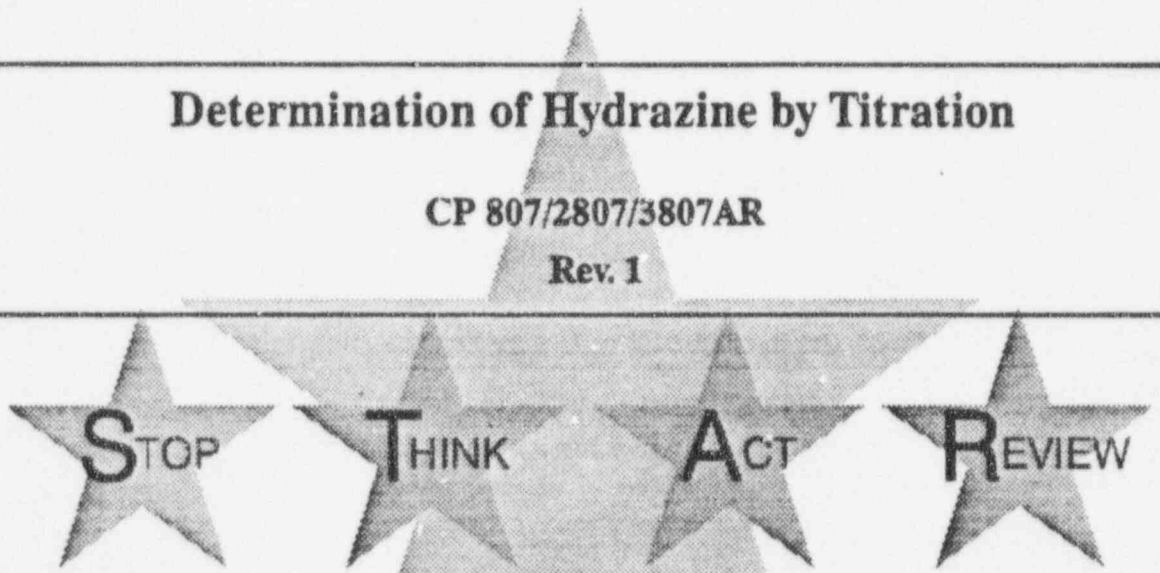
MILLSTONE NUCLEAR POWER STATION
CHEMISTRY PROCEDURE

(ec)

Determination of Hydrazine by Titration

CP 807/2807/3807AR

Rev. 1



Approval: _____
Vice President – Nuclear Operations

SORC Mtg. No: 96-18 Date: 5-1-96

Effective Date: 5-15-96

Level of Use
Information

Subject Matter Expert:
J. Peters

Millstone All Units
Chemistry Procedure

Determination of Hydrazine by Titration

TABLE OF CONTENTS

1. PURPOSE

1.1 Objective

Provide instructions for the analysis of hydrazine in water at concentrations greater than 1 ppm by titration.

1.2 Discussion

Hydrazine is readily oxidized by iodine. In this analysis, a measured aliquot of sample is titrated with a standard iodine solution. When all of the hydrazine is consumed, the excess iodine reacts with the starch to form an intensely colored blue complex, indicating the endpoint of the titration.

2. PREREQUISITES

2.1 General

N/A

2.2 Documents

2.2.1 NUC CHM 01, "Chemistry Quality Control Program"

2.3 Tools and Consumables

2.3.1 Euret, 10.0 mL

2.3.2 Buret, 25.0 mL

2.3.3 Cylinder, graduated 100 mL

2.3.4 Flask, Erlenmeyer 250 mL

2.3.5 Buret clamp

2.3.6 Buret base

2.3.7 Flask, Volumetric 1000 mL

2.3.8 Watch glass

2.3.9 Potassium Iodide (KI)

2.3.10 Sublimed Iodine

2.3.11 Sodium Thiosulfate 5-hydrate ($Na_2S_2O_3 \cdot 5H_2O$)

2.3.12 Sodium Thiosulfate N/40 – vendor supplied

2.3.13 Sodium Bicarbonate – Reagent Grade

2.3.14 Stable Starch solution – vendor supplied

3. PRECAUTIONS

3.1 Other oxidizable materials if present, including ferrous iron, sulfite and sulfide will be titrated, resulting in erroneously high values.

