

DUKE POWER COMPANY
PROCEDURE PREPARATION
PROCESS RECORD

(1) ID No: CP/0/A/8100/42
Change(s) 0 to
0 Incorporated

- (2) STATION: Catawba
- (3) PROCEDURE TITLE: Chemistry Procedure for the Determination of Chloride -
Selective Ion Electrode
- (4) PREPARED BY: CW Balin DATE: 11-11-83
- (5) REVIEWED BY: R L Banta DATE: 11-11-83
Cross-Disciplinary Review By: Jw. Cox 11/11/83 N/R: SLC 83/77
- (6) TEMPORARY APPROVAL (IF NECESSARY):
By: _____ (SRO) Date: _____
By: _____ Date: _____
- (7) APPROVED BY: Jw. Cox Date: 11/11/83
- (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/A/8100/42

(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 FSA
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 Babin DATE: 11-11-83
- (7) REVIEWED BY: R. L. Pate DATE: 11-11-83

DUKE POWER COMPANY
ALARA EVALUATION CHECKLIST

- (1) Station Catawba Unit: 1 2 3
Other: Shared
- (2) Checklist Applicable to: CP/O/A/8100/42
- (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: Ch. Selin Date 11-11-83
- (6) Reviewed by: R. R. R. R. Date 11-11-83

DUKE POWER COMPANY
CATAWBA NUCLEAR STATION
CHEMISTRY PROCEDURE FOR THE DETERMINATION
OF CHLORIDE - SELECTIVE ION ELECTRODE

1.0 DISCUSSION

1.1 Scope

This procedure describes the selective ion electrode method for the determination of low level chloride concentration in high purity water.

1.2 Principle

The chloride selective ion electrode is a solid state sensor. The electrode contains a $\text{HgS}/\text{Hg}_2\text{Cl}_2$ crystal at the tip, across which a potential is developed by the chloride ions. This principle is the same as a glass electrode's response to hydrogen ions. The potential varies with the concentration of chloride ions. For each tenfold change in concentration, the electrode will respond with a 59 mV (at 25°C) change in potential. A plot of mV vs. chloride concentration is prepared from standards of known chloride concentration. The chloride concentration of unknown samples can then be determined from this curve.

1.3 Limits and Precautions

- 1.3.1 This method is applicable in the range of 10 ppb to 1000 ppb chloride.
- 1.3.2 NEVER STORE BOTH ELECTRODES TOGETHER IN THE SAME SOLUTION.
- 1.3.3 Mercuric salts are POISONOUS! Gloves should be worn when handling the chloride electrode.
- 1.3.4 Always keep the reference electrode filling solution levels (upper and lower) higher than the level of solution being measured.
- 1.3.5 The upper and lower filling solutions in the double junction reference electrode should be replaced daily.
- 1.3.6 Since electrode potentials are affected by changes in temperature, samples and standards should not differ more than $\pm 5^\circ\text{C}$.

- 1.3.7 When handling radioactive samples, personnel should follow the Directive for Personnel Conduct in the Hot Lab, Atomic Spectroscopy Lab, and Primary Sampling Labs (see Enclosure 6.1).
- 1.3.8 All glassware used in this procedure should be nitric acid washed before use.
- 1.3.9 Safety glasses, rubber gloves, and a lab coat must be worn when handling nitric acid.
- 1.4 Interferences
 - 1.4.1 Changes in sample pH and low ionic strength will affect the chloride electrode response. Therefore, all samples and standards should be treated with pH/Ionic Strength Adjustor (2M nitric acid) to reduce the pH to 2 and insure sufficient ionic strength for proper electrode response.
 - 1.4.2 Never expose the chloride electrode to a solution with a pH greater than 7 or less than 1. If exposed, polish the electrode (see Section 4.2.1).
 - 1.4.3 Ions which form very insoluble salts with mercury (S^{2-} , I^- , Br^- , CNS^-) will interfere if present at sufficiently high levels.

