NUS CORPORATION
CYRUS WM. RICE DIVISION

GENERAL OFFICES:
MANOR OAK TWO
1910 COCHRAN ROAD
PITTSBURGH, PA. 15220
412-343-9200

R-27-10-0-2

FINAL REPORT

ANALYSES FOR DISSOLVED HYDROGEN, DISSOLVED OXYGEN, BORON, CHLORIDE, pH, AND CONDUCTIVITY UNDER NORMAL AND POST-ACCIDENT CONDITIONS

PREPARED FOR

COMMONWEALTH EDISON COMPANY
CHICAGO, ILLINOIS

SUBMITTED BY

P. J. BATTAGLIA
W. LECHNICK
J. R. RIDDLE
R. C. RICE

CLIENT NO. 3620.01

OCTOBER 1980

TABLE OF CONTENTS

III. AUTOMATED ANALYSIS SYSTEM

TABLE OF CONTENTS (CONTINUED)

APPENDICES

LIST OF TABLES

LIST OF TABLES (CONTINUED)

LIST OF TABLES (CONTINUED)

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

I. EXECUTIVE SUMMARY AND RECOMMENDATIONS

A. EXECUTIVE SUMMARY

An analysis system has been developed to provide for in-line analysis of boron, chloride, dissolved hydrogen, dissolved oxygen, pH and conductivity. The system can be operated during regular or post-accident conditions. Analytical procedures have also been developed to provide for boron analyses under post-accident conditions. The boron analyses will be performed in a hood with samples that have been diluted by about a factor of 1000 in the liquid sample panel. All the analyses listed above can be performed within one hour after sampling during post-accident conditions. Cumulative radiation exposure involved to perform the analyses listed above at one hour after core damage occurs is estimated to be less than 1 rem. This recommendation applies to both normal and post-accident conditions.

B. RECOMMENDATIONS

1. Boron Analyses

The boron concentration should be determined in-line, with the DigiChem analyzer described in Section IV of this report. Plant qualification testing is required before the recommendation is implemented. For interim post-accident conditions, the boron concentration should be determined on a diluted sample using the fluoroborate selective ion electrode. The uncertainty factor associated with analyzing a solution containing 2 ppm boron using this procedure is about (+13, -3.3 percent). Analysis time is less than one hour. A colorimetric method utilizing curcumin is recommended as a alternate backup method for boron analysis during post-accident conditions. This method has an uncertainty factor of about ±13 percent, with a total analyses time of two hours.

2. Dissolved Hydrogen Concentration Determination

Hydrogen analyses during both normal and post-accident conditions should be performed with the in-line analysis system shown in Figure III-2. A 30 ml primary coolant sample is stripped with argon gas to yield an end volume of 600 cc of gas at STP conditions. The resulting gas mixture is hard piped to a gas chromatograph to determine hydrogen concentration. This hydrogen concentration is, of course, directly relatable to dissolved hydrogen concentration in the primary coolant.

3. Chloride Analyses

The chloride analyses should be performed with a Dionex ion chromatograph under both normal and accident conditions, using the automated system shown in Figure III-1. The ion chromatograph has the capability to analyze chlorides in the range of 100 ppb to 20 ppm with virtually no radiation exposure to operating personnel. A chloride determination can be made within one hour after sampling under accident conditions.

4. Dissolved Oxygen Analyses

Under accident conditions, dissolved oxygen analyses should be performed with the YSI oxygen analyzer incorporated into the system shown in Figure III-1. This system has the capability to determine dissolved oxygen in the range of 0.1 ppm to 20 ppm. All operations can be performed remotely on the recommended system; consequently, there is minimal radiation exposure associated with its use. An oxygen determination can be performed within one hour after sampling under accident conditions. Continuous monitoring of dissolved oxygen is also possible.

For routine operations, oxygen analysis should be performed with the Rexnord analyzer. This instrument is not used during accident conditions because of the large liquid volume contained within the probe and the slow response times involved in monitoring low level oxygen concentrations. Dual analysis capabilities are included to provide for low oxygen monitoring. The low level sensitivity range for the Rexnord oxygen analyzer is 0-20 ppb.

5. pH and Conductivity

The pH and conductivity measurements should be performed using in-line flow cells under both normal and post-accident conditions. Both measurements can be obtained within one hour after sampling under accident conditions. The system recommended here can be operated continuously or intermittently. The pH and conductivity probes used in the system shown in Figure III-1 are standard commercial designs. The probe holders have been designed to reduce total liquid volumes to 3-4 ml for each probe to minimize shielding requirements. There will be little or no radiation exposure involved in determining pH and conductivity under accident conditions.

II. INTRODUCTION

A. GENERAL

The NUS Corporation in cooperation with William Nestel and Tom Lehmann of Commonwealth Edison and under contract to Commonwealth Edison has designed the system described in this report to provide for improved post-accident analyses capability. The findings of the Nuclear Regulatory Commission's TMI-2 Lessons Learned Task Force have been taken into consideration in developing the system. While design objectives are based in large part on post-accident considerations, the system can also be used for routine analysis operations.

Initially, the work scope was to develop procedures for post-accident analysis for boron and chloride. Later the work scope was expanded to include development of an automated system which would provide for analyses of dissolved hydrogen, dissolved oxygen, chloride, pH and conductivity. The chemical analysis system described here will take effluent flow from the liquid sample panel in the sampling system developed by the Sentry Corporation.

B. DESIGN OBJECTIVES

The major objectives which have all been realized are as follows:

1. To provide the chemical analyses specified in NUREG-0578 during post-accident conditions in a time frame of one hour after sampling.

2. To perform dissolved hydrogen, dissolved oxygen, boron, chloride, pH and conductivity determinations with in-line instrumentation.

3. To develop manual boron analysis procedures that can be performed on a sample that has been diluted by a factor of 1000.

This is to limit radiation exposure involved with handling post-accident samples.

4. To limit the cumulative radiation exposure involved to perform all the analyses listed above at one hour after core damage to less than 1 rem.

5. To use off-the-shelf instruments in designing the system.

6. To provide a system that can be used on a daily basis as well as during post-accident conditions.

7. To demonstrate by laboratory experiments that the proposed analytical methods would be suitable for this application using simulated "post-accident" reactor coolant samples (exclusive of radioactivity) containing various quantities of dissolved gases, chloride and boron.

8. To calculate the dilution factors needed to allow laboratory isotopic analyses of radioactive gases with post-accident conditions.

III. AUTOMATED ANALYSIS SYSTEM

A. GENERAL DESCRIPTION

The automated analysis system that has been developed consists of stainless steel tubing, valves, and instrumentation mounted in a lead shielded panel. Remote indicating flow and pressure meters are mounted on the face of the control panel for monitoring and controlling flow parameters. Readout instrumentation is on an instrument panel located about 20-25 feet from the panel containing the sensor probes.

The in-line instrumentation provides for determination of dissolved hydrogen concentration, boron concentration, chloride concentration, dissolved oxygen concentration, pH, conductivity and temperature. Analytical capabilities and accuracy limitations under regular or post-accident conditions are listed in Table III-1. A simplified flow schematic for the water analyses system is shown in Figure III-1. This system does not include the DigiChem in-line boron analyzer since it has not yet been qualified for in-plant use. It is our understanding that CECO (Tom Lehmann and William Nestel) will perform the plant qualification work for this analyzer. The gas analysis flow schematic is shown in simplified form in Figure III-2.

Undiluted water to be analyzed for chloride, oxygen, pH and conductivity is taken from the Sentry liquid sample panel at about 50-60 psig pressure. Flow rate is maintained in the range of 50-400 ml/min as indicated by the flow meter in the Sentry liquid sample panel. The chemical analysis panel (Figure III-1) also has a flow-no-flow indicator on each of the two sample loops. The dissolved hydrogen in the primary coolant sample contained in a 30 ml sample container in the Sentry liquid sample panel is stripped from solution with argon gas. The gas evolving from solution is collected in a previously evacuated 300 cc container. From here, it is transferred by 1/8 inch tubing to the Baseline gas chromatograph in the automated analysis system for hydrogen determination. The oven, columns and detector of the gas chromatograph are located in back of the lead-shielded chemical analysis panel, above the chloride analyzer. The control system for the gas chromatograph is mounted on the instrument panel located outside the high radiation zone. Simplified operating instructions for overall operation of the automated analysis system are provided later in this section. Operating instructions concerning specific components in the system are provided in Sections IV, V and VI of this report. These instructions are based on the system design used by NUS to check-out the equipment. Changes may be made in the final system to be manufactured by Sentry. In any event, operating instructions for the final system will be issued by Sentry.

In designing the system, the choice of instrumentation was limited to off-the-shelf components. One change was made from conventional design to redesign probe holders to minimize fluid volume and reduce shielding requirements. The system as shown contains a Rexnord oxygen probe which would not be used during post-accident sampling conditions because of the large sample volume contained within the probe. It is included as optional equipment for routine operations. All personnel exposure times involved with operation of this system will be on the order of seconds.

B. FUNCTIONAL DESCRIPTION

1. Liquids

The automated analysis system can provide continuous in-line monitoring of dissolved oxygen, pH and conductivity under normal operative conditions. The system can be expanded to include in-line analyses of boron after plant qualification tests are performed. Chloride analysis is performed on bite samples taken from the sample flow stream. It is anticipated that under accident conditions the system would be operated on an intermittent basis only when analytical data are required.

During post-accident conditions all calibration operations should be performed prior to introducing sample flow to the system to minimize radiation exposure to operating personnel. The calibration and functional operations of the system for liquid analyses are discribed in the following sections. The functional operation for the hydrogen analysis system is provided in Section VI.

a. Calibration

The instruments in the Chemical Analysis Panel will have to be calibrated with frequency as indicated below or just prior to use if the system is operated on an infrequent basis. All calibration operations must be completed prior to admitting flow to the sampling panel during accident conditions.

Instrument	Calibration Frequency
Gas Chromatograph	Daily - 200 ppm standard Monthly - 10% standard
Ion Chromatograph	Daily
pH Determination	Daily
Conductivity Determination	Every three months (Maintenance Operation)
Yellow Springs Oxygen Analyzer	Weekly
Rexnord Oxygen Analyzer	Weekly

Calibration operations are performed after the following initial conditions are established. Valve and sample line designations are as shown in Figure III-1; sample line designations have a "L" prefix.

- If it is not being operated in a continuous mode, the system should be maintained in a water-solid condition for 8-12 hours prior to use to assure pH probe stability.

- The two buffer solution tanks should be filled with pH 7 and 10 buffer solutions.

- The oxygen calibration tank should be filled with demineralized water.

- For PWR plants, the chloride calibration tank should be filled with a standard solution containing 1 ppm chloride and 2000 ppm boron solution in the boric acid form. A 1 ppm chloride standard without boron is used in BWR plants.

- Nitrogen lines L-7, L-8 and L-27 should be pressurized at 50 psi.

- Flush lines L-10 and L-24 should be connected and water available for flushing.

- All instruments should be electrically energized for the minimum period specified in the appropriate instrument manuals.

(1) Gas Chromatograph Calibration

The development work concerning gas stripping operations described in this report was performed with a Fisher gas chromatograph. After this work was complete, the decision was made to use a Baseline gas chromatograph in the final system. Calibration data are not included on the Baseline because NUS has no working experience with this system.

(2) pH Calibration

To calibrate the pH instrumentation buffer solution, flow is established through L-6, L-15, L-16, L-19, L-20 and L-21 by line-up of valves 14 or 6 and valves 3, 4 and 5. Flow rate is controlled with the valve 5, opening the valve until the indicating light on the flow indicator is on. It is only necessary to establish that flow exists. Motive force to establish flow is provided by establishing a nitrogen pressure in the buffer solution tank via by opening valve 15 or 17 dependent on whether pH 7 or 10 buffer solution is used. After the flow rate has been established for 15-20 seconds valve 5 is turned to the off position. The pH meter is adjusted to indicate the proper pH then the procedure is repeated using the other buffer solution. Following calibration the system must be flushed with demineralized water via line L-10.

(3) Calibration of the Rexnord or YSI Oxygen Analyzer

At least two hours prior to performing the calibration operation, the pump in line L-13 must be operational and circulating water through the oxygenated water calibration tank via lines L-13 and L-12. Using the temperature of the water, indicated by a monitor on the tank, the oxygen on the water can be determined from Figure III-3 showing oxygen concentration in the water as a function of water temperature. Calibration of the dissolved oxygen instrumentation is accomplished by flow from the tank through lines L-13, L-9, L-15, L-16, L-17 and L-18 for the Rexnord probe or L-28 for the YSI probe. Exit flow for both probes is through L-19, L-20 and 21. The flow rate should be established by adjusting throttle valve 5 until the indicating light on the flow indicator is on. It is only necessary to establish that flow exists. When operating at a high oxygen level, the oxygen meter of either analyzer will achieve an equilibrium valve in about 3-4 minutes. Several hours may be required to attain equilibrium value on the Rexnord analyzer for oxygen levels in the low ppb range. Adjust the YSI or Rexnord oxygen meters to read the proper concentration after 3-4 minutes of flow.

