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HAL B. Tucker Vice President Nuclear Production (7/4)373-4531



DUKE POWER

September 20, 1988

Document Control Desk U. S. Nuclear Regulatory Commission Washington, D.C. 20555

Subject: Catawba Nuclear Station Docket Nos. 50-413 and 50-414 Environment 1 Protection Plan NPDES Permit

Pursuant to the Catawba Nuclear Station Environmental Protection Plan and NPDES permit, please finds attached the Catawba 316(a) Demonstration. Additionally, please find attached correspondence between Duke Power Company and the South Carolina Department of Health and Environmental Control regarding a modification to the facility NPDES permit.

Very truly yours,

Hal B. Turter you

H. B. Tucker

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Attachments

xc: (with attachment) Dr. J. Nelson Grace Regional Administrator, Region II U. S. Nuclear Regulatory Commission 101 Marietta Street, NW, Suite 2900 Atlanta, Georgia 30323

> W. T. Orders NRC Resident Inspector Catawba Nuclear Station

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DUKE POWER COMPANY PO. BOX 33189 CHARLOTTE. N.C. 28242

WILLIAM A. HALLER MANAGER NUCLEAR TECHNICAL SERVICES 17041 373 8500

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July 18, 1968

Ms. Nancy Weatherup South Carolina Department of Health and Environmental Control Industrial and Agricultural Wastewater Division 2600 Bull Street Columbia, South Carolina 29201

SUBJECT: Catawba Nuclear Station NPDES Permit Modification File: CN-702.13

Regarding your letter dated May 31, 1988, we concur with your recommendation to modify Catawba Nuclear Station's existing NPDES Permit to include effluent limits for Hydrazine and Ethylene Glycol. We have reviewed the draft modifications along with the supporting rationale which you provided. Listed below, please find our comments and suggestions as they pertain to the proposed modification. The changes we have suggested are aimed at structvring the permit language to, (1) assure that our discharge is effectively monitored so as not to impact receiving waters, and (2) provide additional clarification for the requirements in the permit.

RATIONALE

Section 4.8.5. - There is a mistake in the calculation of the Daily Average Limit for Ethylene Glycol (Outfall 002). The correct value should be 11.9 mg/l.

OUTFALL 002

A. Hydrazine

We recommend that the monitoring frequency for hydrazine be reduced to once/occurrence.

Ms. Nancy Weatherup July 18, 1988 Page Two

B. Ethylene Glycol

We recommend that the monitoring frequency for ethylene glycol be reduced to once/occurrence.

Note: Justification for changing the monitoring frequency of this Outfall to "once/occurrence" is because the waste treatment system is released on a batch basis and is homogeneous prior to release. Once/occurrence monitoring will be representative of the entire discharge.

OUTFALL 004

A. Hydrazine

We recommend that the monitoring frequency for hydrazine be reduced to once/occurrence.

B. Ethylene Glycol

The presence of Ethylene Glycol in this system is expected to be very infrequent. We therefore recommend that there be no specific effluent limitations assigned to ethylene glycol for Outfall 004. Instead, we suggest that similar language be used here as was user for the hydrazine (ie: record results and if value is great than 23.8 mg/l, then this permit may be modified to prolimitations on glycol). Furthermore, we suggest that monito frequency for ethylene glycol be reduced to once/occurrence.

Note: Justification for changing the monitoring for this Outfall to once/occurrence is based on the fact that the Radwaste system discharge tank is homogeneous prior to discharge. Once/occurrence monitoring would be representative of the entire discharge.

For convenience of understanding, we have attached copies of affected pages of the NPDES permit incorporating our recommendations. Please note, for better clarification we have suggested that some of the language from the Rationale be included in Part III (page 24 of 24) of the permit.

Attached also, for your review and approval, are the analytical procedures which we intend to use to comply with effluent limitations once they are finalized. The source from which these procedures were obtained, is referenced in Section 5.0 of each procedure.

Ms. Nancy Weatherup July 18, 1988 Page Three

We appreciate the opportunity to comment on this draft of the permit modification. Please review these comments at your earliest convenience. Once you've had an opportunity to perform the review, we would like to meet with you do discuss the specifics of our comments in greater detail. In the mean time, should you have any questions, please contact Mitch Griggs at 704-373-7080. Your attention to this matter is greatly appreciated.