2.0 APPARATUS

- 2.1 pH/mV meter
- 2.2 Beckman Multiple Electrode Selector
- 2.3 Ultra Sensitive Solid State Chloride Electrode (GAM RAD PHI 91100)
- 2.4 Double Junction Reference Electrode (GAM RAD PHE 54473)
- 2.5 Electrode holder
- 2.6 Magnetic stirrer and teflon-coated stirring bars
- 2.7 Stopwatch or clock
- 2.8 Glass beakers, nitric acid washed
- 2.9 Eppendorf pipets with tips: 50 μ l, 100 μ l, 250 μ l, 500 μ l, and 1000 μ l
- 2.10 Glass Graduated Cylinders, nitric acid washed
- 2.11 Thermometer
- 2.12 Polishing Kit (GAM RAD PHA 76518)
- 2.13 1000 ml glass volumetric flask, nitric acid washed

3.0 REAGENTS

3.1 pH/Ionic Strength Adjustor (2M nitric acid)

Slowly add 63 ± 1 mls of concentrated nitric acid to 437 ± 1 mls of demineralized water. Mix thoroughly. This solution is stable for six months.

3.2 Chloride Stock Standard (100 ppm Cl^-)

Dissolve 0.1648 ± 0.0001 grams of sodium chloride (NaCl), oven dried at $105-110^\circ\text{C}$ for one hour, in ~ 500 mls of Super-Q water in a one liter volumetric flask. Dilute to volume. This solution is stable for 1 year.

3.3 Double Junction Reference Electrode Filling Solutions (supplied with the reference electrode)

3.3.1 Lower Filling Solution (gelled saturated KNO_3 ; GAM RAD PHB 1326).

3.3.2 Upper Filling Solution (gelled saturated KCl ; GAM RAD PHB 1322).

4.0 PROCEDURE

4.1 Initial Conditions

4.1.1 Add the upper filling solution to the upper section of the double junction reference electrode each day before use.

4.1.2 Add the lower filling solution to the lower section of the double junction reference electrode each day before use.

4.1.3 Insure that the chloride electrode and the reference electrode are connected to the back of the multiple electrode selector. Place the chloride channel in service by depressing the appropriate channel button.

4.1.4 Place the pH/mV meter in STANDBY and in the mV mode.

4.1.5 Polish the chloride electrode as follows:

4.1.5.1 Wet the cloth-covered acrylic polishing block with Super-Q water. Shake off the excess water.

4.1.5.2 Place a small amount of alumina powder on the polishing block to form a paste.

4.1.5.3 Using light pressure and a circular motion, polish the surface of the crystal for 30 seconds.

4.1.5.4 Rinse the electrode thoroughly with Super-Q water.

4.2 Standard Curve

- 4.2.1 Soak the electrodes in a solution comprised of 99 mls of Super-Q water and one ml of pH/Ionic Strength Adjustor (Section 3.1) for 30 minutes to pre-condition both electrodes.
- 4.2.2 Rinse the electrodes with Super-Q water.
- 4.2.3 Immerse the electrodes and a thermometer into the blank comprised of 99 ml. of Super-Q water and 1 ml of pH/Ionic Strength Adjustor (Section 3.1).
- 4.2.4 Insert a stirring bar and adjust the stirring rate until there is no vortex. Release the STANDBY switch.
- 4.2.5 Record the temperature of the solution.
- 4.2.6 Make a 50 ppb Cl^- solution by adding 50 μl of 100 ppm Cl^- standard to the blank. Wait 3 minutes, then adjust the coarse and fine adjustment as needed until the millivolt display reads +500.
- 4.2.7 Add an additional 100 μl of 100 ppm Cl^- standard, making a 150 ppb Cl^- solution. Wait 3 minutes and record the millivolt reading.

NOTE: There should be ~ 14 mV between the 50 ppb and the 150 ppb Cl^- standards. If not, polish the probe according to Section 4.1.5 then repeat Sections 4.2.1 through 4.2.7.

- 4.2.8 Add an additional 100 μl of 100 ppm Cl^- standard, making a 250 ppb Cl^- solution. Wait 3 minutes and record the millivolt reading.
- 4.2.9 Add an additional 250 μl of 100 ppm Cl^- standard, making a 500 ppb Cl^- solution. Wait 3 minutes and record the millivolt reading.
- 4.2.10 Add an additional 500 μl of 100 ppm Cl^- standard, making a 990 ppb Cl^- solution. Wait 3 minutes and record the millivolt reading.
- 4.2.11 Place the mV meter in STANDBY by depressing the STANDBY switch.
- 4.2.12 Plot the data obtained in Sections 4.2.6 through 4.2.10 on semi-log graph paper. Record the temperature of the solution (blank), measured in Step 4.2.5, on this graph.