(4) Chloride Analyzer Calibration

Chloride calibration can be performed prior to, subsequent to, or in conjunction with the other calibration operations. Flow from the chloride calibration solution tank is provided by 50 psi pressure of nitrogen in line L-7. Flow through the analyzer is through line L-5 and L-25 exiting to waste through line L-26. A flow rate is established by throttling valve 8 until the indicating light on the flow indicator is on. It is only necessary to establish that flow exists. Valves 8 and 9 are closed after one minute of operation with flow in line L-25. The inject switch on the ion chromatograph is then activated to automatically inject 0.2 ml of the chloride standard solution into the instrument. This begins the sequence of operation required for the analysis. The peak height for the chloride peak recorded on the strip chart six minutes after injection is used as the reference point for determining the concentration of chlorides in samples. The chloride standard solution will be automatically flushed from the analyzer through a sequence of steps with the eluent solution contained in the ion chromatograph. The complete calibration operations including flushing requires about 30 minutes. No analyses can be performed until this operation is complete.

(5) Conductivity Calibration

The cell constant of the conductivity cell will be checked every three months as part of a maintenance operation. A buffer solution tank will be thoroughly rinsed with demineralized water, then with a known conductivity standard containing KCl in water. Next, this standard will be injected into the system as described under pH calibration; the conductivity as measured under flowing conditions will be compared to the known value. Finally, the system will be rinsed with demineralized water.

b. Analysis of Liquid Samples

Sample flow through the automated analysis system (Figure III-1) comes from line L-2, connecting to the liquid sample panel, to L-4 where the flow is split to go to valves 2 and 3 for the conductivity, oxygen, and pH analyses and to valve 7 for the chloride analyses. Flow rate to valves 7 and 2 is controlled by the Sentry liquid panel and typically will be of the order of 200 ml/min. However, the flow can vary between 50 and 400 ml/min without significantly affecting instrument accuracy. Flow from valve 3 is through lines L-15, L-16, L-17, L-18, L-19, L-20 and L-21 for analyses during normal operation with the Rexnord oxygen analyzer. Under post-accident conditions, flow is directed through lines L-15, L-16, L-28, L-19, L-20 and L-21 to use the YSI oxygen probe. Following the analysis; valve 1 is closed and valves 7 and 3 opened to align lines L-24 and L-10 respectively to flush the system for approximately 10 minutes.

Analysis of liquid samples for pH, conductivity, dissolved oxygen and chloride under post-accident conditions should be performed following a 5-10 minute purge of the sample line. Dissolved oxygen readout should be obtained in the final minute of purge flow. System flow in the range of 50-400 ml/min is required to obtain accurate oxygen results. The pH and conductivity measurements are preferrably obtained when there is flow past the probes; however, readings can be obtained within a few minutes after flow has stopped. The chloride analysis sample should be obtained by pressing the "inject" button on the analyzer during the final minute of purge flow.

C. DESCRIPTION OF INDIVIDUAL INSTRUMENTS

1. Chloride Analyses

Chloride analyses will be performed by the use of the Dionex Model 10 ion chromatograph. This is the only approach that can be used to analyze for chlorides that will not add significantly to personnel radiation exposure. A discussion of the methods investigated for chloride analyses under post-accident conditions is presented in Section V. Other available methods for chloride analysis involve substantially higher radiation exposure to the analyst and for this reason were discarded. Analyzing a sample by IC is fairly straight forward requiring about 1 ml of undiluted sample transferred via hard piping into the sampling module to the IC. A fixed amount (0.2 ml) of the sample is automatically transferred to the separator column for analysis. Excess sample is discharged to the waste disposal system via gravity drain. Eluent solutions containing sodium tetraborate or sodium carbonate and regenerant solutions containing sulfuric acid are also discharged to this same drain line. Analytical results obtained on tests performed on a system mockup are discussed in Section V.

The ion chromatograph in the analytical panel can be used to analyze for chlorides in the range of 100 ppb to 20 ppm without pretreatment of the sample. This system must be modified from the norm to eliminate a boron peak interference and to reduce radiation exposure. The columns must be changed as described in Section V to separate the boron and chloride peak. Also, shielding must be provided for that portion of the unit which will process the radioactive solution. Partial enclosure in a hood is required in the event of leakage.

Operating procedures have been developed for chloride analysis with the ion chromatograph that are relatively simple and have a high degree of precision. The step by step procedure described in Section V will enable operation of this system by personnel that have only limited training in analytical chemistry.

2. Dissolved Hydrogen Analyses

The gas analysis system shown in Figure III-2 provides for the analysis of dissolved hydrogen concentration in the primary coolant. The system designed by NUS measures dissolved hydrogen concentration in the range of 5 cc H_2/kg to 2000 cc H_2/kg. The gas is stripped from a 30 ml liquid sample with argon gas to yield an end volume of 600 cc of gas at STP conditions. The resulting gas mixture is collected in a 300 cc container. Hydrogen concentration of the gas mixture as determined by the Baseline gas chromatograph is related to dissolved hydrogen concentration in the primary coolant.

The gas analyses will be performed using a gas chromatograph manufactured by the Baseline Corporation. No data are provided for this instrument since qualification testing has been performed by Sentry. Results with this system should be similar to that obtained from the Fisher gas partitioner used in the testing described in this report. This development work is discussed in Section VI.

3. Dissolved Oxygen Analyses

a. Yellow Springs Analyzer

Under accident conditions, the analyses will be peformed using an in-line dissolved oxygen meter manufactured by the Yellow Springs Instrument Company. During normal operation, this system will be operated on a once per week basis to assure that the system is properly maintained. It can measure dissolved oxygen concentration in water for the range of 0.1 to 20 ppm. Qualification testing of the instrument is described in Section VII of this report.

The probe holder has been redesigned to minimize fluid volume and reduce radiation exposure. A double O-ring seal is used to prevent leakage. The probe can be easily removed for replacement or repair. Also, the probe holder is designed so that it can be flushed after it is used in this application. The system design provides for in-line calibration to achieve accurate oxygen determinations. The calibration solution is an oxygen saturated demineralized water source. Demineralized water is oxygen saturated by being continuously recirculated and ejected as a spray through air into a tank. The oxygen concentration in this water will be a constant, based on the temperature of the water. Since water temperature is monitored, oxygen concentration can be determined from a solubility chart relating dissolved oxygen concentration to temperature of the water.

(1) This calibration method was selected for the following reasons:

  (a) It is simple in operation.

  (b) The calibration can be verified by Winkler analysis of the water. The tank has a drain valve which can be used to obtain a water sample.

  (c) Variations in barometric pressure will affect results to a minor degree; however, the degree of error would not be important.

Other approaches, as identified below, were considered in selecting a method to provide for calibration of the dissolved oxygen monitor:

(2) The dissolved oxygen monitor can be calibrated by purging air through the probe. This was considered undesirable for the following reasons:

  (a) If the valving is mishandled and air is blasted through the system, the dissolved oxygen membrane could be damaged.

  (b) After the system is flooded with air, some time would be required before it would be possible to obtain low level oxygen readings.

  (c) Purging air through a contaminated system can create airborne contamination levels.

(3) Calibration can be performed by an introduction of oxygen-free water or water from a closed tank with known oxygen levels. This approach was not used for the following reasons:

(a) Most plants do not have known sources of oxygen-free water conveniently available.

(b) Oxygen levels of water from almost any closed tank source in a nuclear plant vary with time; consequently, it would be necessary to perform a colorimetric or Winkler analysis to determine the oxygen concentration before the water can be used for calibration. This approach can lead to error if there is stratification of oxygen concentration in the water. This writer participated in one experiment where oxygen levels in a water storage tank were found to vary by several ppm over a distance in height of about 6-10 inches.

b. Rexnord Analyzer

The Rexnord oxygen analyzer will not be used during post-accident conditions, because the relatively large volume in the probe will result in a radiation shielding problem. Also, the delay time of 30 minutes or more for the instrument to reach equilibrium is unacceptable under post-accident conditions.

The Rexnord analyzer will be on stream during normal operating conditions to measure dissolved oxygen concentration in the low ppb range. No qualification testing was performed with this instrument. Operating instructions for the instrument are provided by the vendor.

The Rexnord system will be calibrated on a weekly basis using the same procedure indicated for the YSI instrument. Calibration can also be performed by exposing the membrane in the probe to air. However, this approach is not recommended because of contamination considerations.

4. pH Determination

An industrial grade in-line probe with a sealed reference electrodes that never needs refilling is used to determine pH. A Cole - Parmer pH probe (Catalog No. 5993-2) and readout instrumentation was used in the test work performed by NUS. The vertical probe holder has a flow inlet at the bottom with exit flow from the top. This design feature prevents entrapment of gas bubbles in the holder. The probe holder has been redesigned to minimize fluid volume. A double O-ring seal is used to prevent leakage. The probe can be easily removed for replacement. Calibration of the pH probe is performed in place using pH 7 and 10 buffer solutions. Loop design provides for the addition of buffer solutions to the pH probe and for flushing of this solution from the system after calibration is complete. Readout indication for pH is provided by an industrial grade meter. The meter is mounted in the remote instrument panel.

Qualification testing performed was limited to establishing that the pH probe selected would work in a flowing stream and to determine the effect of air bubbles on system operation. Air was continuously injected in the sample flow stream at a rate to make up about 5 percent of the water volume. No effect on pH readout was noted in this test.

5. Conductivity Measurement

Conductivity measurements are provided by an in-line probe with a cell constant of 0.1. A Beckman probe and readout instrumentation was used in the test work performed by NUS. The probe holder has been redesigned to minimize fluid volume. A double O-ring seal is used to prevent leakage. The probe can be easily removed for replacement. Calibration of the conductivity probe to determine cell constant should be performed every three months as part of a maintenance procedure. Readout indication for conductivity as provided in the end system is with a Leeds and Northrup meter with a nonlinear scale of 0-500 μmhos/cm. The instrument has high accuracy for the low end of the range (0-2 μmhos/cm), with decreasing accuracy at the other end of the scale.

Qualification testing performed was limited to establishing that the system would work in a flowing stream and to determine the effect of air bubbles on system operation. This work was performed in conjunction with the air bubble test performed with the pH probe. No effect on conductivity readout other than an occasional needle perturbation was noted when air bubbles were introduced to the sample flow.

6. Flowmeter

The flowmeters used in this system are flow-no-flow types. They are provided by the Sentry Corporation.

D. OTHER DESIGN CONSIDERATIONS

1. System Flushing

Design of the analysis system provides two entrance points for flushing the entire system with demineralized water. This is to provide for radiation control and to clean the system prior to opening the system for repair or maintenance. Chemical cleaning with a chelant or organic acid can also be easily performed using the oxygen calibration tank to charge the solution into the system. Materials of construction within the system are compatible with most chelants or organic acids.

2. Radiation Control

Lead shot will be used to provide for complete shielding on the front of the analysis panel. All components will be accessible from the back for ease of maintenance.

A hood is used to provide for gaseous activity control in the event of leakage of radioactive gases and iodine from valves and fittings.

3. Pressure and Temperature Limitations

The analytical system operating pressure limitation is 75 psi. This is based on an operating pressure limitation of 100 psi for the pH probe. A margin of safety was arbitrarily added for conservative reasons.

Optimum temperature range for operation of the analytical system is in the range of 75-90 °F. There will be a loss in accuracy for the pH and conductivity determinations when operating in a variable temperature range; this loss in accuracy cannot be tolerated for a BWR plant. Constant temperature control of the sample stream is required for a BWR and is preferably installed for a PWR. Maximum operating temperature for the analytical system is 125 °F.

4. Radiation Damage

A study made to determine the effect of radiation on equipment in the NUS analysis system indicates that the radiation levels anticipated will have no effect on accuracy of measurement and very little, if any, effect on operating lifetime of the individual components within the system. The study included a survey of personnel who have performed similar analysis under high radiation levels in hot cell conditions and a review of the literature concerning irradiation effects on materials of construction. In addition, laboratory experiments were performed to determine the effect of concentrations of hydrogen peroxide on the conductivity of the reference solution. No effect was noted. The laboratory work was performed because there could be trace concentrations of peroxide in the coolant under zero or near zero hydrogen concentrations in the primary coolant.

