

MILLSTONE NUCLEAR POWER STATION  
CHEMISTRY PROCEDURE

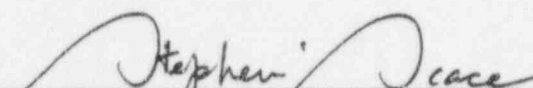


**Boron Analysis**

**CP 807/2807/3807AA**

**Rev. 0**

Approval:

  
Vice President - Millstone Station

SORC Mtg. No:

93-36

Effective Date:

9-13-93

Level of Use  
**General**

Subject Matter Expert:  
Greg D'Auria

**Millstone All Units  
Chemistry Procedure**

**Boron Analysis**

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**ATTACHMENTS AND FORMS**

Chem Form 807/2807/3807AA-1, "Boron Analysis Log Sheet"

Chem Form 807/2807/3807AA-2, "Boron Control Chart"

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## 1. PURPOSE

### 1.1 Objective

This procedure provides a method for boron analysis, for all nuclear plant applications with boron concentrations above 1.0 mg/liter (1.0 ppm).

### 1.2 Discussion

A sample containing boric acid or borate is weighed and results are transferred to the autotitrator. Demineralized water and mannitol is then added to sample. The mannitoboric acid formed is then titrated with a standard NaOH solution to a pH of 8.5. The milliliters of titrant used is proportional to the amount of boron present in the sample.

### 1.3 Frequency

1.3.1 A quality control check of the method is performed daily by analyzing a 1000 ppm boron standard.

## 2. PREREQUISITES

### 2.1 General

2.1.1 N/A

### 2.2 Tools and Consumables

2.2.1 Autotitrator

2.2.2 Collapsible container ("cubitainer")

2.2.3 Demineralized water

2.2.4 Dropper bottles for HCl and NaOH

2.2.5 Electronic Balance

2.2.6 Magnetic stirrer and teflon bars

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### 2.2.7 Solutions

- 1000 ppm Boron Standard – Certified, vendor supplied
- Buffer solution – pH 4.00
- Buffer solution – pH 7.00
- pH probe reference solution

### 2.2.8 pH-mV meter equipped with pH electrode

### 2.2.9 Plastic beaker

### 2.2.10 Potassium Biphthalate (KHP)

### 2.2.11 Reagents

- 0.025 N Sodium Hydroxide Solution
- 0.05 N Sodium Hydroxide Solution
- 0.2 N HCL
- 0.001 N HCL
- 50% W/W Analytical Reagent NaOH
- Mannitol

## 2.3 Definitions

2.3.1 Potassium Biphthalate – Other common chemical names, Potassium Hydrogen Biphthalate (KHP) or Potassium Acid Phthalate (KAP)

2.3.2 W/W – Weight per Weight

## 3. PRECAUTIONS

3.1 The exposure of a specific ion electrode to acidic or alkaline gases, such as HCL or NH<sub>3</sub> from laboratory air, can cause meter drift and error in analysis.

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- 3.2 When preparing a gravimetric standard of boric acid, the boric acid should not be heated. When boric acid is heated, it gradually loses water, changing first to meta boric acid ( $\text{HBO}_2$ ) and finally dehydrating completely to anhydrous oxide ( $\text{B}_2\text{O}_3$ ).
- 3.3 The method stored in the autotitrator must *not* be altered without a Chemistry Supervisor's or designee's approval.

#### 4. INSTRUCTIONS

##### 4.1 Sample Analysis by Autotitrator

##### 4.1.1 START the autotitrator as follows:

- a. IF pH probe is being placed in service, **PERFORM** the following:
  - 1) **REMOVE** protective cap from pH probe filling port.
  - 2) **CHECK** reference solution level.
  - 3) IF reference solution level is below halfway point, **FILL** pH probe with reference solution.
- b. **ENERGIZE** titrator and balance.
- c. **PERFORM** pH probe calibration as follows:
  - 1) **REMOVE** titrant dispensing tip from its holder.
  - 2) **RINSE** pH probe.
  - 3) **IMMERSE** probe in approximately 50 mL pH 4.00 buffer solution.
  - 4) **PRESS** "pH Calib" button ("Buffer A" light will blink).

#### **NOTE**

When "RUN" is pressed, stirrer will start and millivolts will be displayed.  
When millivolts reading is stabilized, "Buffer B" light will blink.

- 5) **PRESS** "RUN."
- 6) WHEN "Buffer B" light blinks, **REMOVE** probe from pH 4.00 buffer and **RINSE** probe.
- 7) **IMMERSE** probe in approximately 50 mL of pH 7.00 buffer solution.

## NOTE

When "RUN" is pressed, stirrer will start. When reading stabilizes the unit will beep and the calibration will display.

