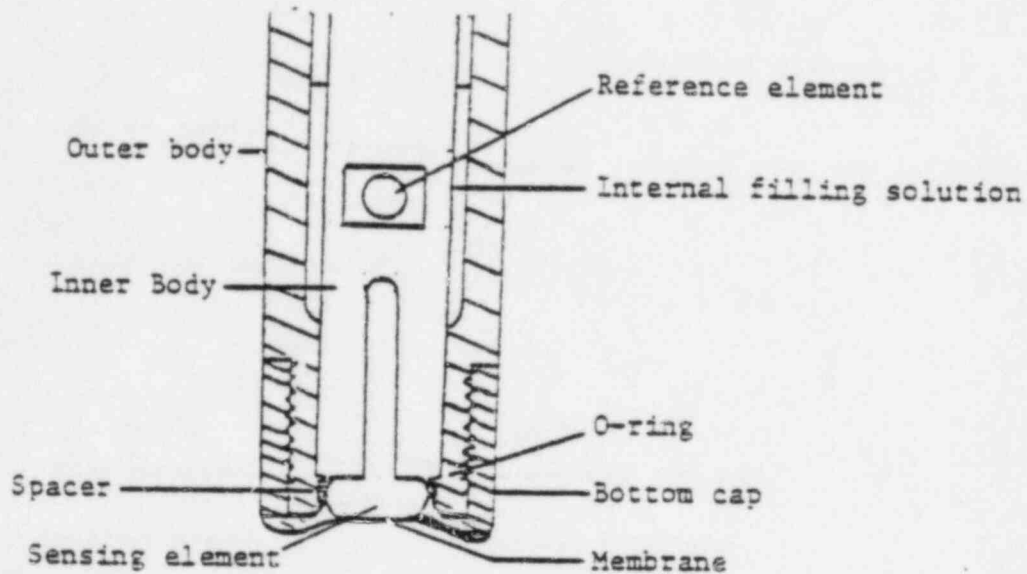
- 6.1 Relative Millivolt Change vs. Temperature
- 6.2 Construction of the Ammonia Electrode
- 6.3 Calibration Curve and Data for the Ammonia Electrode

RELATIVE MILLIVOLT CHANGE WITH TEMPERATURE

Values for the Nernst factor, $2.3 RT/F$, the change in electrode potential for a ten-fold change in the ammonia concentration of the sample as a function of temperature.

Temp.	Slope (mv)	Temp.	Slope (mv)	Temp.	Slope (mv)
0°C	54.20	15	57.18	30	60.16
5	55.20	20	58.17	35	61.15
10	56.19	25	59.16	40	62.14

CONSTRUCTION OF THE AMMONIA ELECTRODE



ASSEMBLY DIRECTIONS:

This electrode is shipped dry and without a membrane in place. When initially placing the electrode into service, it should be assembled and allowed to stand in 0.05 MNH_3 solution for at least 1 hour (preferably overnight) before use.

- STEP 1: Remove top cap. Lift out inner body. Pour out old internal filling solution. Remove bottom cap.
- STEP 2: Remove "O" ring and old membrane.
- STEP 3: Place a new membrane in the electrode, with the "dull" side toward the inner sensing element and the "shiny" side down, towards the sample solution.
- STEP 4: In addition to the red "O" ring, a second black "O" ring is an integral part of the spacer, trapped by a small groove on the bottom surface. When assembling, be sure that the black "O" ring is firmly in place in this groove. Place the spacer in the cap top of the new membrane with the black "O" ring down. Place red "O" ring on top of spacer. Screw body into bottom cap.
- STEP 5: Fill the outer body with the dilute internal filling solution 1 + 9 to about 1cm above the line between the body and the bottom cap. When the inner body is inserted into the outer body, any excess filling solution will flow out of the vent hole.
- STEP 6: Put inner body into outer body. Screw top cap on.

ENCLOSURE 6.3
CP/O/B/8100/20
CALIBRATION CURVE FOR THE AMMONIA ELECTRODE