In performing the survey, personnel were contacted at Battelle-Northwest and Oak Ridge Laboratories. In addition, a former employee of the naval test facility in Idaho was contacted concerning his hot cell experience with radiation chemistry at this location. Operational experience exists within the three laboratories concerning all phases of the analyses performed by the subject system. Results from these laboratories are consistent as all indicate the analytical measurements in question can be made at much higher radiation levels than will be experienced under post-accident conditions in the automated analysis system. One general conclusion that can be made from this survey, is that analytical instruments can be operated in a hot cell without loss to accuracy of results. There will be some reduction in operating lifetime of the system where continuing exposure at very high radiation levels is involved. Results of this survey as it applies to the individual analytical components within the system are discussed below:

a. Conductivity Determination

Readout equipment for this system is located remotely, thus, will not be exposed to significant radiation levels. The equipment exposed to radiation includes the following:

Platinum electrodes enclosed in a glass holder
Connecting wires to the electrodes
Stainless steel probe holder
Synthetic rubber O-ring seals

Operating experience at Oak Ridge and the naval test facility indicate that conductivity measurements can be made in hot cell conditions under very high radiation levels without problem. Battelle-Northwest could not recall an experience in measuring conductivity under hot cell conditions. Oak Ridge has noted that ruthenium in solution can result in a problem since it will ultimately plate out and thus poison the electrodes. This is a very slow process occurring only in solutions having a much higher radiation level than would be present under post-accident conditions.

Incipient damage to the insulation on the connecting wires to the platinum electrodes could be anticipated at about 10^7 rad based on information presented in reference (a). Total radiation exposure to this insulation during post-accident conditions would probably not exceed 1000 rads and would be less than 10,000 rads. Thus, the insulation on the wire has a 1000X factor of safety.

The synthetic rubber O-ring seals could suffer incipient damage at about 10^6 rads based on data listed in reference (b). Total radiation exposure for these O-ring seals during post-accident conditions would be less than 10,000 rads resulting in a 100X safety factor. The glass and stainless steel would not be affected by the radiation. Glass will darken with time on exposure to radiation; however, this would not affect its performance in this application.

In the absence of dissolved hydrogen in the primary coolant, it is possible that there will be low ppm concentrations of peroxide present from radiolysis of the water. Testing was performed to determine if this peroxide would have an effect on the conductivity of boron-containing waters. No effect was noted on boric acid solutions with peroxide concentrations of 100 and 200 ppm. A 1 percent increase in conductivity was observed for basic boron solutions containing 100 and 200 ppm peroxide. These data are reported in Table III-2.

b. Dissolved Oxygen Determination

Readout equipment for this system is located remotely. The equipment exposed to radiation contained in the oxygen and temperature detection probe includes the following:

Gold cathode and silver anode
Membrane made of 2 mil Teflon
Electrolyte - saturated KCl

Two metal-oxide thermistors
Connecting wires to anodes
Synthetic rubber O-ring seals
Stainless steel probe holder
PVC block and Hysol epoxy cement

The most sensitive component to radiation damage in the above list is the two-mil thick Teflon membrane. Unpublished data from Oak Ridge indicates that Teflon is resistant to radiation damage to about 10^6 rads. This data is supported by irradiation tests performed in connection with the nuclear plane development effort. Results of this work indicate that high pressure (1400 psi) Teflon hoses would show incipient leakage at 10^6 rads exposure levels. Cumulative exposure levels for the Teflon membrane during post-accident conditions would be less than 10,000 rads. Thus, there is a safety factor of at least 100X associated with this component. It should be noted that the probe or the membrane itself can be easily replaced with very minimal exposure after the system is flushed, drained and blown dry.

The two anodes and stainless probe holder are not sensitive to radiation other than perhaps high-intensity neutron irradiation. There will be no neutrons present in the analytical system. The two metal-oxide thermistors are not expected to be affected by radiation; however, no problem would result if damage occurred. The temperature indication provided by the thermistors is not a critical measurement.

No radiation damage is anticipated to the PVC block below 10^6 rads based on data concerning the general resistance of organics to radiation presented in references (a) and (b). The Hysol epoxy cement is stable to radiation at exposure levels to 10^7 rads. Concerning other components (O-ring seals, insulation), the cumulative exposure levels anticipated are far below the area where damage will occur.

c. pH Determination

Readout equipment for this system is located remotely. The equipment exposed to radiation includes the following:

- Glass pH probe - Gel type with internal reference cell
- Connecting wires to probe
- Synthetic rubber O-ring seals
- Stainless steel probe holder

Experimental work reported in reference (c) indicates that pH electrodes of the type used in this system are stable at cumulative dosages up to 10^7-10^8 rads. These results are in agreement with data presented in reference (d) and experience reported by Battelle and the naval test facility in Idaho. Concerning selective ion electrodes, it was observed that the potential response of a fluoride electrode shifted with time at very high cumulative exposures; however, the affected electrode did not lose its effectiveness as long as calibrations were made periodically with standard solutions. A nitrate electrode began to give erratic readings as the cumulative dose approached 10^7 rad.

Cumulative exposure levels to the pH probe in the automated analysis panel during post-accident conditions will be less than 10,000 rads. Thus, there is a factor of at least 1000X below the point where incipient radiation damage can be anticipated.

It is worthy to note, that the data reported in the literature indicate that valid pH readings can be obtained even where a radiation effect was noted provided that the system is calibrated periodically. Operating instructions to be included with the automated analysis equipment will specify daily calibration when the system is in regular use. Calibration prior to use will be specified for intermittent operation. Other components within the pH probe assembly will not be affected by the radiation exposure levels involved.

d. Chloride Determination

Radiation levels for the chloride analysis equipment (ion chromatograph) will be lower than is the case for the other equipment in the analytical system. The reasons for this are as follows: (1) the maximum primary coolant volume contained within the ion chromatograph will be on the order of 1 ml, and (2) the system will be located further away from the radiation source than are other components in the system. Components in the ion chromatograph receiving relatively high radiation exposure include the following:

Cation resin
Anion resin
Conductivity cell
Transistors
Capicitors
Wire-would pots
Circuit board

No radiation damage is anticipated with the resins based on experience developed at Battelle. Resins are conventionally used to separate various isotopes at Battelle without problems. Damage occurs after extended exposure; however, the degradation process is slow. Anion resin will start to degrade at about 10^8 rads and cation resins at 5×10^8 rads. This is several orders of magnitude higher than will be encountered for the resins in the ion chromatograph. It is anticipated that electronic components of the type included in the ion chromatograph will be resistant to cumulative exposure well above 10^5 rads based on data presented in reference (a).

In the absence of dissolved hydrogen, it is possible the primary coolant will contain low ppm concentrations of hydrogen peroxide from radiolysis of water. The effect of this peroxide on readout of the conductivity cell in the ion chromatograph was investigated by adding peroxide to a solution containing 2 ppm HCl and measuring conductivity before and after the addition of peroxide. The justification for using a 2 ppm HCl solution is noted below. Essentially no effect was observed on conductivity within the limits of the accuracy of the instrumentation. Results are presented in Table III-3.

Chloride determinations on an ion chromatograph are obtained by processing the water through resin columns and monitoring the conductivity of the effluent. The chloride (or other anions) will pass through the resin column in wave form at known time intervals after injection of the solution to be analyzed. Cations are removed by the suppressor column resulting in the formation of the corresponding acids from the anions in solution. Consequently, there will be a series of acids such as HCl, H_2SO_4, etc., passing through the conductivity cell in wave form, each at a different, though known time interval after the injection of the solution to be analyzed. Conductivity of the solution at a specific time interval is then related to acid concentration for the anionic species which passes through at that time.

Information developed in testing performed by NUS indicates that 5-10 ppm chloride in the sample size used will result in a maximum HCl concentration of about 2 ppm after it is separated in peaks as it passes through ion exchange columns in the ion chromatograph. The 2 ppm HCl concentration used in the peroxide test is based on the reasonable assumption that chloride level in the primary coolant will generally be below 10 ppm.

e. Pressure Indicator

A pressure transducer incorporating a strain gage is used to sense pressure and transmit this pressure to the readout equipment which is located remotely. Only the transducer is exposed to radiation. This contains the following material:

Diaphragm made of 17-4 PH stainless steel
A strain gage made of silicon doped with phosphorous
Synthetic rubber O-ring seal
Circuit board with resistors, capacitors and transistors
Die-cast aluminum housing for electronic components
Insulation on lead-in wire

The most sensitive component to radiation damage in the pressure transducer is probably the transistors. These should be resistant to cumulative exposure above 10^5 rads based on data presented in reference (a). Maximum cumulative exposure for the transistors will be below 10,000 rads. There are no data available concerning radiation resistance of the strain gage. Principle of operation for a strain gage involves a change in resistivity that is proportional to the deflection in the gage. It is very unlikely that resistivity of an element will be affected by radiation exposures that will be experienced in the pressure-transducer driving a post-accident condition.

All other components in the pressure transducer can withstand cumulative exposure on the order of 10^6 rads or more.

Operation of the pressure indicator is not required for any of the post-accident analyses performed with the NUS system. The pressure indicator is included so that operating personnel can maintain a back-pressure of 40-50 psi or more in the system by suitable adjustment of the throttling valve. Back-pressure is required to keep dissolved gases in solution. Adjustment of the throttling valve to control back-pressure will be made during calibration of the system performed during normal power operations. Flow adjustment will be required only infrequently since inlet pressure will be relatively constant at about 60 psi. In the event that there was a significant change in pressure and the transducer failed, the change in pressure would be manifest by a change in flow rate. There can be no buildup of excess pressure since the system is pressure relief valve protected with valves in the Sentry system.

f. Flow Meters and Dissolved Hydrogen Analysis System

These systems are provided by Sentry.

g. Valves

All valves use Teflon packing. The use of Teflon packing is specified because of its good sealing characteristics. Oak Ridge prefers Teflon-packed valves for handling radioactive solutions containing high levels of radioactive iodine. Some radiation damage to the teflon may be anticipated at 10^6 rads cumulative exposure; however, it is unlikely these valves will ever have 10,000 rads exposure. It is recognized that there are packing materials available that are more resistant to radiation than is Teflon. These were not specified because the primary concern is to maintain leak-tightness.

TABLE-III-1

ANALYSES AND SYSTEM MONITORING CAPABILITIES OF AUTOMATED ANALYSES SYSTEM

Analyses or Instrumentation	Range	Accuracy(1)	Readout(2)
Chloride Concentration (Dionex Model 10 Ion Chromatograph)	0.100-1.0 ppm 0-20 ppm	± 15 % ± 20%(3)	Recording
Dissolved Hydrogen Concentration (Fisher Model 1200 Gas Chromatograph)	5-2000 cc/kg	±15%	Recording
Dissolved Oxygen Concentration (Rexnord)	0-20 ppb 0-200 ppb	±1% Repeatability (Vendor Claim)	Indicating
Dissolved Oxygen Concentration (YS1)	0.1-5 ppm 1-10 ppm 1-20 ppm	± 10%	Recording
Temperature (YSI)	-5 to 45°C	± 0.4°C (Vendor Claim)	Recording
pH Determination (Cole - Palmer)	pH 1 to 13	± 0.1 (Based on Previous Experience)	Indicating
Conductivity (Leeds and Northrup)	1-500 µmho/cm	(5)	Indicating
Flowmeter, Line L-25	Flow - No Flow	(5)	Indicating
Flowmeter, Line L-20	Flow - No Flow	(5)	Indicating
Pressure Gauge (Kulite Pressure Transmitter)	0-100 psig	±1% (Vendor Claim)	Indicating
Temperature - Dissolved Oxygen Calibration System (Cole - Palmer Thermometer)	0-50°C	±1% (Vendor Claim)	Indicating

(1) Unless indicated otherwise, this is based on flow tests performed with equipment assembled by NUS. Ten and one-half inch wide paper was used in the strip chart recorders for the chloride and dissolved hydrogen concentration.

(2) All instrumentation concerning chemistry readout is installed outside the high radiation zone.

(3) This can be reduced to ± 10% if the system is calibrated for operation in this range.

(4) Nonlinear range with high accuracy at the low end of the range. Accuracy decreases at the other end of the range.

(5) Supplied by Sentry.