- 4.2.13 Proceed with Section 4.3 or store the electrodes in separate beakers containing Super-Q water.

4.3 Standard Curve Check

NOTE: A standard curve check should be done daily when the probe is in use in which two 150 ppb Cl^- standards will be run for Q-sum.

- 4.3.1 Rinse the electrodes with Super-Q water.
- 4.3.2 Soak the electrodes in a solution comprised of 99 ml of Super-Q water and 1 ml of pH/Ionic Strength Adjustor (Section 3.1) for 30 minutes to pre-condition both electrodes. If the electrodes have already been soaked, proceed to Section 4.3.4.
- 4.3.3 Rinse the electrodes with Super-Q water.
- 4.3.4 Prepare two 150 ppb standards by adding 150 μl of 100 ppm standard to two beakers containing 99 ml of Super-Q water and 1 ml of pH/Ionic Strength Adjustor.
- 4.3.5 Immerse the electrodes and a thermometer in the blank solution of 99 ml of Super-Q water and 1 ml of pH/Ionic Strength Adjustor containing a stirring bar.
- 4.3.6 Adjust the stirring rate so there is no vortex and release the STANDBY switch.
- 4.3.7 Check the temperature of the solution (blank) and compare to the standard curve temperature. The temperature should be $\pm 5^\circ\text{C}$ of the temperature listed on the standard curve.
- 4.3.8 Make a 50 ppb Cl^- solution by adding 50 μl of the 100 ppm Cl^- standard to the blank. Wait 3 minutes, then adjust the coarse and fine adjustments as needed until the millivolt display reads +500.
- 4.3.9 Place the mV meter in STANDBY by depressing the STANDBY switch.
- 4.3.10 Rinse the electrodes with Super-Q water.
- 4.3.11 Immerse the electrodes in the first 150 ppb standard. Adjust the stirring rate until there is no vortex.
- 4.3.12 Release the STANDBY switch. Wait 3 minutes and record the millivolt reading.
- 4.3.13 Place the mV meter in STANDBY by depressing the STANDBY switch.

- 4.3.14 Repeat Sections 4.3.10 - 4.3.13, substituting the second 150 ppb standard.
- 4.3.15 Read the chloride concentration of the two 150 ppb standards from the standard curve.
- 4.3.16 If the results do not fall within the Q-Sum Limits, repeat 4.3.3 - 4.3.15. If the results are still unacceptable, polish the probe according to Section 4.1.5 and repeat Section 4.3. If results are still unacceptable, repeat Section 4.2.
- 4.3.17 If results are within Q-Sum Limits, proceed with Section 4.4 or Section 4.5 or store the electrodes in separate beakers containing Super-Q water.
- 4.4 Sample Concentration Measurement (>50 ppb)
- NOTE: Check the temperature of the sample and compare it to the standard curve temperature. The sample temperature should be $\pm 5^{\circ}\text{C}$ of the temperature listed on the standard curve. If the sample temperature is outside the $\pm 5^{\circ}\text{C}$ limit, the temperature should be adjusted by placing the sample container in a water bath.
- 4.4.1 Rinse the electrodes with Super-Q water.
- 4.4.2 Add 1 ml of pH/Ionic Strength Adjustor (Section 3.1) to 100 ml of the sample to be analyzed.
- NOTE: Samples containing more than 1 ppm chloride should be diluted using Super-Q water. Exposure to high chloride concentrations can cause a loss of sensitivity in the electrode.
- 4.4.3 Immerse the electrodes, a thermometer, and a stirring bar into the sample solution. Adjust the stirring rate until there is no vortex and release the STANDBY switch.
- 4.4.4 Wait 3 minutes and record the millivolt reading.
- 4.4.5 Place the mV meter in STANDBY by depressing the STANDBY switch.
- 4.4.6 Find the millivolt reading(s) obtained in Section 4.4.4 on the standard curve and read the chloride concentration in ppb.
- 4.4.6.1 If the millivolt reading obtained is >500, proceed to Section 4.5.
- 4.4.6.2 If samples have been diluted, results from 4.4.6 should be multiplied by the dilution factor.

- 4.4.7 If additional samples are to be analyzed, repeat Sections 4.4.2 through 4.4.7.
- 4.4.8 If no additional samples are to be analyzed, rinse the electrodes with Super-Q water and store in separate beakers of Super-Q water.