3.2 A watch glass must be used when weighing sublimed iodine to prevent the loss of analyte during transfer from the reaction of iodine with various materials other than glass.

3.3 Samples must be analyzed immediately after collection to prevent the hydrazine from reacting with atmospheric oxygen resulting in erroneously low values.

4. INSTRUCTIONS

4.1 Preparation of Sodium Bicarbonate Solution

4.1.1 DISSOLVE 50.0 grams of reagent grade sodium bicarbonate in 950 mL of demineralized water.

4.1.2 Refer To NUC CHM 01, "Chemistry Quality Control Program," and LABEL bottle.

4.2 Preparation of Iodine Titrating Solution

4.2.1 In a 500 mL volumetric flask, DISSOLVE 20.0 grams of potassium iodide in 50 mL of demineralizer water.

4.2.2 ADD 1.60 grams of sublimed iodine to volumetric flask containing potassium iodide solution.

4.2.3 MIX solution until iodine is completely dissolved.

4.2.4 DILUTE to 500 mL with demineralized water and MIX solution thoroughly.

4.2.5 TRANSFER iodine titrating solution to a bottle.

4.2.6 LABEL bottle with a 1 month expiration date.

4.3 Preparation of Sodium Thiosulfate Solution

4.3.1 In a 1 liter volumetric flask, DISSOLVE 6.20 grams of reagent grade soidum thiosulfate in approximately 500 mls of demineralized water.

4.3.2 DILUTE to 1 liter with demineralized water and MIX solution thoroughly.

4.3.3 TRANSFER solution to an amber bottle.

4.3.4 Refer To NUC CHM 01, "Chemistry Quality Control Program," and LABEL bottle.

4.4 **Weekly Standardization of Iodine Titrant**

4.4.1 ADD the following solutions to a 250 mL Erlenmeyer flask:

- 10.0 mL of sodium thiosulfate solution

OR

10.0 mL of sodium thiosulfate N/40 solution

- 2.0 mL of vendor supplied stable starch solution
- 90 mL of demineralized water

4.4.2 MIX solution thoroughly,

NOTE

When color of the sample remains blue and does not fade with swirling, the titration should be stopped, the end point has been reached.

4.4.3 SWIRL flask and TITRATE with the iodine titrating solution until a blue color end point is obtained.

4.4.4 READ the mL of iodine solution required to reach the end point from the burette.

4.4.5 RECORD the following information on Chem Form 807/2807/3807AR-2:

- Date
- Time
- mL of titrant for standardization
- Week ending date
- Technician initials

4.5 **Sample Analysis**

4.5.1 ADD the following solutions to a 250 mL Erlenmeyer flask.

- 100 mL of sample
- 2.0 mL of vendor supplied stable starch solution
- 5 mL of sodium bicarbonate solution

NOTE

When color of the sample remains blue and does not fade with swirling, the titration should be stopped, the end point has been reached.

4.5.2 SWIRL flask and TITRATE with the iodine titrating solution until a blue color end point is obtained.

4.5.3 READ the mL of iodine solution required to reach the end point from the burette.

4.5.4 CALCULATE the ppm hydrazine as follows:

$$\text{PPM hydrazine} = \frac{20\,(\text{mL of titrant} - 0.1\ \text{mL})\,D}{A}$$

D = Dilution Factor = 100/number of mL of sample used in dilution.

A = number of mL required for weekly standardization (Chem Form 807/2807/3807AR-2).

4.5.5 RECORD the following information on Chem Form 807/2807/3807AR−1:

- Date
- Time
- Sample point
- mL of titrant for sample
- Dilution factor
- ppm Hydrazine
- Technician initials

5. REVIEW AND SIGNOFF

5.1 The review and signoff for this procedure is located on:

5.1.1 Chem Form 807/2807/3807AR-1, "Hydrazine Titration Log"

5.1.2 Chem Form 807/2807/3807AR-2, "Weekly Iodine Titrating Solution Standardization Log"

6. REFERENCES

6.1 Calgon Corporation, "Determination of Hydrazine in Boiler Water (Direct Iodine Titration Method)," Test No. 35-166-C, March 1989

6.2 NUC CHM 01, "Chemistry Quality Control Program," Rev. 0

7. SUMMARY OF CHANGES

7.1 The content of this procedure was modified to incorporate new format criteria specified in Revision 1 of DC-2, "Developing and Revising Millstone Procedures and Forms."