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W.A. Haller, Manager Nuclear Technical Services

MCG/28/rhm

Attachment

xc: Al Williams, Catawba District

bc: T.B. Owen R.H. Charest S.W. Rogers R.L. Painter C.L. Therrien S. Biswas R.F. Wardell M.L. Birch R.W. Eaker R.W. Ouellette

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J.E. Lansche G.S. Rice R.M. Glover R.R. Wylie M.B. Baron, Jr. R.E. Baker Staff CN-3000.02-01 CN-3000.02-02 MODIFICATION DATE

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A. EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

During the period beginning on the effective date and lasting through the expiration date the pennittee is authorized to discharge from outfall(s) serial number(s)002, wastewater treatment system discharged Lake Wylie (Low volume wastes, chemical metal cleaning Such discharge shall be limited and monitored by the permittee as specified below: waste (#005).

Effluent Characteristics	Discharge Limitations Other Units (Specify)		Monitoring Requirements	
	Daily Avg.	Daily Max.	Measurement Frequency	Sample Type
Flow-m ³ /day (MGD)		-	1/week	Flow Indicator
011 and Grease	15 mg/l	20 mg/1	2/month	Grab
Total Suspended Solids	30 mg/l	100 mg/1	2/month	Grab
liverazine		.43 mg/1	*1/securrence	Grab
Ethylene Glycol	11.9mg/1	23.809/1	*1/occurrence	Grab

"Measurement frequency is once per occurrence, but need not be more than twice per month.

The radiological components of this discharge is regulated by the United States Nuclear Regulatory Commission (NRC 10 CFR 50 Appendix 1) and is monitored and reported to the NRC.

Based on a design flow of 3.4 MGD.

The pH shall not be less than 6.0 standard units nor greater than 9.0 standard units and shall be monitored: once per week by grab sample.

There shall be no discharge of floating solids or visible foam in other than trace amounts.

Samples taken in compliance with the monitoring requirements specified above shall be taken at the following location(s): discharge from the wastewater treatment system prior to mixing with any other waste streams.

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Bureau of Water Pollution Control

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A. EFFLUENT LIMITATIONS AND BOULTORING REQUIREMENTS

During the period beginning on the effective date and fasting through the expiration date the permittee is authorized to discharge from outfall(s) serial number(s)004: Radwaste System Discharge

Such discharge shall be limited and monitored by the permittee as specified below:

Effluent Characteristics	Discharge Limitations Other Units (Specify)		Monitoring Requirements	
CTTTUCKE STATE			the second second	Samla
	Bonthly Avg.	Dally Max.	frequency	Туре
011 and Grease	15 mg/1	20 mg/1	1/ year	Grab
Total Suspended Solids	30 mg/l	100 mg/1	./ year	Grab
A			1/quarter	30 Day Composite
Boron Nydrazine Ethylene Glycol			**1/accurrence	Grab
			**1/occurrence	Grab

This discharge is regulated by the United States Nuclear Regulatory Commission (NRC 10 CFR 50 Appendix 1) and is monitored and reported to the NRC. However, in the event that chemical metals cleaning wastes as defined in 40 CFR Part 423 are discharged through this serial number, treatment shall be provided to assure that discharges are in compliance with requirements of Part 423.13.

Based on a Design of .140 MGD. Samples taken in compliance with the monitoring requirements specified above shall be taken at the following location(s): Wastewater treatment system prior to mixing with any other waste stream. Boron shall be sampled from the radiological sample location.

