

DUKE POWER COMPANY  
PROCEDURE PREPARATION  
PROCESS RECORD

(1) ID No: CP/O/A/8100/11  
Change(s) 0 to  
0 Incorporated

- (2) STATION: Catawba
- (3) PROCEDURE TITLE: Chemistry Procedure for the Determination of  
Dissolved Oxygen
- (4) PREPARED BY: Richard H. Chavet DATE: 7-26-79
- (5) REVIEWED BY: Larry D. Evans DATE: 8-7-79  
Cross-Disciplinary Review By: Jw. Cox 8/7/79 N/R: SRC-79-21
- (6) TEMPORARY APPROVAL (IF NECESSARY):  
By: \_\_\_\_\_ (SRO) Date: \_\_\_\_\_  
By: \_\_\_\_\_ Date: \_\_\_\_\_
- (7) APPROVED BY: M.S. Tuckman by Jw. Cox Date: 8/14/79
- (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 X 2 X 3       
OTHER:       
(2) CHECK LIST APPLICABLE TO: CP/O/A/8100/11

## (3) SAFETY EVALUATION - PART A

The item to which this evaluation is applicable represents:

Yes      No X A change to the station or procedures as described in the FSAR  
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 X 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 X Will the probability of an accident previously evaluated  
in the FSAR be increased?  
Yes      No X Will the consequences of an accident previously evaluated  
in the FSAR be increased?  
Yes      No X May the possibility of an accident which is different  
than any already evaluated in the FSAR be created?  
Yes      No X Will the probability of a malfunction of equipment  
important to safety previously evaluated in the FSAR  
be increased?  
Yes      No X Will the consequences of a malfunction of equipment  
important to safety previously evaluated in the FSAR  
be increased?  
Yes      No X May the possibility of malfunction of equipment  
important to safety different than any already evaluated  
in the FSAR be created?  
Yes      No X 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: Richard H. Chaust DATE: 7-26-79  
(7) REVIEWED BY: Larry D. Evans DATE: 8-7-79

DUKE POWER COMPANY

(1) Station: Catawba Unit: 1 X 2 X 3

Other: \_\_\_\_\_

(2) Checklist Applicable to: CP/O/A/8100 11

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

Flushing and draining was 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: Richard H. Chaust Date 2-18-80

(6) Reviewed by: Larry D. Evans Date 2-19-80

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

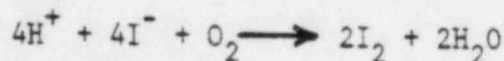
## 1.0 DISCUSSION

### 1.1 Scope

This procedure covers three methods (Indigo Carmine, modified Winkler, and Chemets) for the determination of dissolved oxygen.

### 1.2 Principle

- 1.2.1 Indigo Carmine - Dissolved oxygen reacts with a solution of indigo carmine dye to produce color changes. The concentration of dissolved oxygen can be determined by the color produced.
- 1.2.2 Winkler - Dissolved oxygen can be determined by an indirect titration method. Direct titration of dissolved oxygen in water would be difficult since no indicator of adequate sensitivity is known. To overcome this difficulty, the oxygen is quantitatively reacted with iodide to form iodine. The concentration of iodine is more easily determined. The quantitative reaction taking place for dissolved oxygen determination is:



- 1.2.3 Chemets - Dissolved oxygen Chemets, using indigo carmine or Rhodazine D reagents, react to produce a progressive color change when oxygen is present.

### 1.3 Interferences

- 1.3.1 Indigo Carmine - Hydrazine up to 1 ppm and ferric ion up to 4 ppm will not interfere. Boric acid does not interfere up to 250 ppm as boron. Above 250 ppm additional potassium hydroxide must be added as shown in Enclosure 6.1.
- 1.3.2 Winkler - The azide modification to this method is used to eliminate interferences from less than 5 ppb nitrate nitrogen and less than 1 ppm ferrous ion. Other oxidizing or reducing agents should not be present. Oxidizing agents will tend to cause high results while reducing agents lead to low results. Boric acid can interfere if an insufficient amount of caustic is added.

- 1.3.3 Chemets - No interferences should occur when this method is used where applicable.