7.2 Incorporated a hydrazine titration log sheet.

7.3 Incorporated an iodine tritrant weekly standardization log sheet.

CALGON CORPORATION
SUBSIDIARY OF MERCK & CO., INC.

WATER MANAGEMENT DIVISION

ANALYTICAL PROCEDURES

DETERMINATION OF HYDRAZINE IN BOILER WATER

(Direct Iodine Titration Method)

SUMMARY OF METHOD

Hydrazine is readily oxidized by iodine. In this test, a measured aliquot of sample is titrated with a standard iodine solution. When all of the hydrazine is consumed, the excess iodine reacts with starch to form an intensely colored blue complex, indicating the endpoint of the titration. The test, which is applicable to waters containing more than 1 mg/L N_2H_4, must be performed immediately after sampling for results to be meaningful. For measurement of hydrazine concentrations below 1 mg/L, refer to test No. 35-241.

SAMPLING REQUIREMENTS

Cool the sample upon collection to 70°F or lower and analyze immediately after collection. Hydrazine tends to react with oxygen in the atmosphere and delay of analysis may result in erroneously low values.

INTERFERENCES

The test is not specific to hydrazine but will measure a variety of oxidizable compounds. Certain organic compounds, ferrous iron, sulfite and sulfide are positive interferences.

ORDERING REAGENTS AND EQUIPMENT

Reagents, certified by Calgon Corporation, and equipment items are obtainable from Calgon Corporation, Pittsburgh, Pennsylvania. When ordering, include description and catalog number.

Description	*Unit Size*	*Catalog No.*
N/40 Thiosulfate Solution	qt	R5095
Stable Starch Solution	pt	R5096
Clamp for Buret, Single	Each	E1029
Cylinder, Graduated (Glass)	100 mL	E1038
or		or
Cylinder, Graduated (Plastic)	100 mL	E1351
Dish, Porcelain	250 mL	E1042
Flask, Erlenmeyer	250 mL	E1050
Graduate, Conical	10 mL	E1057
Stirring Rod, glass	6 in.	E1089
Support, Rectangular Base	Medium	E1094
Buret, Geissler	25 mL	E1186
Buret, Geissler	10 mL	E1434
Sodium Bicarbonate Solution*		N.A.
Standard Iodine Solution*		N.A.
Flask, Volumetric	1000 mL	N.A.

**See Reagents section for information on preparation of these solutions.*
N.A. — Not Available

PROCEDURE

Standardization of Iodine Solution

Add 90 mL of distilled water and 2 mL of Stable Starch Solution to 10 mL of N/40 Thiosulfate Solution in a porcelain dish. Titrate with iodine to the blue starch color. The net volume of iodine required for the titration should be approximately 20 mL. Adjustment of the reagent is not necessary if compensation is made in the calculation. Since this solution is not stable, only an amount sufficient to last a month should be made at one time. Standardize daily.

Sample Analysis

1. To a 250 mL Erlenmeyer flask, add about 2 mL of Stable Starch Solution and 5 mL of Sodium Bicarbonate Solution.

(Procedure Continued)

2. Measure 100 mL of the decanted boiler water sample in a 100 mL graduated cylinder and pour into the 250 mL flask.
3. Slowly add Standard Iodine Solution from a buret, while constantly shaking the sample. Stop the titration when a blue color, which is not removed by further stirring, first appears. From the buret read the mL of Iodine Solution used.
4. The blank on this titration is about 0.1 mL. Calculate the hydrazine concentration in the following manner.

$$\text{mg/L Hydrazine } (N_2H_4) = (\text{mL titration} - 0.1\text{ mL}) \times \frac{20}{A}$$

where A = actual mL of Iodine Solution required to titrate 10 mL of N/40 Thiosulfate Solution.

Reagents

Sodium Bicarbonate Solution — Dissolve 50 grams of reagent grade sodium bicarbonate ($NaHCO_3$) in 950 mL of distilled water.

Standard Iodine Solution — Dissolve 20 grams of reagent grade potassium iodide crystals in *as little water as possible*. Weigh on a watch glass 1.6 grams of iodine crystals then add the iodine crystals to the solution. Shake or stir the contents until all of the iodine is dissolved. Dilute to 1 liter.

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Determination of Hydrazine in Boiler Water (Direct Iodine Titration Method) Test No. 35-166-C