PART 111 Page 24 of 24 Permit No. SC0004278

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- U. A monitoring program will be implemented to determine downstream concentrations of <u>boron</u>. A downstream sample shall be collected at the radiological sample location and analyzed for boron once per quarter. If there is no significant impact on water quality after 5 years of data collection, the monitoring requirement will be eliminated.
- V. Monitoring of the rad waste discharge for oil and grease and total suspended solids will be implemented for one year. If shown that the above parameters are not in significant amounts in the rad wastewater the monitoring requirement will be eliminated.
- W. Duke will perform a 316(a) study to assess any measurable thermal effects on the biota of Lake Wylie. The first year pre-operational data was collected by a consultant, Industrial Biotest, Inc. Duke implemented the second year of pre-operational data collection in May, 1983 and will continue through May, 1984. The operational impact, assessment phase of the study will be similar to the second year pre-operational phase with only minor changes made if the results indicate modifications are necessary. The plan and any significant change must be approved by Department of Health and Environmental Control. The operational phase will commence when Unit 1 reaches 50% power and will continue for one year. Another second year of ata collection will be initiated when Unit 2 reaches 50% power. A report will be submitted to DHEC upon completion of each one-year operational phase study.
 - X. The rad waste discharge will be required to be monitored and results reported of the discharge concentration for Hydrazine (Part I Page 7 of 24). If values are greater than 15 mg/l, this permit may be modified to provide Hydrazine limitations and/or biological monitoring. Reporting requirements, pursuant to Section 402 of the Clean Water Act (Regulation 40 CFR 117), Section 102 of CERCLA (Regulation 40 CFR 302), and Section 302 of SARA Title III (Regulation 40 CFR 355), for an exceedence of the applicable reportable quantity for Hydrazine, will be initiated if the discharge concentration of Hydrazine exceeds 15.0 mg/l, and the reportable quantity has been exceeded.
 - Y. The radwaste discharge will be required to be monitored and results reported of the discharge concentration for Ethylene Glycol (Part I Page 7 of 24). If values are greater than 23.8 mg/l, this permit may be modified to provide Ethylene Glycol limitations.

CP/0/B/8500/09 Revision 1

DUKE POWER COMPANY CATAWBA NUCLEAR STATION CHEMISTRY PROCEDURE FOR THE DETERMINATION OF HYDRAZINE IN WASTE WATER

1.0 DISCUSSION

1.1 Scope

This procedure describes the colorimetric method for the determination of hydrazine in waste water.

1.2 Principle

Para-dimethylaminobenzaldehyde produces a specific yellow reaction with bydrazine as shown:





para-dimethylaminobenzaldehyde azine (yellow)

The intensity of the yellow color is proportional to the amount of hydrazine in the sample within the specified concentration range.

1.3 Limits

Sample concentration should be between 0.005 and 0.25 ppm bydrazine. Higher concentrations must be proportionally diluted prior to analysis. The lower limit of detectable bydrazine is 0.005 ppm.

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- 1.4 Precision and Accuracy
 - 1.4.1 The precision and accuracy of this method will be determined by Q-Sum data.
 - 1.4.2 A new calibration curve should be generated at least once a year.
- 1.5 Interferences
 - 1.5.1 Hydrazine content may be diminished by oxidizing agents.
 - 1.5.2 Turbidity may cause high results. If turbidity is a problem, filter the sample through a .45µm membrane filter prior to analyzing.
 - 1.5.3 Coloration in a sample may interfere with the quantitative determination of hydrazine.
- 1.6 Precautions
 - 1.6.1 Labcoat, eye and hand protection shall be worn when working with para-dimethylaminobenzaldehyde or hydrochloric acid (HCL).
 - 1.6.2 Hydrazine is a skiu irritant and a potential skin sensitizer; therefore, precautions must be taken to avoid skin contact. Lab coat, hand and eye protection will be worn when working with hydrazine dihydrochloride and hydrazine containing solutions and samples. If skin contact occurs, wash the affected area immediately with soap and water.
 - 1.6.3 The light path surfaces of cuvettes should be buffed with a lint free tissue such as "Kimwipes" prior to being placed into the spectrophotometer.
 - 1.6.4 If matched cuvettes are not available, correct the sample absorbance by subtracting the absorbance caused by the cuvette.

2.0 AFPARATUS

- 2.1 Spectrophotometer, with wavelength set at 458 nm. Allow spectrophotometer to warm up for 30 minutes before use.
- 2.2 Erlenmeyer flasks
- 2.3 Graduated cylinder
- 2.4 Eppendorf pipets with required tips
- 2.5 Pipet dispenser
- 2.6 Balance
- 2.7 Two matched 1.0 cm cuvettes

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3.0 REAGENTS

3.1 Hydrazine Stock Solution (100 ppm)

Dissolve 0.3280 \pm 0.0005 grams of hydrazine dibydrochloride (N_H_ . 2HCl) in a 1000 ml volumetric flask with demineralized water. Add 10 \pm 0.5 ml of concentrated HCl, then dilute this solution to volume with demineralized water and mix. Shelf life is 6 months.