4.5 Sample Concentration Measurement - Internal Addition (<50 ppb)

NOTE: Check the temperature of the sample solution and compare it to the standard curve temperature. The sample temperature should be $\pm 5^{\circ}\text{C}$ of the temperature listed on the standard curve. If the sample temperature is outside the 5°C limit, it should be adjusted by placing the container in a water bath.

- 4.5.1 Soak the electrodes in a solution comprised of 99 ml of Super-Q water and 1 ml of pH/Ionic Strength Adjustor for 3 minutes.
- 4.5.2 Rinse the electrodes with Super-Q water.
- 4.5.3 Add 1 ml of pH/Ionic Strength Adjustor to 100 ml of the sample in a beaker.
- 4.5.4 Immerse the electrodes and a stirring bar into the sample solution. Adjust the stirring rate until there is no vortex.
- 4.5.5 Add 50 μl of 100 ppm Cl^{-} standard to the sample solution.
- 4.5.6 Release the Standby Switch, wait 3 minutes, and record the millivolt reading.
- 4.5.7 Find the millivolt reading obtained in Section 4.5.6 on the standard curve and read the chloride concentration in ppb.
 - 4.5.7.1 Calculate the sample concentration as follows:
$$\text{Smp. Concentration} = \text{Measured Concentration} - 50 \text{ ppb}$$
 - 4.5.7.2 Record anything under 10 ppb as < 10 ppb.
(This allows for a 1% volume error.)
- 4.5.8 If additional samples are to be analyzed, repeat Sections 4.5.2 through 4.5.8.
- 4.5.9 If no additional samples are to be analyzed, rinse the electrodes with Super-Q water and store in separate beakers of Super-Q water.

5.0 REFERENCES

- 5.1 Gam Rad Inc. Ultra-Sensitive Solid State Chloride Electrode
PHI 91100 Instruction Manual
- 5.2 Ocone Nuclear Station, Chemistry Procedure for the Determination
of Chloride by Specific Ion Electrode Using Beckman 4500 Meter,
OP/O/A/2004/03A
- 5.3 McGuire Nuclear Station, Chemistry Procedure for the Determination
of Chloride in Water, Alternate Method, CP/O/A/8100/06B

6.0 ENCLOSURES

- 6.1 Directive for Personnel Conduct in the Hot Lab, Atomic Spectroscopy
Lab, and Primary Sampling Labs

DUKE POWER COMPANY
CATAWBA NUCLEAR STATION
CP/O/A/8100/42
ENCLOSURE 6.1

DIRECTIVES FOR PERSONNEL CONDUCT IN THE HOT LAB, ATOMIC SPECTROSCOPY LAB,
AND PRIMARY SAMPLING LABS

1. Eating, drinking and smoking are prohibited.
2. Pipetting is not to be done by mouth suction. A pipet bulb or aspirator is to be used.
3. Before a worker leaves the Hot Lab, hands must be washed and then checked with a beta-gamma survey meter. Contamination remaining after thorough washing is to be reported to Health Physics.
4. If, in the course of work, personnel contamination is suspected, a survey with a suitable instrument is to be made immediately. This is to be followed by the required cleansing and a further survey. Routine precautionary surveys should be made at intervals.
5. No person is to work with radioactive materials unless he is wearing rubber gloves.
6. Radioactive liquid waste is to be disposed of in radioactive sinks only.
7. Radioactive solid waste and contaminated material are to be placed in trash containers labeled "Contaminated."
8. Good housekeeping must be observed at all times. In the event of a spill, the following procedure is to be followed:
 - a. The liquid is to be blotted up; wear gloves and shoe covers.
 - b. All disposable materials contaminated by the spill and the cleaning process are to be placed in a "Contaminated" trash can.
 - c. The area of the spill and the type of activity is to be clearly marked if fixed contamination results.
 - d. Contact Health Physics to swipe test the area for cleanliness.
9. All apparatus used in the analysis of radioactive material is to remain in the Hot Lab unless certified clean for removal by Health Physics.
10. Radioactive materials and contaminated materials are to be retained within the radioisotope locker or a specific location within the lab.
11. All wounds, spills and other emergencies are to be reported to Health Physics immediately.
12. Before leaving the lab, be sure all written records have been completed.
13. If you have a cut or open wound, notify a Chemistry Supervisor prior to handling any radioactive material.
14. Entry and exit from the Hot Lab is to comply with Health Physics procedures.