- 8) PRESS "RUN."
- 9) WHEN "Buffer B" light goes out AND 3 beeps are heard, REMOVE probe from pH 7.00 buffer.
- 10) RINSE pH probe.
- 11) INSTALL titrator tip in holder.

### 4.1.2 CHECK pH as follows:

- a. IMMERSE probe in approximately 50 mL of sample.
- b. PRESS "3."
- c. PRESS "pH Calib."
- d. WHEN sample pH has stabilized, PRESS "reset."
- e. REMOVE sample and RINSE pH probe.

### 4.1.3 CONDUCT a quality control check as follows:

- a. TARE a clean, dry, plastic beaker.
- b. PRESS "RUN" and WAIT for weight light to blink.
- c. ADD 8 to 12 grams of 1000 ppm Boric acid standard to a clean, dry plastic beaker.
- d. WHEN weight has stabilized, PERFORM the following:
  - 1) PRESS "RUN" to enter sample weight into the autotitrator.
  - 2) WAIT for "BUSY" light to blink.
  - 3) RECORD sample weight on Chem Form 807/2807/3807AA-1.



- e. REMOVE beaker from balance.
- f. ADD 6 to 7 grams mannitol.
- g. FILL to 50 mL with demineralized water.
- h. RINSE probe.
- i. ATTACH sample cup to autotitrator collar.
- j. PRESS "RUN" to start titration.
- k. ADJUST stirring rate to between 4 and 5.
- l. WHEN unit beeps AND displays boron ppm value, RECORD value and initials on Chem Form 807/2807/3807AA-1.
- m. PLOT boron ppm value on Chem Form 807/2807/3807AA-2.
- n. IF Boron Control Chart on Chem Form 807/2807/3807AA-2 is new, ENTER start date.
- o. IF Boron Control Chart on Chem Form 807/2807/3807AA-2 is complete, PERFORM the following:
  - 1) ENTER end date.
  - 2) SUBMIT Chem Form to Chemistry Supervisor or designee.
  - 3) REVIEW data on Chem Form.
  - 4) SIGN "Reviewed By."
  - 5) RECORD title.
- p. RECORD the following data on Chem Form 807/2807/3807AA-1.
  - Sample date
  - Sample time
  - Sample type

Chemistry  
Supervisor or  
Designee

Technician

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- Normality of titrant
  - Dilution factor
- q. IF the concentration of the control is less than 990 ppm OR greater than 1010 ppm, CONSULT Chemistry Supervisor to outline corrective action.
- r. REMOVE sample and RINSE pH probe.

4.1.4 CONDUCT a sample analysis with the autotitrator as follows:

- a. RECORD the following data on Chem Form 807/2807/3807AA-1.
- Sample date
  - Sample time
  - Sample type
  - Normality of titrant
  - Dilution factor
- b. MEASURE sample pH.
- c. IF pH is less than 4.0, ADJUST pH to approximately 5.5 using 0.025 N NaOH.
- d. IF pH is greater than 8.0, ADJUST pH to approximately 5.5 using one of the following:
- 0.001 N HCl
  - 0.2 N HCl
- e. TARE a clean, dry, plastic beaker.
- f. PRESS "RUN" and WAIT for weight light to blink.

### NOTE

For dilute aqueous solutions, 1 gram of solution is equivalent to 1 milliliter of solution.

- g. Refer To Table 1, "Sample Size for Anticipated Boron Concentrations" and ADD an appropriate volume of sample to beaker.

Table 1 – Sample Size for Anticipated Boron Concentrations

Anticipated Sample Concentration, ppm	Sample Size grams
> 3000	0.1 – 1
1500 – 3000	4
500 – 1500	5 – 15
100 – 500	15 – 20
10 – 100	20 – 40
< 10	100

- h. WHEN weight has stabilized, PERFORM the following:
- 1) PRESS "RUN" to enter sample weight into the autotitrator.
  - 2) WAIT for "BUSY" light to blink.
  - 3) RECORD sample weight on Chem Form 807/2807/3807AA-1.
- i. REMOVE beaker from balance.
- j. ADD 6 to 7 grams mannitol.

### NOTE

Samples containing less than 10 ppm boron *do not* require addition of demineralized water.

- k. IF anticipated sample concentration is greater than 10 ppm, FILL to 50 mL with demineralized water.

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- l. RINSE probe.
- m. ATTACH sample cup to autotitrator collar.
- n. PRESS "RUN" to start titration.
- o. ADJUST stirring rate to between 4 and 5.
- p. WHEN unit beeps AND displays boron ppm value, RECORD value and initials on Chem Form 807/2807/3807AA-1.
- q. IF boron needs to be reported in different units, PERFORM the following:
  - 1) Refer To Chem Form 807/2807/3807AA-1, page 2, and CALCULATE boron concentration in units desired.
  - 2) RECORD boron concentration on Chem Form 807/2807/3807AA-1 in "Reported as" column.