3.2 Hydrazine Reagent (PAB)

Dissolve 16.0 ± 0.1 grams para-dimethylaminobenzaldehyde in 800 ± 10 ml of methyl alcohol and 80 ± 0.5 ml of concentrated HCL. Store in an amber bottle. This solution is stable indefinitely.

3.3 Hydrochloric Acid Solution (1% V/V)

In a volumetric flask, dilute 10 \pm 0.5 ml concentrated HCl to 1 liter with demineralized water. This solution is stable indefinitely.

4.0 PROCEDURE

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- 4.1 Generation of Calibration Curve
 - NOTE: Generation of a new calibration curve is not required if this procedure is in current use; however, a new calibration curve should be generated at least once a year. Two (2) .050 ppm Q-sum standards should be run daily when using this procedure.
 - 4.1.1 Prepare a series of hydrazine standards by diluting suitable volumes of hydrazine stock solution (Section 3.1) with 1% V/V HCl (Section 3.3) in 100 ml volumetric flasks to produce solutions of the desired concentrations as follows:

pl of 100 ppm stock solution diluted to 100 ml = ppm N,H,

10	µ1	0.010	ppm
50	HI	0.050	ppm
00	μ1 μ1	0.100	ppm

- 4.1.2 Transfer 50 ml of each standard and a demineralized water blank into separate Erlenmeyer flasks.
- 4.1.3 Add 5.0 ± 0.5 ml of para-dimethylaminobenzaldehyde solution (Section 3.2) to each flask. Mix by swirling the flasks. Lot the mixture stand 10 minutes, but not more than 100 minutes.
- 4.1.4 Adjust the spectrophotometer to the 458 nm wavelength.
- 4.1.5 Place the reagent blank in the spectrophotometer in a clean 1.0 cm cuvette.

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- 4.1.6 Set zero absorbance.
- 4.1.7 Transfer the standards into the 1.0 cm cuvette in appropriate order and read the absorbance on the spectrophotometer checking the zero with the reagent blank before each measurement. Standard concentration measurements are to be made in order of increasing concentration. Rinse the cuvette with the subsequent sample before each measurement.
- 4.1.8 Prepare a calibration curve by plotting the absorbance vs concentration on a piece of graph paper. Indicate on the graph the date generated, analysis name, procedure number and spectrophotometer instrument number. This graph is particular to the instrument it was generated on.

4.2 Determination of Unknown Concentrations

- CAUTION: If the analysis is of a sample with turbidity and/or coloration that might interfere with the analysis (RL, WC, and etc.), analyze a second portion of the sample with no PAB added. Subtract the absorbance valve obtained from this sample with no PAB from the absorbance valve obtained from the sample with PAB added.
- 4.2.1 Prepare two (2) .050 ppm standards for Q-Sum by diluting 50 µl of the 100 ppm hydrazine standard (Section 3.1) to 100 ml with 1% HCl (Section 3.3) in a volumetric flask. Measure 50 ml of the .050 ppm bydrazine standard into two (2) separate Erlenmeyer flasks. (To be done once per day when procedure is in use.)
- 4.2.2 Transfer 50 ml of each unknown sample and a demineralized water blank into separate Erlenmeyer flasks.
- 4.2.3 Add 5.0 ± 0.5 ml of para-dimethylaminobenzaldebyde solution (Section 3.2) to each flask. Mix by swirling the flasks. Let the mixture stand for 10 minutes, but not more than 100 minutes.
- 4.2.4 Adjust the spectrophotometer to 458 nm. wavelength.
- 4.2:5 Place the reagent blank in the spectrophotometer in a 1.0 cm cuvette.
- 4.2.6 Set zero absorbance.
- 4.2.7 Transfer the unknown sample or standard into a 1.0 cm cuvette. Read the absorbance.
- 4.2.8 Determine the hydrazine concentration of the sample by comparing the sample absorbance to the calibration curve.