1.4 Limits and Precision

- 1.4.1 Indigo Carmine - Dissolved oxygen can be determined by this method from 0 ppb to 60 ppb. The precision ranges from  $\pm 1$  ppb at 5 ppb to  $\pm 3.8$  ppb at 60 ppb.
- 1.4.2 Winkler - The lower limit of this method is approximately 50 ppb with no upper limit. The precision of this method varies with the type of sample to be analyzed. Precision of  $\pm 20$  ppb can be expected with distilled water to  $\pm 60$  ppb in waste water.
- 1.4.3 Chemets - Dissolved oxygen can be determined from 0 to 1000 ppb with the low range kit and from 100 ppb to 12,000 ppb with the high range kit.

1.5 Precautions

Analysts should wear eye protection when handling chemicals.

2.0 APPARATUS

2.1 Indigo Carmine

- 2.1.1 25 ml buret
- 2.1.2 300 ml BOD sample bottles
- 2.1.3 Color chart or standards

2.2 Winkler

- 2.2.1 Sewage sampler with rope
- 2.2.2 300 ml BOD bottle
- 2.2.3 500 ml Erlenmeyer flask
- 2.2.4 10 ml buret
- 2.2.5 3 pipets to deliver 2 ml each

- 2.3 Chemets - All equipment needed is supplied with the dissolved oxygen Chemets kit.

3.0 REAGENTS

3.1 Indigo Carmine

- 3.1.1 Indigo Carmine Solution - Add  $0.45 \pm 0.005$  grams of indigo carmine and  $4.5 \pm 0.1$  grams of dextrose to a one liter volumetric flask. Add  $500 \pm 5$  ml of glycerin, dilute to 1 liter with demineralized water and mix thoroughly. This solution is stable for 30 days when refrigerated.
- 3.1.2 Potassium Hydroxide Solution - Dissolve  $530 \pm 1$  gram of potassium hydroxide in water and dilute to 1 liter. Store in a polyethylene bottle. This solution is stable indefinitely.
- 3.1.3 Color Reagent - In a 150 ml beaker, mix  $40 \pm 0.5$  ml of indigo carmine solution (Section 3.1.1) with  $10 \pm 0.1$  ml of potassium hydroxide solution (Section 3.1.2) and pour into a buret. Allow the solution to stand until red color changes to bright yellow. Renew daily.
- NOTE: When the sample contains more than 250 ppm boron, adjust KOH according to Enclosure 6.1.
- 3.1.4 Hydrochloric Acid Solution (1%) - Pipet 10 ml of concentrated HCl into a 1 liter volumetric flask containing demineralized water and dilute to volume with demineralized water.
- 3.1.5 Red Stock Solution - In a 250 ml volumetric flask, dissolve 14.82 grams of cobaltous chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) in approximately 200 ml of 1% v/v HCl and dilute to 250 ml with 1% v/v HCl. Store in an amber bottle. This solution is stable indefinitely.
- 3.1.6 Yellow Stock Solution - In a 250 ml volumetric flask, dissolve 11.26 grams of ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in approximately 200 ml of 1% v/v HCl and dilute to 250 ml. Store in an amber bottle. This solution is stable indefinitely.
- 3.1.7 Blue Stock Solution - In a 250 ml volumetric flask, dissolve 15.61 grams of cupric sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in approximately 200 ml of 1% v/v HCl and dilute to 250 ml. Store in an amber bottle. This solution is stable indefinitely.
- 3.1.8 Standard Color Solutions - Prepare a series of color standards by placing the following amounts in a 500 ml volumetric flask.

| Final Color of Solution | Equivalent Dissolved Oxygen in PPB | Ml of Stock Solution |       |       |
|-------------------------|------------------------------------|----------------------|-------|-------|
|                         |                                    | Yellow               | Red   | Blue  |
| Yellow                  | 0                                  | 58.35                | 1.25  |       |
| Orange                  | 5                                  | 33.35                | 8.35  |       |
| Orange-pink             | 10                                 | 20.85                | 10.4  |       |
| Pink                    | 15                                 | 16.65                | 15.65 |       |
| Pink-red                | 25                                 | 6.35                 | 24.0  |       |
| Red-purple              | 50                                 | 2.85                 | 30.5  | 13.5  |
| Blue purple             | 94                                 | 1.25                 | 50.85 | 70.45 |
| Blue                    | > 100                              |                      | 47.5  | 86.7  |



Add 2.3 ml of concentrated HCl to each bottle and dilute to the neck with water. Stopper, seal, label (including date prepared) and retain for 1 year.