TABLE III-2

THE EFFECT OF PEROXIDE ON THE CONDUCTIVITY OF BORON CONTAINING SOLUTIONS

Solution ID	Conductivity (μmhos/cm)	
Basic Boron Solution with:		
a.) 0 ppm H_2O_2	93.9	93.0
b.) 100 ppm H_2O_2	94.0	94.0
c.) 200 ppm H_2O_2	94.0	95.0
Boric Acid Solution with:		
a.) 0 ppm H_2O_2	38.0	39.0
b.) 100 ppm H_2O_2	39.0	39.0
c.) 200 ppm H_2O_2	39.0	39.0

TABLE III-3

THE EFFECT OF PEROXIDE ON THE CONDUCTIVITY OF DILUTE HCl SOLUTIONS (ION CHROMATOGRAPH SOLUTIONS)

2 ppm HCl with:	Conductivity (μmhos/cm)	
a.) 0 ppm H_2O_2	24.0	23.5
b.) 10 ppm H_2O_2	24.5	25.0
c.) 25 ppm H_2O_2	25.0	25.0
d.) 50 ppm H_2O_2	25.0	25.0
e.) 100 ppm H_2O_2	25.0	25.0
f.) 200 ppm H_2O_2	25.0	25.0

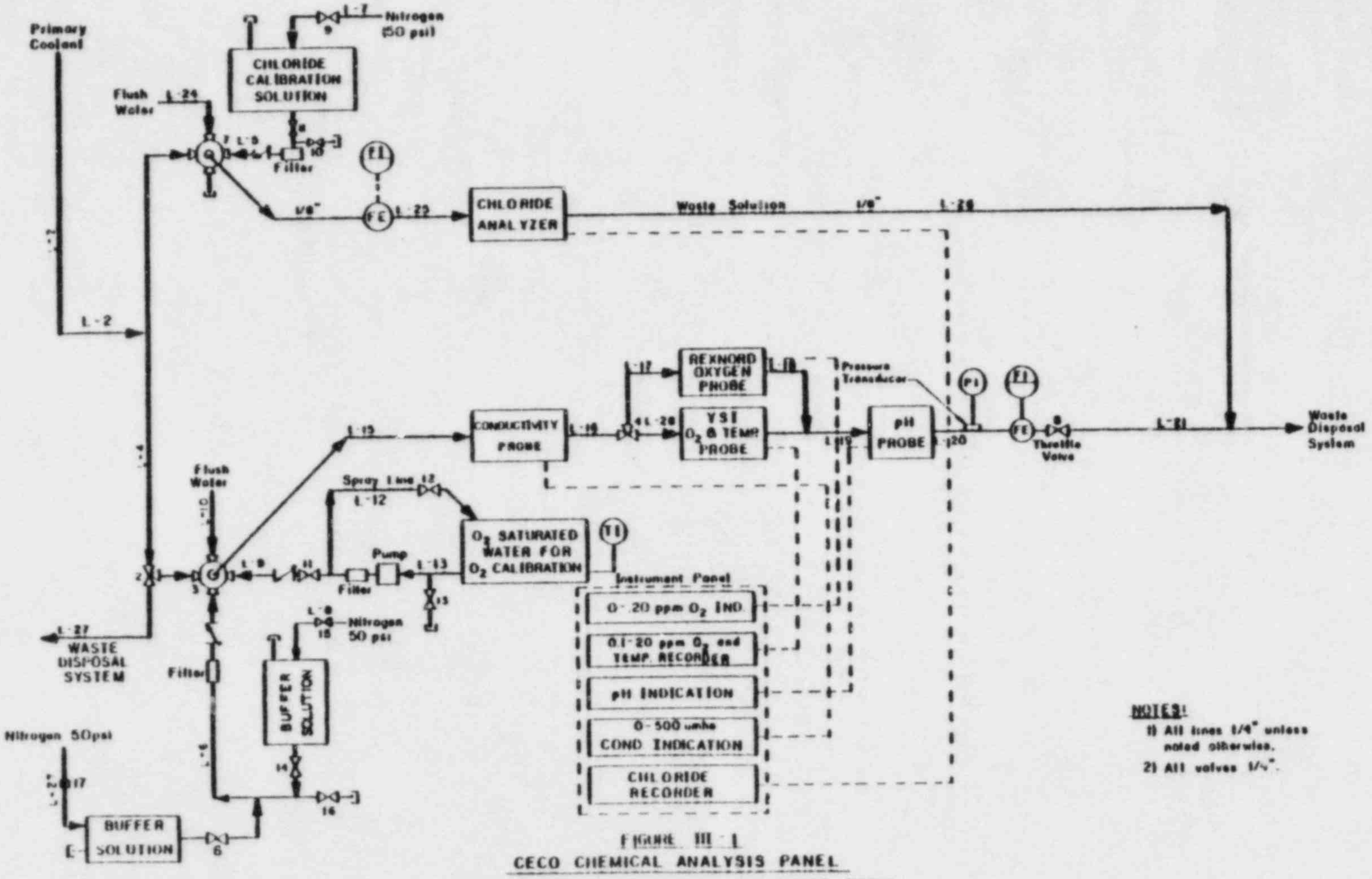


FIGURE III-1

CECO CHEMICAL ANALYSIS PANEL

PRELIMINARY SCHEMATIC IN SIMPLIFIED FORM

NOTES:

1) All lines 1/4" unless noted otherwise.
2) All valves 1/4".

PRELIMINARY SCHEMATIC IN SIMPLIFIED FORM

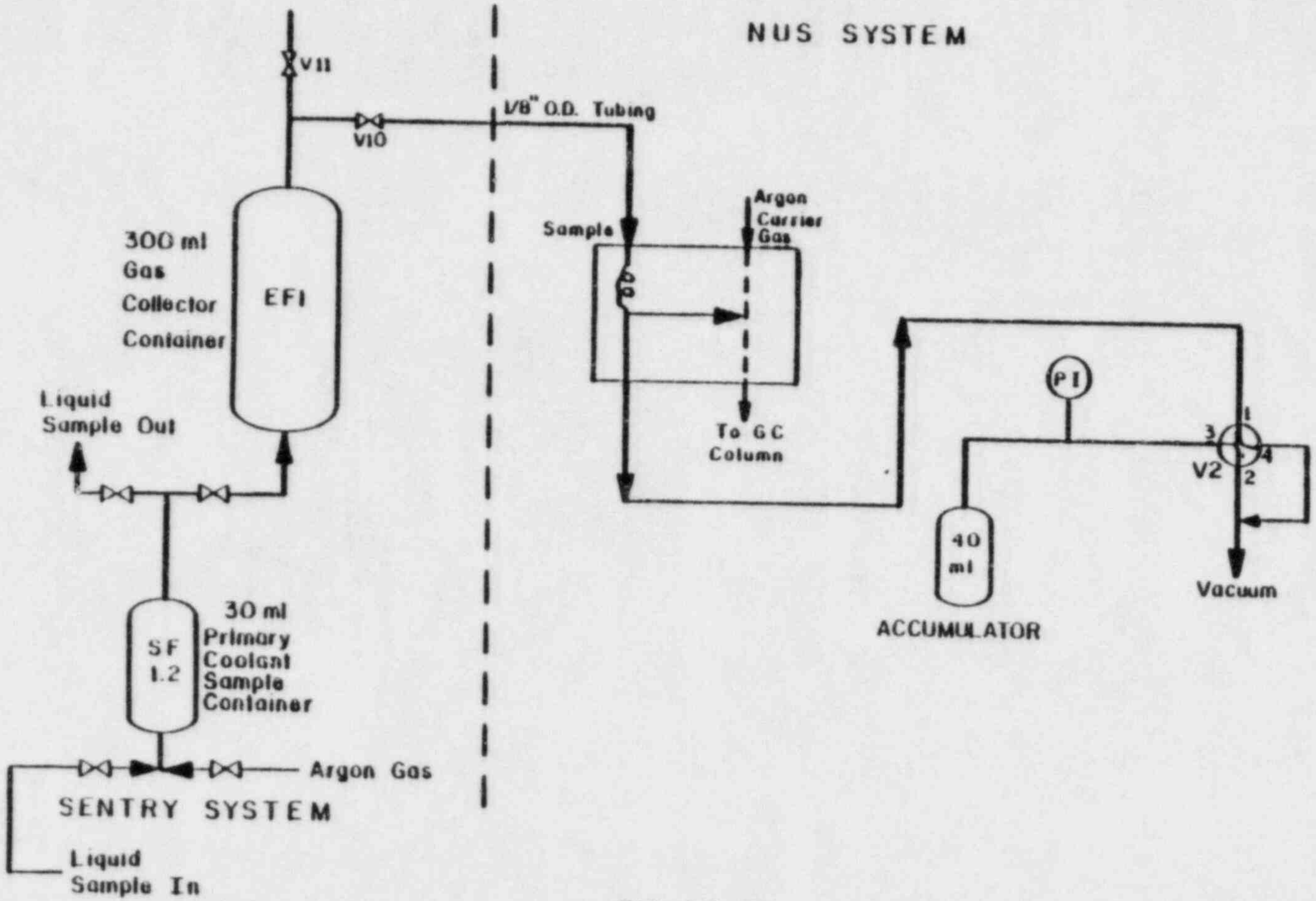


FIGURE III-2

DISSOLVED HYDROGEN GAS FLOW

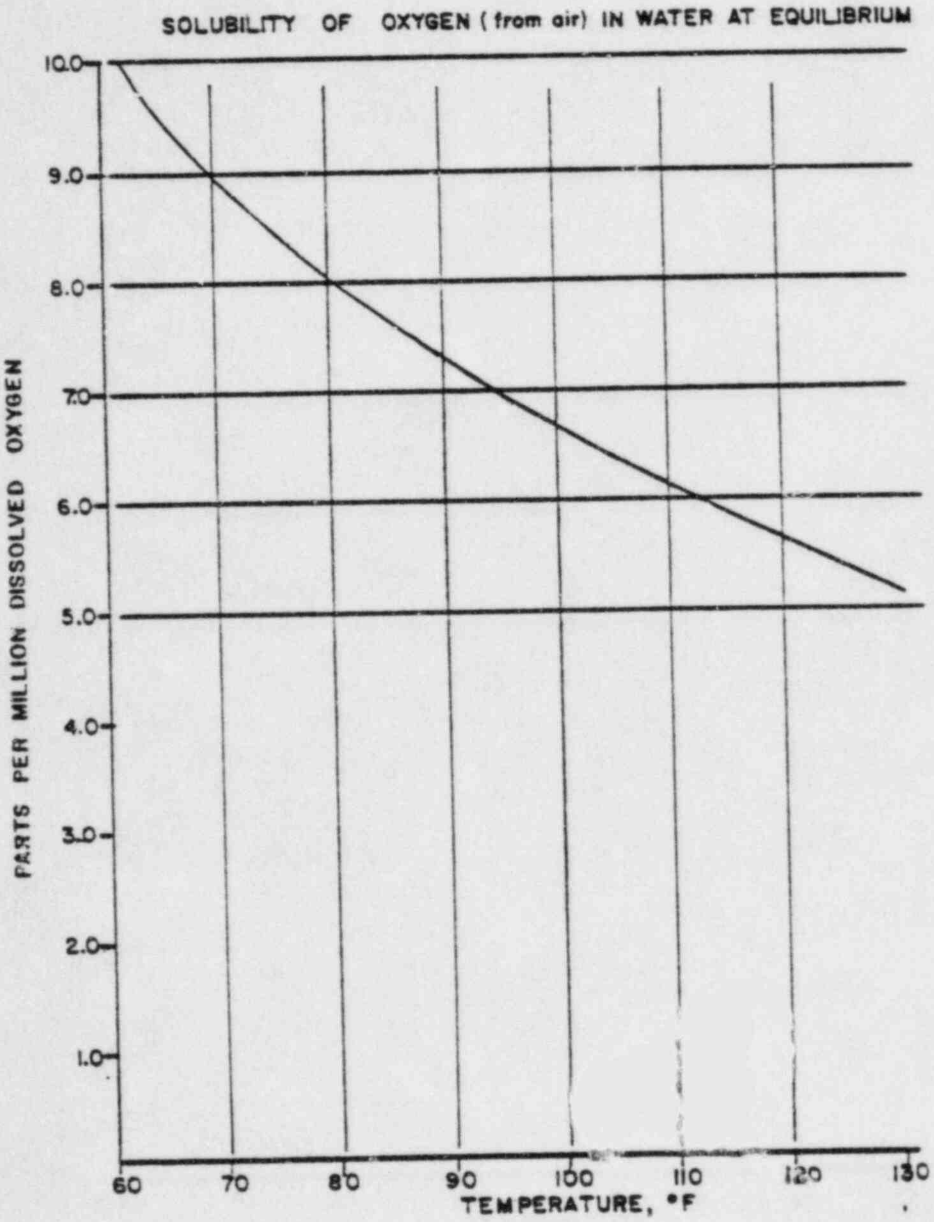

SOLUBILITY OF OXYGEN (from air) IN WATER AT EQUILIBRIUM
PARTS PER MILLION DISSOLVED OXYGEN
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
60
70
80
90
100
110
120
130
TEMPERATURE, °F

FIGURE III - 3

IV. EVALUATION OF ANALYTICAL METHOD FOR BORON

A. APPLICABLE SYSTEMS

The NRC has indicated that BWR's will not require boron analyses under accident conditions. Accordingly, development of analytical methods for boron analyses as discussed in this section, apply only to PWR systems. In the event that requirements change to include boron analyses for BWR's as is apparently indicated in Rev. 2 of Reg. Guide 1.9,(1) the following methods identified in this section can be used for boron analyses:

1. Remote titration with the DigiChem analyzer

2. Curcumin method

3. Dionex Ion Chromatograph

Use of the fluoroborate method is not recommended for BWR's since the response of the boron probe to the pentaborate solutions used in a BWR during accident conditions has not been extensively investigated. No work is recommended to develop the fluoroborate method for BWR's since the three methods identified above are available. Remote titration with the DigiChem analyzer is recommended over the ion chromatograph or Curcumin method.