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5.0 REFERENCES

5.1 American Society for Testing and Materials, 1987 Annual Book of ASTM Standards, D 1385-86, Page 514-517.

6.0 ENCLOSURES

None

DUKE POWER COMPANY CATAWBA NUCLEAR STATION CHEMISTRY PROCEDURE FOR THE DETERMINATION OF ETHYLENE GLYCOL CP/0/B/8500/29

1.0 DISCUSSION

1.1 Scope

This procedure describes the colorimetric determination of Ethylene Glycol in small concentrations.

1.2 Principle

Ethylene Glycol is reacted with Sodium meta-Periodate to yield formaldehyde:

HOCH2CH2OH + NaIO4 + 2CH2O + NaIO3+H2O

The formaldehyde is then determined colorimetrically.

1.3 Limits

This method is applicable to samples having a concentration of 1 to 7500 ppm. Samples containing higher concentrations must be diluted accordingly.

1.4 Precision and Accuracy

Precision and Accuracy will be determined by Q-Sum data.

- 1.5 Interferences
 - 1.5.1 Some waters purified by ion exchange techniques cannot be used because of the presence of minute particles of resin that might react to form formaldehyde. Demineralized water has not been found to cause this problem and should be used for this analysis.
 - 1.5.2 Turbid samples will interfere. All samples shall be - filtered before analysis.
- 1.6 Precautions
 - 1.6.1 Eye protection, gloves and labcoat should be worn when performing analysis.
 - 1.6.2 Concentrated Sulfuric Acid is very corrosive. Extreme care should be exercised when working with this chemical. Follow precautions given in CP/0/B/8300/09.



2.0 APPARATUS

- 2.1 Spectrophotometer
- 2.2 1.0 cm cuvettes
- 2.3 Eppendorfs 200, 400, 600, 800 and 1000 µ£
- 2.4 Pipets 10 ml disposable
- 2.5 Automatic dispensers 2ml
- 2.6 Glass stoppered graduated cylinders 50 and 100 ml
- 2.7 Volumetric flasks 50, 200 and 1000 ml
- 2.8 Clamp or holder for Nitrogen cylinder
- 2.9 Bubbling Apparatus
- 2.10 ... crogen Regulator
- 2.11 Analytical Balance

3.0 REAGENTS

- 3.1 Sodium Chromotropate (Sodium 1, 8 dihydroxy napthalene 3, 6 disulfonate) C10H70sS2 · Na · Reagent Grade.
- 3.2 Concentrated Sulfuric Acid (H2SO4)
- 3.3 Sodium Sulfite (Na2SO3) 5.5%

Dissolve 11.0 \pm .5 grams of Sodium Sulfite (Na₂SO₃) into a 200 ml volumetric flask, dilute to volume with demineralized water and mix. Shelf life is one week.

3.4 Sodium meta-Periodate (NaIO.) 0.1M

Dissolve 21.0 2.5 grams of Sodium meta-Periodate (NaIO₄) into a 1000 ml volumetric flask, dilute to volume with demineralized water and mix. Shelf life is six months.

3.5 Ethylene Glycol (HOCK2CH2OK) Stock Solution (100 ppm)

Dissolve .500 \pm .005 g of Ethylene Glycol into a 50 ml volumetric flask, dilute to volume with demineralized water and mix. Pipet 10 mls of this solution and transfer it to a 1000 ml volumetric flask, dilute to volume with demineralized water and mix. This solution should be made daily.





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3.5 Demineralized Water



- 3.7 Nitrogen
- 4.0 Procedure
 - 4.1 Generation of Standard Curve

Generation of a standard curve is not required if method is currently in use; however, a new standard curve should be generated at least once a year. Two (2) 1.0 ppm Q-Sum standards should be run daily when procedure is in use.

4.1.1 Prepare a series of standards by diluting suitable volumes of Ethylene Glycol solution to 20 mls with demineralized water in a 100 ml glass stoppered graduated cylinder. Include a graduated cylinder with 20 mls of demineralized water to be used as a blank.