### 3.2 Winkler

#### 3.2.1 Winkler Method Using Powder Pillows

- 3.2.1.1 Phenylarsine oxide (PAO) 0.0375N, commercially available.

NOTE: This must be standardized according to Section 3.2.2.3.2. If the normality is high, dilute according to Section 3.2.2.3.4. If the normality is low, the calculation in Section 4.2.2.8 can be adjusted to compensate for the low normality.

- 3.2.1.2 Powder pillows (alkaline-iodide-azide, manganous sulfate, and sulfamic acid) premeasured, commercially available.

- 3.2.1.3 Potassium hydroxide, solid, reagent grade.

- 3.2.1.4 Starch Solution - Dissolve 1 gram of soluble starch in 100 ml of boiling water while stirring. Boil for 1 minute after addition of starch. Cool and use.

NOTE: This must be made daily since aqueous-starch suspensions decompose within a few days due to bacterial action.

#### 3.2.2 Winkler Method Using Laboratory Chemicals

- 3.2.2.1 Manganous sulfate solution - Dissolve  $364 \pm 0.5$  grams of manganous sulfate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) in demineralized water. Filter and dilute to 1 liter.

NOTE:  $400 \pm 0.5$  grams of  $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$  or  $480 \pm 0.5$  grams of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  can be used.

- 3.2.2.2 Iodide-azide Solution - Dissolve  $700 \pm 0.5$  grams of potassium hydroxide (KOH) in sufficient demineralized water to make approximately 700 ml of solution in a 1 liter volumetric flask and cool to room temperature. Dissolve  $150 \pm 0.5$  grams of iodate-free potassium iodide (KI) in 200 ml of demineralized water and mix with the KOH solution in the volumetric flask. Dilute to 1 liter. To this solution add  $10 \pm 0.1$  gram of sodium azide ( $\text{NaN}_3$ ) dissolved in 40 ml of demineralized water. Mix the solution and store in a dark polyethylene bottle.

## 3.2.2.3 Phenylarsine Oxide (PAO) 0.0375N

3.2.2.3.1 Dissolve  $45 \pm 0.1$  grams of PAO ( $\text{C}_6\text{H}_5\text{AsO}$ ) in 750 ml of demineralized water containing  $12 \pm 0.1$  grams of sodium hydroxide.

NOTE: Some of the PAO will not dissolve. However, after 1 to  $1\frac{1}{2}$  hours of stirring (magnetic stirrer), enough will have dissolved to continue.

Decant 650 ml of this solution into a 1500 ml beaker. Very slowly adjust the pH between 6 and 7 with 50% v/v HCl ( $6N \approx 40$  mls), then dilute to about 1100 ml with demineralized water and stir for about 5 minutes (at this point, there will be a fluffy white precipitate). Filter this solution through qualitative filter paper and add 1 ml of chloroform to the filtrate as a preservative. Standardize this solution according to Section 3.2.2.3.2. Commercial PAO can be used, but it must also be standardized.

3.2.2.3.2 Standardization of 0.0375N PAO Solution - Dissolve  $1.2188 \pm 0.0005$  grams of potassium biniodate [ $\text{KH}(\text{IO}_3)_2$ ] in demineralized water and dilute to 1 liter. This is a 0.0375N solution of [ $\text{KH}(\text{IO}_3)_2$ ]. Dissolve  $2 \pm 0.1$  grams of iodate free potassium iodide (KI) in an Erlenmeyer flask with about 150 ml of demineralized water. Add exactly 20.00 ml of 0.0375N standard biniodate solution followed by  $10 \pm 0.5$  ml of 10% v/v  $\text{H}_2\text{SO}_4$ . Dilute to 300 ml and titrate the liberated iodine with the 0.0375N PAO titrant. When a pale yellow color appears, add approximately 2 ml of starch solution. If the prepared PAO solution (Section 3.2.2.3.1) is exactly 0.0375N, then it will require exactly 20 ml of biniodate to reach the end point.