B. BACKGROUND INFORMATION

During a postulated reactor accident in which fuel damage results, fission products are released to the reactor coolant in sufficient concentration to contribute to the ionic characteristics of the solution. To investigate the possible effects of fission products on analytical procedures, an estimate was made of expected post-accident fission-product levels based on TMI experience. Calculated reactor coolant ionic levels under design basis post-accident conditions are listed in Table IV-1. Fission product levels listed in this table are higher than are the concentrations assumed in earlier work performed on this project. The change was made to be consistent with changing requirements. The original work was performed with fission product concentrations listed in Table IV.

During a PWR accident borated water will be charged into the reactor loops for cooling and reactivity control. Caustic solution from the spray additive tank is mixed with borated water and sprayed into the containment to scavenge radioiodine and condense steam. After the accident, the borated water, sodium hydroxide solution, and reactor water will mix in the containment sump. The RHR pumps will take their suction at this point and the matrix solution is established.

Table IV-2 lists the PWR parameters used to calculate the matrix effects. The PWR parameters are for a 1100 MWe Westinghouse plant under various accident conditions. The boron contribution from the boron injection tank (BIT) is not included, as the reactor coolant boron level was assumed to be 2000 ppm, a high value for operating conditions. (Boron levels decrease during a fuel cycle from about 2000 ppm to about 10 ppm.) Including the BIT contribution would bias the boron level after the postulated accident using an initial 2000 ppm reactor coolant boron level.

The sodium hydroxide used in the PWR spray additive tank is "rayon grade." This contains chloride as an impurity. A series of measurements made at two plants indicate the chloride concentration in spray additive tank water in these plants is below 50 ppm. This chloride inventory when combined with reactor and RWST water should result in sump water chloride concentrations below 1 ppm. This does not consider the contribution resulting from leaching of chloride from insulation and concrete. End levels could, in fact, be in the order of 10 ppm based on Three-Mile Island experience.

NUS prepared matrix solutions for the boron analysis development program based on normal coolant additives, the expected fission-product levels listed in Table IV-1, and dilution and plant parameters listed in Table IV-2. The matrix conditions simulated PWR reactor plant water after a postulated accident and the effects of injecting cooling water with additives mixing and collecting in the sumps. Boron procedures under consideration were evaluated using the boron and fission product concentrations listed in Table IV-1. Solutions listed in this table contained different chloride levels including the contribution of chloride impurities from leaching action on insulation and concrete.

Sump water will be diluted 1000 fold for analyses with resulting concentrations as indicated in Table IV-3. As part of the developmental effort, boron analyses were performed on the solutions listed in this table and in Table IV-4.

Based on the overall results of this study, the fluoroborate selective ion electrode technique using sulfuric acid as a catalyst, is the recommended method for boron analysis under post-accident conditions with the curcumin spectrophotometric procedure as a backup. It is anticipated that titration analyses with the DigiChem analyzer will be recommended as the primary method, once this system is qualified for in-plant use. NUS also investigated and developed other analytical procedures to meet post-accident requirements.

C. TEST OPERATIONS

1. Fluoroborate Selective Ion Electrode

Tetrafluoroborate ion is formed upon reaction of boric acid with hydrofluoric acid:

(1) $B(OH)_3 + 3HF \rightarrow H(BF_3OH) + 2HOH$
(2) $H(BF_3OH) + HF \rightleftharpoons H(BF_4) + HOH$
(3) $H(BF_4) \rightleftharpoons + BF_4^- + H^+$

The first reaction is rapid, whereas the second reaction is rate controlling and slow. The net reaction rate is a function of the matrix pH, temperature, fluoride ion concentration, boric acid concentration, and other effects. At high and low pH levels (i.e., 12 and 2) the tetrafluoroborate ion is subject to hydrolysis. Thus, reproducible formation of the tetrafluoroborate ion is subject to many variables.

Orion Research, Inc. manufactures a selective ion electrode sensitive to the tetrafluoroborate ion. The sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a fluoroborate ion-selective ion exchanger. The theoretical response of the electrode system should result in about -59.2 millivolts change for a factor of 10 increase in effective tetrofluoroborate ion concentration.

The manufacturer does not give firm instructions for using the probe for measuring boron in the boric acid form. Because the electrode responds to anions other than tetrafluoroborate ion, Orion recommends the use of a double junction reference cell with ammonium sulfate solution in the outer jacket to prevent chloride ion interference from the potassium chloride solution used in conventional single junction cells. Ions in post-accident matrix solutions which could give a 10 percent error at the 1.0 ppm boron level are:

Anion	Interference Level, ppm
I^-	0.06
Br^-	7
NO_3^-	28
$CO_3^=$	166
Cl^-	164
F^-	1060
$SO_4^=$	8900

Thus, any procedure for using the fluoroborate probe must consider the kinetics for forming tetrafluoroborate ion and the effect of other anions in the solution.

2. Procedure Development

NUS selected the following criteria for using the Orion fluoroborate selective ion electrode:

a. Accuracy must be adequate to confirm the boration level in a timely manner.

b. Reagents must be easily obtained and not include hydrofluoric acid, a very hazardous acid if improperly used by inexperienced personnel.

c. The procedure must not use more than 5 ml of a 1 to a 1,000 dilution of post-accident solutions.

d. Steps must be simple and easy to follow.

Initial investigation showed that reproducible results could be obtained by reacting a 5 ml sample with saturated sodium fluoride solution and dilute hydrochloric acid for 20 minutes. The hydrochloric acid catalyst provided a relatively constant chloride ion interference, and thus, a conventional single junction reference cell could be used. By using concentrated hydrochloric acid, the reaction rate was sufficient for reproducible results to be obtained in 10 minutes. Developmental work performed using HCl as a catalyst is not described here in the interest of simplifying this report. The test results are available upon request.

Figure IV-1 shows the response of the fluoroborate probe when used with different reference cells. The Orion single junction reference cell provides the best sensitivity of the cells tested.

Because the chloride ion from the hydrochloric acid catalyst could cause electrode drift at low tetrafluoroborate ion levels, NUS investigated the use of 10 N sulfuric acid. This resulted in substantial improvement in electrode response. Interferences from chloride ions are not necessarily important if calibration solutions and samples have the same levels. However, interferences can reduce the system sensitivity in addition to causing drift in the electrode response. Figure IV-2 shows the improved responses when 10 N sulfuric acid is used as the catalyst.

Figure IV-3 shows the relative reaction rates/electrode responses when sulfuric acid is used. The millivolts difference (as a function of time after the acid is added) for various standard solutions and the 5.0 ppm standard verify that a constant response can be measured after 10 minutes. However, the blank solution shows possible electrode drift. Sluggish response is characteristic of low sample concentrations. Thus, 0.5 ppm boron is recommended as the lower level for useful analysis on the basis of Figure IV-3 data. Determining lower boron levels in diluted post-accident samples is not necessary, as the 0.5 ppm level in a diluted sample will clearly define boration requirements.

3. Reproducibility of Procedure

The basic post-accident boron procedure consists of adding 1.0 ml of saturated sodium fluoride solution to 5.0 ml of boron standard and noting the time when 0.5 ml of 10 N sulfuric acid is added. Five minutes after the acid addition to the standard, the same reagents are added to the sample. At eight minutes, the electrodes are inserted into the standard solution, which is stirred, and at 10 minutes the millivolts response is adjusted to give the value on the calibration curve. The millivolts response for the sample is recorded at 10 minutes after the acid addition and related to the ppm boron from the calibration curve. This analysis sequence takes approximately 20 minutes.

Once a calibration curve has been established for an electrode pair, its use in the future is limited by the change in slope over time. The change in slope with time should not be a major problem unless the electrode is used frequently. Orion gives six months as the normal electrode life.

To evaluate the electrode slope for the boron levels of concern, NUS performed several calibration curves under different conditions as listed in Table IV-5. The absolute response in millivolts should change slightly, but the slope should be relatively constant over the useful life of the electrode pair.

Table IV-5 gives the differences in millivolts between the 5.0 ppm standard and other standards. This difference is a measure of the electrode slope. The average difference and standard deviation for the boron standards measured with the Orion single junction reference cell after the sulfuric acid addition show that lower boron levels give greater standard deviations. When these standard deviations in millivolts are converted to the two sigma (95 percent) confidence intervals and related to the calibration curve, the millivolts response uncertainty can be related to boron level. This evaluation shows on the basis of 10 sets of data that an unknown can be determined within the following two-sigma limits once the meter is adjusted to the 5.0 ppm response on the calibration curve:

0.5 ppm	34%, -24%
3.0 ppm	13%, -3.3%

Figure IV-4 gives the average calibration curve for the 10 analysis sets and the two-sigma confidence intervals. These data show that reproducible responses can be obtained in terms of absolute millivolts. Figure IV-5 illustrates the average slope as given by the difference between the 5.0 ppm standard and other standard. The two-sigma millivolt spread for a given standard is higher in Figure IV-4 (absolute millivolts) than in Figure IV-5 (difference in millivolts), showing that small fluctuations from day to day can be accounted for by an adjustment to give the calibration curve response.

Table IV-6 gives the analysis results of the Table IV-4 matrix solutions. The average results are well within the stated boron levels when the standard deviations are converted to the two sigma intervals. Table IV-6 data were obtained during calibrations.

Table IV-3 matrix solutions were analyzed by using the Figure IV-4 average calibration curve and the fluorborate post-accident boron procedure recommended in this report. The analysis results are given in Table IV-7. These data verify the adequacy of the post-accident boron procedure to give the correct concentration within the stated intervals and the minimal effect of matrix conditions. Thus, the fluoroborate selective ion electrode procedure is suitable for post-accident analysis conditions.

D. CORROSION POTENTIAL OF FLUORIDE CONTAINING WASTE SOLUTIONS

The waste solution from one set of analyses (including six standards to develop calibration curve) to determine boron concentration of an unknown sample will contain about 0.19 grams of fluoride ion. For training operations, it is assumed that one calibration curve would be developed and 20 unknowns would be analyzed in one day resulting in a total end release of about 0.5 gram of fluoride. Since this solution will ultimately come in contact with stainless steel, it is necessary to consider the corrosion potential associated with the use of fluorides.

Under normal operating conditions, waste solutions containing these fluorides will be discharged to a radwaste facility for concentration by evaporation followed by solidification in concrete. For accident conditions, the waste solutions would be solidified directly or processed by other means. Concentration by evaporation could not be permitted because the end solution will be too radioactive to handle. The corrosion potential associated with each method of disposal is discussed separately below.

1. Normal Operating Conditions

Under normal operating conditions, solutions dumped to a radioactive drain will ultimately discharge to an evaporation tank containing 500-1000 gallons of water. Assuming the evaporation tank contains 500 gallons, the addition of 0.5 gram of fluoride ion from 20 analyses to this volume will result in an end fluoride concentration of about 0.25 ppm. The volume reduction achieved in evaporation varies between utilities; however, a reduction of 80 percent in volume can be considered reasonable. This volume reduction would result in an end fluoride concentration of about 1 ppm in the waste solution from 20 boron analyses.

With respect to pitting attack on stainless steel, Sedriks indicates in reference (g) that most equipment failures due to pitting are caused by chlorine and chlorine-containing ions. Of the other halogen ions, bromides will also cause pitting, but fluoride and iodide solutions show little pitting tendencies. In general, chloride concentrations of above 100 ppm are required to achieve pitting of stainless steel. Since fluorides are less aggressive in this respect than are chlorides, it is concluded that a 1 ppm fluoride contribution in the waste disposal system, resulting from the fluorobrate boron analyses, will have no effect on pitting potential of the stainless steel in the evaporator.

There is little direct information concerning the cracking potential of fluorides on stainless steel, and the work that has been done is not well documented. Several calls were made to people who have direct experience on this topic and they indicate that fluorides are considered less of a problem with respect to stress cracking of stainless steel than are chlorides. Since fluorides are less aggressive in this respect than are chlorides, it can be assumed that the fluoride concentration required to produce cracking must at least, approach the chloride concentrations required.

Temperature in a radwaste evaporator during operation is in the range of 200°F. Oxygen concentration in the water will be low because the oxygen is stripped from the waste solution as it is heated for evaporation. Under these low temperature, low oxygen conditions, it is very unlikely that chloride stress-cracking could develop at chloride concentrations below 25 ppm. Comparing this with the 1 ppm fluoride concentration expected as a maximum in the radwaste system it is concluded that the use of the fluoroborate method of analysis is not likely to cause stress-cracking of the stainless steel in the system.

2. Accident Condition

There will be lower concentration of fluorides in waste solutions associated with the fluoroborate method of analysis under accident conditions because solutions will not be concentrated through evaporation. There is virtually no potential for fluoride solutions to reach a concentration where pitting of stainless steel is a problem.

Stress-cracking will not be a problem under accident conditions because waste solution temperature will not exceed 100-125 °F. This temperature is too low to promote stress corrosion cracking.