#### 4.2 Preparation and Standardization of 0.05 N NaOH Solution for Autotitrator

4.2.1 PREPARE the 0.05 N NaOH titrating solution as follows:

- a. PIPETTE 5.25 mL of 50% W/W Analytical Reagent NaOH into 2 liter volumetric flask.
- b. DILUTE 50% W/W Analytical Reagent NaOH to 2 liters with demineralized water.
- c. STORE solution in collapsible container ("cubitainer").

4.2.2 STANDARDIZE the 0.05 N NaOH titrating solution as follows:

#### NOTE

When drying KHP in oven, do *not* exceed 6 hours of drying time.

- a. DRY KHP in oven for at least 1 hour.

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- b. WHEN KHP has dried, REMOVE KHP from oven and ALLOW to cool in desiccator.
- c. PRESS "MODE" key (The light above "CONC" will light).
- d. ENSURE that 0.2042 is entered as "CONST REAG".
- e. TARE a clean, dry plastic beaker.
- f. In the clean, dry, tared plastic beaker, WEIGH 0.2g of KHP.
- g. To enter the mass of KHP, PRESS "RUN" key twice.
- h. DISSOLVE KHP with 50 mL demineralized water.
- i. ENSURE the KHP is completely dissolved.
- j. RINSE probe.
- k. ATTACH sample cup to autotitrator collar.
- l. To begin titration, PRESS "RUN".
- m. REMOVE sample cup and RINSE probe.

#### NOTE

A new blank should be determined each time NaOH is standardized.

#### 4.2.3 DETERMINE a blank as follows:

- a. ADD 6 to 7 grams of Mannitol to a plastic sample beaker.
- b. DILUTE to 50 mL.
- c. ATTACH sample to sample attachment collar.
- d. PRESS "2" and "RUN" to start stirrer.
- e. ADJUST stirring rate to between 4 and 5.
- f. WHEN Mannitol is completely dissolved, PRESS "RESET."
- g. To light "BLANK" indicator, PRESS "MODE" key twice.

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- h. PRESS "RUN" key twice.
- i. WHEN titration is finished, CHECK that blank is displayed.

4.2.4 IF NaOH has just been prepared OR difficulty is experienced in the analysis of the control standard, PERFORM a control check of the normality of NaOH solution against 1000 ppm boron standard as follows:

- a. RECORD the following data and results on Chem Form 807/2807/3807AA-1.
  - Sample date
  - Sample time
  - Sample type
  - Normality of titrant
  - Dilution factor
- b. TARE a clean, dry, plastic beaker.
- c. PRESS "RUN" and WAIT for weight light to blink.
- d. ADD 10 grams of 1000 ppm boron standard to beaker.
- e. WHEN weight has stabilized, PERFORM the following:
  - 1) PRESS "RUN" to enter sample weight into the autotitrator.
  - 2) WAIT for "BUSY" light to blink.
  - 3) RECORD sample weight on Chem Form 807/2807/3807AA-1.
- f. REMOVE beaker from balance.
- g. ADD 6 to 7 grams mannitol.

## NOTE

Samples containing less than 10 ppm boron *do not* require addition of demineralized water.

- h. IF anticipated sample concentration is greater than 10 ppm, FILL to 50 mL with demineralized water.
  - i. RINSE probe.
  - j. ATTACH sample cup to autotitrator collar.
  - k. PRESS "RUN" to start titration.
  - l. ADJUST stirring rate to between 4 and 5.
  - m. WHEN unit beeps and displays boron ppm value, RECORD value and initials on Chem Form 807/2807/3807AA-1.
- 4.2.5 COMPARE results with actual concentration of Boron standard.
- 4.2.6 IF the concentration of the control is less than 990 ppm OR greater than 1010 ppm, CONSULT Chemistry Supervisor to outline corrective action.

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## 5. REVIEW AND SIGNOFF

- 5.1 The review and signoff for this procedure is located in Chem Form 807/2807/3807AA-1 and -2.

## 6. REFERENCES

- 6.1 Boron In Water, Reactor Plant Chemistry Manual, CE NPD-28.
- 6.2 Operating Instructions, Mettler DL 21 and DL 25 Titrator, Mettler Instruments AG, ME-703175.
- 6.3 CP 800/2800/3800, "Quality Control Program".

## 7. SUMMARY OF CHANGES

- 7.1 The content of this procedure was modified to incorporate new format criteria specified in Revision 0 of the "Millstone Procedure Writer's Guide."

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