3.2.2.3.3 Calculate the normality of the PAO solution by the following formula:

$$N_{\text{PAO}} = \frac{20 \text{ ml} \times 0.0375\text{N}}{\text{ml PAO used}} \quad \text{or} \quad \frac{0.75}{\text{ml PAO used}}$$

NOTE: If the PAO solution is less than 0.0375N, discard and start over.



3.2.2.3.4 If the normality of the PAO is greater than 0.0375, prepare 1 liter of working solution by the following formula:

$$X = \frac{0.0375N \times 1000 \text{ ml}}{\text{Normality of PAO (Section 3.2.2.3.3)}}$$

where X = the number of milliliters of PAO to be diluted to 1 liter

3.2.2.4 Sulfuric Acid - concentrated (36N)

3.2.2.5 Starch Solution - Prepare according to Section 3.2.1.4.

3.3 Chemets - all reagents necessary are supplied with the dissolved oxygen Chemets kits.

#### 4.0 PROCEDURE

##### 4.1 Indigo-Carmine

- 4.1.1 Determine that reagents 3.1.1, 3.1.3 and 3.1.8 have not expired.
- 4.1.2 Collect a sample in a 300 ml BOD bottle by running the sample line to the bottom of the BOD bottle with a sample flow of 500 - 1000 ml per minute. Allow for 10 changes of sample bottle volume while sample is flowing. Extreme care must be taken to prevent entrapment of air in the sample. Maintain BOD bottle full to overflowing while removing the sample line.
- 4.1.3 Insert the tip of the buret containing the color reagent (Section 3.1.3) below the neck of the bottle and add 2 ml of the color reagent.
- 4.1.4 Remove the buret tip from the BOD bottle and stopper the BOD bottle exercising care in preventing the entrapment of air in the sample.
- 4.1.5 Invert the bottle several times and compare the color of the sample with the color of the standards (Section 3.1.8) or color chart.

##### 4.2 Winkler

###### 4.2.1 Collection of Sample

###### 4.2.1.1 Sample Collection Using Sewage Sampler

4.2.1.1.1 Secure 300 ml BOD bottle in the sampler.

4.2.1.1.2 Place the sampler under water and hold there until no air bubbles can be seen escaping from the sampler (about 2 minutes).

4.2.1.1.3 Lift the sampler out of the water and remove the top.

4.2.1.1.4 Place glass stopper into the BOD bottle and remove the bottle from the sampler.

4.2.1.2 Sample Collection at Sample Panel

4.2.1.2.1 Collect a sample in a 300 ml BOD bottle by running the sample line to the bottom of the BOD bottle with a sample flow of 500 - 1000 ml per minute. Allow for 10 changes of sample bottle volume while sample is flowing. Extreme care must be taken to prevent entrapment of air in the sample. Maintain BOD bottle full to overflowing while removing the sample line.

4.2.1.2.2 Remove the sample line from the BOD bottle and stopper the BOD bottle exercising care in preventing the entrapment of air in the sample.

4.2.2 Determination of Dissolved Oxygen Using Powder Pillows

4.2.2.1 Empty one premeasured Hach capsule of manganous sulfate and one capsule of alkaline-iodide-azide into the BOD bottle.

NOTE: Add 3 grams of solid KOH if the sample is borated.

4.2.2.2 Shake bottle well and allow the contents to settle.

NOTE: Water high in chlorides requires a 10 minute contact with the precipitate.

4.2.2.3 Empty one (1) premeasured capsule of sulfamic acid into the BOD bottle and again shake well.

NOTE: Use two powder pillows if the sample is borated.

4.2.2.4 Transfer the entire 300 ml into a 500 ml Erlenmeyer flask.

NOTE: High iodine concentrations decompose starch to products which do not have good indicator properties. The light yellow color indicates that most of the iodine has been reduced.