3. Conclusions on the Corrosion Potential of Fluoride Solutions

a. There is no potential for pitting of stainless steel associated with the fluoroborate method of analysis for boron under normal or accident conditions.

b. No problem with stress-cracking of stainless steel is anticipated from the fluoride waste solutions resulting from the use of the fluoroborate method for boron determinations.

E. TITRIMETER ANALYSES WITH THE DIGICHEM ANALYZER

The DigiChem analyzer manufactured by Ionics is designed for process control applications, providing on-line analyses and control for continuous, semicontinuous and batch process. It automatically performs titrimetric, colorimetric or selective-ion analyses. A microcomputer controls the automatic functions of sample and reagent dispensing, solution mixing, and concentration sensing through a programmed sequence of analyses. The work performed here was limited to the investigation of titrimetric analyses since titration in the presence of mannitol is used to determine boron concentration with this system.

1. System Operation

The test work was performed by NUS and Ionics at the Ionics Laboratory in Watertown, Massachusetts. The goal was to perform on-line boron analyses on acid or basic solutions containing up to 6000 ppm boron. To perform the tests, the microcomputer was programmed by Ionics to perform the sequence of operations required. Information concerning the chemical parameters involved was provided by NUS.

The instrument as it would be used in this application takes and measures a sample from an on-line stream and performs the following programmed operations automatically:

a. A fixed but programmable volume of sample is forced into the reaction vessel. Sample volume required is on the order of 0.5 -2 ml for boron concentrations in the range of 1000 to 6000 ppm. Low boron concentrations require higher sample volumes.

b. Next the instrument adds dilution water to flush the sample line and provide sufficient volume to cover the tip of the pH probe.

c. If the solution is basic, as could be the case during an accident, acid is added automatically to reduce pH to about 4.4.

d. A programmed volume of mannitol solution is added to the reaction vessel. Mixing is achieved by rotation of the reaction vessel.

e. The solution is titrated with NaOH to an end point pH of 8.5. The inflection points resulting at pH 4.4 and the end point are derived automatically to determine the volume of titrant used in titrating the boron-mannitol complex.

f. The microcomputer takes the information concerning sample size and NaOH titrant volume used and computes the boron concentration. Boron concentration is printed out as ppm boron on a computer tape. Digital readout of boron concentration can also be provided locally or at some distant point.

g. At the conclusion of each analysis, the rotary speed of the reaction vessel is increased to spin out the solution in the vessel. Water is added at this time to flush the vessel by centrifugal force. Waste solutions can go to a gravity drain or waste tank. The reaction vessel is manufactured of Teflon with a smooth finish that is amenable to cleaning by simple flushing action.

2. Test Results

A series of boron standards and post-accident matrix samples were prepared by Ionics and NUS and analyzed automatically with the DigiChem analyzer. Each analysis required about seven minutes. All operations were controlled with the microcomputer. Chemical and volume parameters for this test were as follows:

HCl Titrant	1.0 N
NaOH Titrant	0.25 N
Mannitol Concentration	1 Molar
Mannitol Volume	5.4 ml
Sample Volume	4.3 ml

In the interest of time, one sample volume was used for all boron concentrations. Results of the tests performed, as shown in Tables IV-8 through IV-10, indicated this was a reasonable choice for sample volume. It is anticipated that better results could have been achieved with 0.1 N acid and caustic titrants since the inflection point in the titration curve is more easily detected with a more dilute acid and base. However, results obtained are acceptable for either routine or accident analysis conditions.

Results of analyses performed on a variety of boron standards prepared by and tested by Ionics are presented in Table IV-10. These results are from the initial analyses performed to check out the system. Both acid and basic boron solutions were evaluated in this test. Average error observed was generally within ±2 percent. Maximum error observed was +3 percent.

Results of testing performed by Ionics to determine reproducibility of analyses for a 2000 ppm boron concentration are presented in Table IV-9. The average error observed was -1.04 percent. Maximum error observed was -1.35 percent. These results were obtained over a six-hour period of continuous sampling from a single sample source. The machine was left unattended during this period.

Results of testing performed with matrix solutions prepared by NUS are presented in Table IV-10. These analyses were performed by NUS with the DigiChem analyzer. The data shown in this table indicate that fission-product species released to the coolant during accident conditions will not add significantly to the range of error for boron analyses.

It should be emphasized that the precision and accuracy of the analyses probably can be improved on routine applications by utilizing lower concentrations for the acid and base titrants. This can be verified by in-plant testing. Note in particular, the low range of error associated with the analyses of basic boron solutions. This deserves attention because concern has been expressed that it would be difficult to analyze basic boron solutions under accident conditions.

3. System Construction

The DigiChem systems are modular instruments that can be wall or panel mounted. A simplified flow diagram of the system is shown in Figure IV-6. The overall system consists of a microcomputer, a rotary reaction cell assembly, a measurement sensor (pH probe in this application), and up to five sample and reagent addition modules.

The microcomputer consists of a series of plug-in circuit boards and the keyboard control panel devices. A motherboard of bus lines and connectors spread along the inside rear for plugging in the circuit boards as needed. The CPU board, sensor input board, analog board, stepper control boards, and display auxiliary board are standard items. Other boards such as the valve control boards and current transmitter boards are options in configuring a particular DigiChem. All boards are easily replaced and are quickly available from the vendor.

The rotary reaction cell assembly is located at the lower left of a DigiChem enclosure. The reaction cell, fabricated from Teflon, forms the heart of the assembly. As programmed, the microcomputer controls a variable speed motor which spins the reaction cell. A cover to the reaction cell provides entrances for the sample and reagent addition lines and the measurement sensor. Reagent addition and sensing occurs below the surface of the sample. The reactor cell module can be replaced as a single unit within five minutes. The module itself can be disassembled and reassembled within 10 minutes. Little or no special training would be required to provide for repair or maintenance of this module. It is assumed that the person performing repairs would have some background in instrument repair.

The sample and reagent addition modules are located on the bottom right hand side of the DigiChem enclosure. All modules are interchangeable with each other. The sealed plug-in modules provided a dispensing capability for up to five fluids, such as samples, reagents, and buffers. Three reagent and one sample addition modules would be used in this application. The digital controlled dispensing modules utilize a stepper-motor which pushes a plunger through a burette for the volumetric measurement and dispenses fluids in precise microliter increments. This method results in the highest analysis accuracy and minimizes reagent consumption. Each pair of these addition modules require one stepper control board in the electronics housing for electronic and pneumatic control.

The sample and reagent addition modules can be replaced with a plug-in module in about five minutes. Disassembly and reassembly of the module itself requires 10-15 minutes. The steps required to take this module apart and reassemble it are almost self-apparent. It is anticipated that little or no special training would be required to provide for repair of this module.

Sliding valves are used to provide for sample or reagent addition control. These valves are easily removable from the system. Disassembly of the valve itself for inspection or cleaning can be accomplished within two or three minutes. The valves are simple in construction and should cause little problem in this application.

One very attractive feature of this system, is that it has manual override capabilities for addition of the sample, titrating, rinsing, and performing other functions. The switches involved are located with the microcomputer and would be outside the high radiation zone.

4. Operation in a Radiation Environment

For operation in a high radiation environment, it will be necessary to separate the microcomputer and controls from the analyzer section. These two units can be separated up to 25 feet without loss of signal. Separation poses no problem if performed at the factory since the units are of modular construction. Dimensions of the analyzer section which would be located behind the panel shielding are
* 24x9x15 inches. The microcomputer and control section is 30x15x11 inches. The microcomputer and control section has a self-contained panel and can be wall mounted.

* Installation of the DigiChem analyzer can be accomplished in the chemical analysis panel designed by NUS. It would require installation of a tee in the sample line downstream of the five port valve. A loop arrangement such as used for the Rexnord oxygen analyzer can be utilized in this application.

5. Conclusions and Recommendations Concerning DigiChem Analyzer

The results of this work indicate that the DigiChem analyzer can be used for boron determinations under routine or accident conditions. The system has significant advantages over other approaches now available for routine or accident condition boron analysis. A digital readout in ppm boron is available within 5 to 10 minutes after calibrating the system. Calibration requires about 10 minutes, performed on a once per day basis. Analysis time requirements are essentially the same for accident or routine conditions. There would be virtually no radiation exposure involved because the equipment can be operated remotely.

The DigiChem analyzer should be qualified for performing on-line boron analyses under routine or accident conditions. Qualification should be performed with an in-plant installation after operating personnel had been trained in its operation. Prior to qualification testing, the system should be lab-tested to optimize reagent normality and sample size. NUS has submitted a proposal to CECO by separate letter to perform a plant qualification test.

F. CURCUMIN SPECTROPHOTOMETRIC BORON PROCEDURE (ALTERNATE METHOD)

1. General Procedure

The purpose of this section is to indicate the steps taken to verify the suitability of the spectrophotometric curcumin procedure for post-accident boron analysis requirements. Actual results are not included to reduce the size of this report. These data were reported in the preliminary report to Commonwealth Edison. The basic goal was to develop a quick analysis procedure for determining the boron level within one hour of obtaining a diluted reactor water sample. The boration of a PWR plant should result in about 2000 ppm boron, and a 1:1000 dilution would give a boron concentration suitable for the curcumin method.

The curcumin spectrophotometric boron analysis procedure is commonly used for low-level determinations. Briefly, the normal procedure is performed as follows. A water bath is set up at 55 ± 2°C. One ml of sample and 4 ml of curcumin reagent are pipetted into an evaporating dish. Boron standards may be processed with the samples.

The solutions are evaporated to dryness in the water bath. After cooling to ambient temperatures, the residues are dissolved in isopropyl alcohol and diluted to 25 ml. The percent transmittance at 540 nm is read with a spectrophotometer. The intensity of the orange color is a function of the boron concentration (i.e., a plot of the logarithm of the percent transmittance versus the concentration is linear). The analysis range is from 0.2 to about 2.0 ppm. Total analysis time is about 120 minutes.

2. Effects of Analysis Conditions and Matrix Effects

Because the PWR reactor coolant will contain about 2.0 ppm lithium-7, and this water will be mixed with caustic in the sump after a postulated accident, NUS determined the effect of analysis variables on 1:1000 dilutions of PWR matrix samples. Three matrix conditions were studied: reactor coolant after the accident, RWST water plus 30 percent caustic in the sump to simulate the effect of the containment spray additive, and sump water plus reactor coolant in the final stage of the accident. All samples with simulated reactor water contained an ionic (nonradioactive) fission-product matrix.

Analysis variables, which may be critical during "panic" conditions after an accident, included the following:

a. The effect of 100 percent isopropyl alcohol rather than 95 percent alcohol.

b. Reduction of the water bath time from 80 minutes, the normal procedure requirement.

c. Sensitivity of temperature control.

d. The benefits of an additional dilution to give a 1.0 ppm boron solution.

Test results when statistically evaluated, show the following:

a. Poor sensitivity is achieved with 100 percent isopropyl alcohol should be used.

b. Additional dilution of the 2.0 ppm solutions to 1.0 ppm will improve the precision, but is unnecessary.

c. Eighty minutes total time in the bath will give better precision than removing the samples 15 minutes after dryness. However, removing the sample 15 minutes after dryness will reduce the analysis time by about 20 minutes.

d. 1.0 cm spectrophotometer cells are adequate; 1.9 cm cells would result in lower detection limits (and also could require sample dilution) and increased radiation exposure.

e. The procedure is sensitive to many variables, including the curcumin reagent, development time and temperature, and analysis conditions.

3. Statistical Evaluation of Procedure

The matrix samples were analyzed under different conditions to develop precision data. A total of 64 analyses were performed on eight different samples to investigate how deviation from the procedure will affect analyses results. The relative standard deviation for multiple analysis is about +13 percent for post-accident matrix solutions. The standard deviation increases to about +17 percent if color development time is reduced or 100 percent isopropyl alcohol is used as opposed to 95 percent alcohol recommended.

G. BORON ANALYSES WITH THE ION CHROMATOGRAPH

Development work has been performed by Dionex and NUS indicating that it will be possible to perform boron analyses with the Dionex ion chromatograph. System modifications will be required involving installation of another pump and ion exchange column if the analyses are to be performed on basic boron solutions. Both boron and chlorides can be performed with the same system. The eluent consists of a mannitol-sodium hydroxide-sodium carbonate solution.

Results of this work have been published with conclusions drawn as follows:

1. The ion chromatograph in its modified form represents a viable means for performing boron and chloride analyses under accident conditions.

2. The ion chromatograph does not have the accuracy required for performing boron analyses under routine conditions.

3. This method of analyses should be qualified for use under accident conditions by an in-plant installation. NUS has submitted a proposal to CECO by separate letter to perform a plant qualification test.

H. PLASMA SPECTROSCOPY ANALYSIS FOR BORON

This method of analysis can be used to determine boron concentrations of solutions in the range below 1 ppm. The analysis is performed by vaporizing the sample in a plasma jet with atomic emission analysis of the spectra generated at the boron resonance wavelength of 249.7 or 249.8 nm. Readout of the unknown is compared to a known standard. Good reproducibility can be achieved for boron analyses. Time required for analyses is in the range of 15 to 30 minutes.