Mls	of Ethylene	f Ethylene Glycol Solution		Concentration	
		.2 .4 .8 1.2 1.6 2.0		1.0 2.0 4.0 6.0 8.0 10.0	ppa ppa ppa

- 4.1.2 Dispense 2.0 ± .1 ml of Sodium meta-Periodate solution into each 100 ml glass stoppered graduate, stopper and mix. Allow to react for 15 minutes at room temporature.
- 4.1.3 Dispense 2.0 ± .1 ml of Sodium Sulfite solution to each graduate, dilute to volume, stopper and mix.
- 4.1.4 Pipet 10.0 mls of each of the above dilutions into 50 ml glass stoppered graduates.
- 4.1.5 Add approximately 0.06 gms of Sodium Chromotropate to each graduate and dissolve.
- 4.1.6 CAUTION: Extreme care should be taken when handling acids.

Add 10 mls of concentrated Sulfuric Acid by means of a pipet and allow the normal heat rise to occur.

4.1.7 By means of the bubbling apparatus immersed in the solution, bubble vigorously with Nitrogen for 10 minutes. Allow the contents of each graduate to cool to room temperature.

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- 1.8 Adjust the spectrophotometer to a wavelength of 570 nm.
- 4.1.9 Place the blank in the spectrophotometer in a clean 1.0 cm cuvette.
- 4.1.10 Set the "zero" absorbance.
- 4.1.11 Read the absorbance of the standards, in order of increasing concentration. Rinse the cuvette with each subsequent standard before each measurement. Recheck "zero" absorbance with the blank before each standard.
- 4.1.12 Frepare a standard curve by plotting absorbance vs ppm Ethylene Glycol.
- 4.2 Determination of Unknown Concentrations
 - 4.2.1 Prepare two (2) 1.0 ppm standards for Q-Sum by diluting .2 mls of Ethylene Glycol solution to 20 mls with demineralized water in a 100 ml glass stoppered graduated cylinder. (To be done once per day when procedure is in use).
 - 4.2.2 Into a glass stoppered graduated cylinder introduce the amount of sample indicated in the table below, diluting to 20 mls with demineralized water, if necessary.

Concentration, ppm	Sample Size, mls
1-35	20.0
35-75	10.0
75-150	5.0
150-750	1.0
750-7500	0.1

For concentrations of Ethylene Glycol greater than 7500 ppm (.75%) use a suitable dilution of the sample in demineralized water. Include one graduated cylinder containing 20 ml of demineralized water for a blank.

- 4.2.3 Dispense 2.0 ± 1 ml of 0.1 M Sodium meta-Periodate solution each graduate, stopper and mix, allow to react for 15 minutes room temperature.
- 4.2.4 Dispense 2.0 ± .1 mls of Sodium Sulfite solution to each graduate, dilute to the 100 ml mark with demineralized water, stopper and mix.
- 4.2.5 Pipet 10 mls of each unknown sample or standard into a 50 ml glass stoppered graduated cylinder.
- 4.2.6 Add approximately .06 gms of Sodium Chromotropate to each graduate and dissolve.

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4.2.7 CATTION: Extreme care should be taken when handling acid.

Add 10 mls of concentrated Sulfuric Acid by means of a pipet and allow the normal heat rise to occur.

- 4.2.8 By means of the bubbling apparatus immersed in the solution, bubble vigorously with Nitrogen for 10 minutes. Allow the contents of each graduate to cool to room temperature.
- 4.2.9 Adjust spectrophotometer to a wavelength of 570 nm.
- 4.2.10 Place the blank in a clean 1.0 cm cuvette.
- 4.2.11 Set the "zero" absorbance.
- 4.2.12 Read the absorbance of the standards, in order of increasing concentration. Rinse the cuvette with each subsequent sample before each measurement. Recheck "zero" absorbance with the blank before each sample.
- 4.2.13 Determine the Ethylene Glycol concentration by comparing the sample absorbance to the standard curve.

5.0 REFERENCES

5.1 Union Carbide, Technical So vice Bulletin - Ethylene Glycol, Colorimetric Determination of Low Concentrations by the Sodium Periodate Procedure.

6.0 ENCLOSURES

6.1 Bubbling Apparatus