- 4.2.3.7 Add 1 - 2 ml of starch solution and continue titration until the blue color disappears.
- 4.2.3.8 The number of ml of titrant used equals the dissolved oxygen content in ppm according to the formula:

$$\text{D.O. in ppm} = \frac{(8000)(0.0375)(\text{ml of titrant})}{300}$$

where 8000 = milliequivalents for oxygen  
0.0375 = normality of titrant (PAO)  
300 = volume of sample in ml

#### 4.3 Chemets

- 4.3.1 Procedure for Sewage Waters Using High Range Chemets Kit
- 4.3.1.1 Fill the sample cup to 25 ml with sample.
- 4.3.1.2 Add 2 - 3 drops of neutralizer solution and stir.
- 4.3.1.3 Snap Chemet tip in sample and mix contents.
- 4.3.1.4 Compare with color standards to determine  $\text{O}_2$  in ppm.
- 4.3.2 Procedure for Secondary Systems Using Low Range Chemets Kit
- 4.3.2.1 Place Chemet in sample.
- 4.3.2.2 Snap Chemet tip and mix contents.
- 4.3.2.3 Compare with color standards to determine  $\text{O}_2$  in ppm.

#### 5.0 REFERENCES

- 5.1 American Society for Testing and Materials, 1978. Annual Book of ASTM Standards, Part 31, D 88866, Pages 445-454.
- 5.2 Standard Methods for the Examination of Water and Wastewater, 14th Edition, 1975, Part 442, Pages 440-449.
- 5.3 Skoog, D.A. and West, D.M., 1965. Analytical Chemistry, An Introduction; Holt, Rhinehart, and Winston, pp 393 and 398.

- 4.2.2.5 Titrate the sample with 0.0375N PAO until the sample is light yellow. Add a few ml of starch solution to the sample, then titrate until the blue color disappears.

NOTE: High iodine concentrations decompose starch to products which do not have good indicator properties. The light yellow color indicates that most of the iodine has been reduced.

- 4.2.2.6 Since the PAO solution is 0.0375N, then the number of ml used equals the dissolved oxygen content in ppm.

$$\text{D.O. in ppm} = \frac{(8000)(0.0375)(\text{ml of titrant})}{300}$$

where 8000 = mg/l milliequivalents for oxygen

300 = volume of sample (ml)

0.0375 = normality of titrant (PAO)

#### 4.2.3 Determination of Dissolved Oxygen Using Laboratory Chemicals

- 4.2.3.1 To the sample collected in a 300 ml BOD bottle, add 2 ml of  $\text{MnSO}_4$  solution followed by 2.0 ml of the alkaline-iodide-azide solution, well below the surface of the liquid.

NOTE: Add 3 grams of KOH for borated samples.

- 4.2.3.2 Replace the stopper, carefully excluding air bubbles, and mix.

- 4.2.3.3 Repeat the mixing a second time after the floc has settled, leaving a clear supernate solution.

NOTE: Water high in chlorides requires a 10 minute contact with the precipitate.

- 4.2.3.4 When the floc has settled, leaving at least 100 ml of clear supernate, remove the stopper and add 2.0 ml of  $\text{H}_2\text{SO}_4$  and mix. Allow this solution to stand for a minimum of 5 minutes before proceeding. Do not allow it to stand more than 2 hours.

NOTE: Add 4 ml of  $\text{H}_2\text{SO}_4$  for borated samples.

- 4.2.3.5 Transfer the entire contents of the BOD bottle into a 500 ml Erlenmeyer flask.

- 4.2.3.6 Titrate the sample with 0.0375N PAO solution to a pale yellow.

- 5.4 McGuire Nuclear Station Chemistry Procedures CP/O/A/8100/17A and CP/O/B/8100/18A.
- 5.5 Oconee Nuclear Station Chemistry Procedure CP/O/A/300/17.
- 5.6 Steam Production Department System Power Chemistry Procedures CP/31 and CP/33.

6.0 ENCLOSURES

- 6.1 Graph for KOH Addition In The Presence Of Boric Acid.

## Enclosure 6.1

Graph for KOH Addition in the  
Presence of Boric Acid