NUS analyzed several samples of the reference matrix solutions containing boron at the Spectrometric, Inc. Laboratory. Results indicate that this approach has merit as a possible backup method for boron analyses. If the plasma spectroscopy method were used, installing the instrument in a hood would be necessary to provide for containment of gaseous activity that would be generated in the plasma arc. About 5 ml of a 2,000-fold dilution would be required to perform an analysis. About 1 ml of this liquid would be vaporized with an associated release of activity. The remaining liquid, consisting in a large part of spray droplets, would be collected in a waste container, thus, providing protection against release of gaseous activity, as well as liquid activity, would be necessary. The system as designed, lends itself to the use of a hood to contain the vaporized liquid.

The first analysis performed would involve minimal exposure. Personnel exposure would increase with subsequent analyses because the activity, which is vaporized in the plasma jet area, would deposit on surfaces around and above this area, creating an ever increasing radiation field. The contaminated components could be replaced at periodic intervals; how ever, this could only be accomplished through direct manual contact with the components. Again, radiation exposure could be significant since shielding would not be possible while making the replacement.

One added disadvantage of the plasma spectroscopy system is working with an open or semi-open container of radioactive solution would be required. This creates a potential for spills with the use of this instrument. The instrument design is such that providing hard piping to the system would be difficult. Redesign of the sampling port and of the plasma flame head area would be required for using hard piping. Such a design effort would be expensive. Since a titrimeter, electrode, ion chromatograph, and a colorimetric method are available for boron analyses that have the advantages of lower radiation exposure and lower equipment cost, NUS concludes that these methods should take precedent over plasma spectroscopy.

I. BORONOMETER

Boron determination with a boronometer is provided by relating neutron attenuation in the analysis stream to boron concentration in the water.

The neutron count rate from the detector tube is converted to direct boron concentration on the readout instrumentation. The readout instrumentation and detector can be separated by up to 600 feet.

Westinghouse, Combustion Engineering, Inc., and Babcock & Wilcox Company, have boron analyzers qualified for nuclear plant use. The Westinghouse unit has a 100 gallon constant temperature bath with a sample flow rate of 0.1 to 0.4 gpm. One detector is used. Sample volume in the detector assembly is about 0.6 gallon. The instrument must be secured if sample flow is low because overheating will occur which can damage the instrumentation. The Combustion Engineering and Babcock & Wilcox units do not use a temperature bath. Temperature compensation is provided in the readout instrumentation.

Combustion Engineering recommends the use of an 8 gpm sample flow rate for their boron analyzer. Sample volume in the detector assembly is about nine gallons. Supposedly, the larger volume provides for increased sensitivity of detection. Four boron trifluoride tubes are used in their detector arrangement.

The Babcock & Wilcox device uses polyethylene for moderation and a neutron reflector to maximize utilization of the neutron population. With this arrangement sample volume requirements are reduced to approximately one liter. A sample flow rate of 2 gpm is recommended to provide for rapid sample line turnover. However, the instrument can be operated with a static sample volume after the lines have been properly purged. The Babcock & Wilcox analyzer has the advantages of low sample volume requirements and system capability of operation in the static mode. Sample volume requirements on post-accident analyses are at least a factor of two lower than that needed for the Westinghouse or Combustion systems.

The use of presently available boronometers is not applicable to boron analyses during post-accident conditions because the high gamma radiation fields will increase the indicated concentration. This statement is based on theory and supported in fact by testing performed by Combustion

Engineering. A small change in the neutron signal strength was detected when the Combustion Engineering unit was tested in a 1000 R/hr gamma field by the vendor. The correct readout was obtained by lowering the detector voltage and increasing the discriminator setting. Gamma radiation levels in the detector assembly could be several orders of magnitude higher during post-accident conditions than the 1000 R/hr used in the Combustion Engineering test. Consequently, the noise level will increase by some unknown value. Theory indicates that correcting for this noise level will be possible with appropriate changes to circuit design.

J. MANUAL TITRATION PROCEDURE

PWR plants commonly use the boric acid titration procedure for most plant boron analyses. Mannitol is added to an appropriate sample to partially ionize the boric acid so that the sample can be titrated with a base. The sample size ranges from 2 ml for 1600 to 3500 ppm boron to 100 ml for less than 50 ppm boron. The sample is titrated with 0.1 M sodium hydroxide to pH 8.5. The volume of standard base is related to the boron concentration. An analysis takes about five minutes. This is not recommended for use during post-accident conditions because of the high radiation exposure associated with its use.

K. ALTERNATE SPECTROPHOTOMETRIC METHOD

A low-level spectrophotometric boron analysis method is available which uses carminic acid for color development. The optimum range is 0.2 to 5 ppm boron. A 5-ml sample is pipetted into a flask and a few drops of hydrochloric acid and 30 ml of concentrated sulfuric acid are added. The mixture is cooled for 30 minutes. Carminic acid is then added and the optimum color is developed for one hour. The color intensity is determined with a spectrophometer. The boron level is related to the color intensity.

The carminic acid method shows more variability than the circumin procedure. Also a larger sample size is required. Consequently, the curcumin method is preferred over the carminic acid procedure.

POST-ACCIDENT BORON PROCEDURE USING FLUOROBORATE SELECTIVE ION ELECTRODE AND SULFURIC ACID

1.0 OBJECTIVE

This procedure is to be used for measuring post-accident diluted reactor water boron concentration. Boron concentration in the diluted sample should be greater than about 0.5 ppm. The estimated precision at the 95 percent confidence level is +13 percent, -3.3 percent at 2 ppm boron and +34 percent, -24 percent at 0.5 ppm boron for "stirring" samples. The analysis time is less than 20 minutes excluding sampling, reagent preparation, and calibration curve preparation.

2.0 REFERENCES

None

3.0 INITIAL CONDITIONS

3.1 A diluted reactor water sample or sump sample has been obtained.

3.2 Samples have been prepared for analysis.

3.3 The following equipment must be available:

3.3.1 Ion meter capable of measuring in the relative millivolt mode.

3.3.2 Fluoroborate Selective Ion Electrode, Orion Model 93-05.

3.3.3 Plastic Single Junction Reference Electrode, Orion Model 90-01 with 4 M KCl/saturated AgCl.

3.3.4 Magnetic stirrer and micro stirring bars.

3.3.5 Plastic 30-ml beakers.

3.3.6 Micro sample dishes for electrodes, Orion Catalog No. 92-00-14.

3.3.7 Pipets:
1. Oxford or equivalent with disposable tips, 5, 1, 0.5 ml
2. Glass, 10, 5, 3, 2, 1, 0.5 ml

3.3.8 Volumetric flasks, 100 ml (six).

3.3.9 Medicine droppers, plastic.

3.3.10 Thermometer, degress Celsius

3.3.11 Two cycle semi-logarithmic graph paper and French curve.

3.3.12 Timer

3.4 The following reagents must be available or prepared:

3.4.1 Saturated sodium fluoride - add 30 grams of reagent grade sodium fluoride to 100 ml of deionized water. Mix and store in a clearly labeled plastic bottle.

3.4.2 Sulfuric acid, 10<u>N</u> - add 28 ml of concentrated sulfuric acid to approximately 50 ml of deionized water in a 100-ml volumetric flask. Mix well and dilute to volume with deionized water when cooled to room temperature.

3.4.3 Boron standard, 100 ppm (Fisher SO-B-155, or equivalent).

3.5 The following standard solutions must be available or prepared:

3.5.1 Reference electrode filling solution, Orion 90-00-01.

3.5.2 Dilute 10.0 ml of 1000 ppm stock boron (as boric acid) solution to 100 ml with deionized water and mix. Prepare standard boron solutions as follows from this 100 ppm stock solution.

ml of 100 ppm Boron Solution Diluted to 100 ml	ppm Boron Working Boron Standards
0.5	0.5
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0

4.0 PRECAUTIONS

4.1 After a reactor accident, very high dose rates and high levels of airborne radioactivity may be present in unexpected locations in the sampling building. Take precautions to keep internal and external exposure to a minimum. These may include, but are not limited to the following precautions:

4.1.1 Air sampling should be performed to determine the iodine concentration in the sampling building.

4.1.2 When the radiological conditions in the sampling building are uncertain, at least two individuals shall be sent for sampling and analyses.

4.1.3 At least one functioning high-range dose rate instrument shall be available at all times. This normally means carrying a suitable spare instrument.

4.1.4 The instruments used for survey purposes should be ion chamber type instruments. If an instrument with a sealed chamber (such as the PIC-6A) is not available, bag the instrument to preclude internal contamination with radioactive gases.

4.1.5 Dosimetry monitoring of extremities will be required during sampling and analysis operations.

4.1.6 Normally, if vent release conditions are serious enough to activate post-accident procedures, airborne conditions in the auxiliary building would require the use of pressure demand type supplied air respirators by all personnel involved.

4.2 Assume that all reactor coolant samples are extremely radioactive unless determined otherwise by survey. Handle all liquids collected during post-accident sampling/analysis, including dilutions, with extreme care to prevent unnecessary personnel exposure.

4.3 Check dosimeters periodically to determine approximate exposure.

4.4 Carry out all operations in an operating fume hood to contain activity.

4.5 The following parameters directly affect the reproducibility of the measurements, and are items to be observed and controlled.

4.5.1 Temperature variance between standards and samples must be controlled to within a 5°C spread. Maximum temperature at which the fluoroborate SIE method can be used is 40°C.

4.5.2 Control stirring action at a rate to preclude vortex formation or bubbles. Mount the magnetic stirrer in a chassis that does not conduct heat to the sample beakers. The stirring rate with the micro stirring bar must be constant.

4.5.3 The electrodes, being in plastic sheaths, are sensitive to electrostatic effects. Control factors affecting humidity, temperature, and air flow over the electrode to reasonable limits of fluctuation.

4.5.4 Ensure that no bubbles are adhering to the electrode bottom near the membrane when making a measurement.

4.5.5 Ensure that the reference electrode is filled with Orion 90-00-01 filling solution and that no crystals have formed inside the reservoir. Store the reference electrode in deionized water while not in use. Alternately 4M potassium chloride solution may be used.

4.5.6 Do not energize the pH-millivolt meter if the electrodes are not immersed in liquid. Use the STANDBY mode in this case.

4.5.7 Store the fluoroborate electrode in air. For short periods of time (2-3 weeks), during frequent use, such as training and testing, store the fluoroborate electrode in deionized water. DO NOT STORE IN FLUOROBORATE SOLUTIONS.

4.5.8 Soak the electrodes in deionized water for approximately five minutes before measuring a 0.5 ppm or less boron sample after measuring a 5 ppm standard or sample.

4.5.9 The reactions of this procedure are time dependent. Therefore, reagent additions, electrode equilibrium times, and measurement times must be performed as indicated.

5.0 CHECK OF SHEETS

5.1 None.

6.0 PROCEDURE

6.1 Calibration Curve (all millivolt readings in ABSOLUTE mode)

6.1.1 Soak the electrodes in deionized water for at least 10 minutes prior to use. The reference probe should be soaked several hours prior to use for optimum response.

6.1.2 Pipette 5.0 ml of deionized water (blank), 0.5, 1.0, 2.0, 3.0, and 5.0 ppm boron standard solutions into separate 30-ml plastic beakers. Insert a micro stirring bar into each solution.

6.1.3 Pipette 1.0 ml of saturated sodium fluoride into the water blank. (Do not place the pipet into the bottom of the sodium fluoride solution. Pipette from near the top of the solution.) Immediately pipette 0.5 ml of 10<u>N</u> sulfuric acid into the water blank (first sample) and start the timer. Swirl to mix the reagents. (All times mentioned in this procedure are based on the time after acid addition to the first sample.)

6.1.4 At approximately five minutes, pipette 1.0 ml of saturated sodium fluoride into the 0.5 ppm standard (second sample).

6.1.5 At 6.0 minutes, pipette 0.5 ml of 10<u>N</u> sulfuric acid into the 0.5 ppm standard (second sample) and swirl to mix.

6.1.6 At eight minutes, immerse the electrodes into the water blank (first sample) at a depth of approximately 1/4 inch.

6.1.7 Measure the millivott response (absolute) of the stirring solution at 10.0 ± 0.1 minutes and record the reading.

6.1.8 Immediately transfer approximately 0.3 ml (seven drops) of the solution into the electrode micro dish and measure the millivolt response (absolute) at 12 ± 0.5 minutes.

6.1.9 Rinse the electrodes with deionized water and blot off excess water before proceeding to the next set of measurements.

6.1.10 At 14 minutes, immerse the electrodes into the 0.5 ppm standard (second sample) at a depth of approximately 1/4 inch.

6.1.11 Measure the millivolt response (absolute) of the stirring solution at 16.0 ± 0.1 minutes and record the reading.

6.1.12 Immediately transfer approximately 0.3 ml (seven drops) of the solution in to the electrode micro dish. Measure the millivolt response (absolute) at 18 ± 0.5 minutes and record the reading.

6.1.13 Rinse the electrodes with deionized water and blot off excess water. Immerse the electrodes in deionized water.

6.1.14 Repeat the same sequence of steps (6.1.3 through 6.1.13) for the 1.0 and 2.0 ppm and the 3.0 and 5.0 ppm standards as two sample sets. The time table for the water blank and five standards is illustrated below.

TIMES FOR:

ppm boron	Acid addition	Immersion of Electrodes	Record mV (stirring)	Record mV (microdish)
0	0	8	10.0±0.1	12.0±0.5
0.5	6.0	14	16.0±0.1	18.0±0.5
1.0	0	8	10.0±0.1	12.0±0.5
2.0	6.0	14	16.0±0.1	18.0±0.5
3.0	0	8	10.0±0.1	12.0±0.5
5.0	6.0	14	16.0±0.1	18.0±0.5

6.1.15 Plot the ppm boron on the logarithmic axis versus the millivolt responses for the boron standards on the linear axis of two-cycle semi-logarithmic graph paper. Using a French curve, draw the best-fit curve through the data points. Prepare a calibration curve for the samples in the beakers (stirring) and for measurements in the micro dishes (static).

6.2 Sample Analysis (All millivolts readings in RELATIVE mode)

6.2.1 Ensure that the electrodes have been soaked in deionized water for at least 10 minutes prior to use.

The reference probe should be soaked several hours prior to use for optimum response.

6.2.2 Pipette 5.0 ml of sample and 5.0 ml of a boron standard into separate plastic beakers and insert a micro stirring bar in each solution. (The standard should be approximately the same boron level as the sample.)

NOTE: If the radiation level from a 5.0 ml sample is excessive, the analysis may be performed using 1.0 ml of sample and adding 0.20 ml of saturated sodium flouride solution and 0.10 ml of 10N sulfuric acid, reading the millivolt response in a micro dish as indicated by the note following Step 6.2.7. This method is not recommended and should be used only under extreme conditions.

6.2.3 Pipette 1.0 ml of saturated sodium flouride into the boron standard. Immediately pipette 0.5 ml of 10N sulfuric acid into the standard and start the timer. Swirl to mix. (All times mentioned in this section are based on the time after acid addition to the standard solution.)

6.2.4 At approximately five minutes, pipette 1.0 ml of saturated sodium flouride into the sample.

6.2.5 At 6.0 minutes, pipette 0.5 ml of 10N sulfuric acid into the sample and swirl to mix.

6.2.6 At eight minutes, immerse the electrodes into the boron standard at a depth of approximately 1/4 inch.

6.2.7 Measure the millivolt response (relative) of the stirring boron standard solution at 10.0 ± 0.1 minutes. Using the calibration control knob on the millivolt-pH meter, adjust the meter readout to give the correct response for the standard as given on the calibration curve for stirring samples. Do not make an additional millivolts adjustment after this step and proceed to step 6.2.8.

NOTE: If the radiation level is excessive, transfer approximately 0.3 ml. (7 drops) of the solution to an electrode micro dish and measure the millivolt (relative) response at 12 ± 0.5 minutes. Using the calibration control knob on the pH-millivolt meter, adjust the meter readout to give the correct response for the standard as given on the calibration curve for the micro dishes. Perform step 6.2.8. Measure the millivolt response (relative) of the sample in the micro dish at 18.0 ± 0.5 minutes and record the reading. Proceed to step 6.2.11.

6.2.8 Rinse the electrodes with deionized water and blot off excess water before proceeding to step 6.2.9.

6.2.9 At 14 minutes, immerse the electrodes into the sample at a depth of approximately 1/4 inch.

6.2.10 Measure the millivolt response (relative) of the stirring sample solution at 16.0 ± 0.1 minutes and record the reading.

6.2.11 Determine the ppm boron in the sample from the calibration curve.

6.2.12 Multiply the sample boron level determined from the calibration curve by the dilution factor (normally, 1000 for boron samples).

7.0 FINAL CONDITIONS

7.1 Ensure all sampling bottles and liquid samples have been properly disposed.

7.2 Rinse electrodes with deionized water. Check radiation level of instruments and work area to ensure spillage of sample did not occur.

7.3 Clean work area as necessary to minimize residual radiation levels.

7.4 Store electrodes in deionized water and place the pH-millivolt meter on "off" or "standby."

BACKUP PROCEDURE FOR BORON ANALYSIS BY CURCUMIN SPECTROPHOTOMETRIC METHOD

1.0 OBJECTIVE

This procedure is to be used as a backup method to the fluoroborate method for determining the boron concentration in reactor plant waters after a reactor accident. The method is based on the reaction of boron with curcumin to form a red-colored product called rosocyanine. The product is dissolved in alcohol and the solution transmittance is determined spectrophotometrically. Boron concentration in the diluted sample should be between 0.2 to 2.0 ppm. The relative standard deviation is about ±13 percent for post-accident matrix solutions. The total analysis time is about 120 minutes, excluding sampling and reagent preparation.

2.0 PRECAUTIONS

2.1 Very high dose rates and high levels of airborne radioactivity may be present during sampling. Precautions to keep internal and external exposure to a minimum shall be taken as indicated in Section IV of the Fluoroborate Procedure.

2.2 The following precautions pertain to the analytical procedure:

2.2.1 The same geometry evaporating dishes must be used for all standards and samples to assure that evaporative rates are equivalent.

2.2.2 The temperature of the bath must be controlled so that all samples dry at the same rate.

2.2.3 The curcumin reagent must be stored under refrigeration after preparation and not be more than three days old.

2.2.4 Use 95 percent rather than 100 percent alcohol in preparing the curcumin reagent.

2.2.5 Prepare the water bath using hot tap water to fill the bath as soon as it is known that sampling will be required for boron analyses. The bath must be contained in an operating fume hood because there will be release of radioactive iodine and gases during the analysis procedure. In checking out the procedure, determine the thermostat setting for 55±2°C on the temperature controlling device and mark the setting.

3.0 INITIAL CONDITIONS

3.1 A diluted primary coolant sample has been obtained containing between 0.5 and 2 ppm boron.

3.2 The following equipment must be available:

3.2.1 Water bath set at 55 ± 2°C in an operating fume hood.

3.2.2 Graduated cylinders, 10 or 25 ml and 500 ml

3.2.3 Volumetric flasks, 25 ml, 100 ml, 1000 ml

3.2.4 Evaporating dishes, 100 to 150 ml capacity, Vycor glass (Corning glass), or equivalent (used for boron determination only).

3.2.5 Oxford pipettes with disposable plastic tips, 1 ml, 4 ml, 5 ml, 15 ml, 20 ml and 5 ml Mohr pipette.

3.2.6 Beakers, 250 or 400 ml, wide form

3.2.7 Tongs, 53 cm

3.2.8 Rods, polyethylene

3.2.9 Medicine droppers

3.2.10 Filter paper, Whatman No. 30 or equivalent, and glass or plastic funnel

3.2.11 Cells, 1.0 or 1.9 cm (for spectrophotometer)

3.2.12 Spectrophotometer, Bausch and Lomb Spectronic 20, or equivalent

3.2.13 Semi-logarithmic graph paper, dual cycle

3.3 The following reagents must be available or prepared:

3.3.1 95 percent isopropyl alcohol - Measure 475 ml of 100 percent isopropyl alcohol in a 500 ml graduated cylinder. Dilute to 500 ml with water and mix.

3.3.2 Curcumin Reagent - Dissolve 40 mg of finely ground curcumin (Eastman No. 1179, or equivalent) and 5.0 g of oxalic acid (reagent grade) in approximately 80 ml of 95 percent isopropyl alcohol in a 100 ml volumetric flask. Mix, and add 4.2 ml of concentrated hydrochloric acid (12.1<u>M</u>). Dilute to 100 ml with 95 percent isopropyl alcohol.

NOTE: This reagent is stable for a limited period of time under refrigeration. Storage life under refrigeration is three days, or one day at room temperature. The reagent color changes to a brighter yellow upon degradation.

3.3.3 Boron standard, 1000 ppm (Fisher SO-B-155, or equivalent)

3.4 The following standard solutions must be available or prepared:

3.4.1 Prepare a 10.0 ppm boron solution by pipetting 10.0 ml of the 1000 ppm boron standard into a 1000 ml volumetric flask and dilute with deionized water. Prepare the working standards by diluting the 10 ppm standard boron solution as follows:

ml of 10 ppm Boron Solution Diluted to 100 ml	ppm Boron Boron Standards
5.0	0.5
10.0	1.0
15.0	1.5
20.0	2.0

3.4.2 Prepare fresh curcumin prior to sampling if the existing stock is more than three days old.

3.4.3 Tests show that many variables can affect the color development in this procedure. To minimize these effects, the procedure includes processing standard boron solutions along with the samples. This may not be necessary during a series of analyses provided that identical conditions prevail throughout (same reagents and personnel) and that the personnel involved are totally familiar with this procedure.

4.0 CHECK OFF SHEET

4.1 None.

5.0 PROCEDURE

5.1 Pipette 1.0 ml of water (blank) and 1.0 ml of the 0.5, 1.0, 1.5 and 2.0 ppm boron standards into separate labeled evaporating dishes. Also pipette 1.0 ml of the diluted sample solution into two separate evaporating dishes for duplicate analyses.

5.2 Pipette 4.0 ml of curcumin reagent into each evaporating dish. Swirl the contents gently to mix, using long tongs to handle the two radioactive samples.

5.3 Place each evaporating dish on the bottom of the 250 or 400 ml wide-form beakers, using long tongs to handle the radioactive samples. Float the beakers in a water bath set at 55±2 °C.

5.4 Evaporate the contents of each evaporating dish to complete dryness and note the time of dryness for each sample.

5.5 Remove the evaporating dishes from the bath at 15 minutes after the contents appear dry and allow them to cool to room temperature.

5.6 Add approximately 10 ml of 95 percent isopropyl alcohol to each evaporating dish. Use a polyethylene rod to aid in dissolution of the red-colored reaction product and oxalic acid.

5.7 Using a medicine dropper, transfer the contents of the evaporating dishes to individual 25 ml volumetric flasks which have been previously rinsed with 95 percent alcohol. Rinse the evaporating dishes with 95 percent alcohol and add the contents to the flasks. Dilute the contents of each flask to 25.0 ml using 95 percent alcohol.

5.8 Within one hour of dissolution of the dried product (Step 5.6), measure the percent transmittance at 540 nm against the reagent blank (100 percent transmittance) and record the readings for each sample.

NOTE: If a solution appears turbid, filter through dry filter paper directly into a clean, dry spectrophotometer cell.

5.9 Plot the percent transmittance for the standards on the log axis of dual cycle semilogarimetric graph paper against concentration (linear axis). Draw the best fit straight line through the data points.

5.10 Determine the ppm boron in each sample from the calibration curve.

5.11 Calculate the average boron concentration for the duplicate samples.

5.12 Multiply the average boron level by the dilution factor to determine the sample boron concentration.

6.0 FINAL CONDITIONS

6.1 Ensure all sampling bottles and liquid samples have been properly disposed.

6.2 Secure water bath and spectrophotometer. Check the radiation level of the instruments and work area to ensure spillage of sample did not occur.

6.3 Clean work area as necessary to minimize residual radiation levels.

6.4 All workers should check their dosimeters to determine personnel exposure during the analysis.

TABLE IV-1

BASIS FOR FISSION - PRODUCT MATRIX SOLUTION

Fission Product	Radioactive Decay Constant, Sec^{-1} (1)	^{239}Pu Fission Yield, Atom/Fis. (1)	Percent Release	Calculated Moles per Liter (2)	Calculated ppm (3)
127-I	Stable	4.938 (-3)		7.236 (-5)	
128-I	4.621 (-4)	1.140 (-6)		6.437 (-13)	
129-I	1.304 (-15)	1.511 (-2)		2.214 (-4)	
130-I	1.298 (-3)	1.246 (-5)		2.505 (-12)	
131-I	9.977 (-7)	3.745 (-2)		9.794 (-6)	
132-I	8.426 (-5)	5.274 (-2)		1.633 (-7)	
133-I	9.257 (-6)	6.930 (-2)		1.953 (-6)	
134-I	2.196 (-4)	7.286 (-2)		8.657 (-8)	
135-I	2.924 (-5)	6.312 (-2)		5.632 (-7)	
Total	-		50%	3.063 (-4)	38.9
133-Cs	Stable	6.973 (-2)		6.131 (-4)	
134m-Cs	6.639 (-5)	1.650 (-6)		3.891 (-12)	
134-Cs	1.067 (-8)	3.290 (-6)		2.176 (-8)	
135-Cs	9.556 (-15)	7.473 (-2)		6.570 (-4)	
136-Cs	6.171 (-7)	1.055 (-3)		2.676 (-7)	
137-Cs	7.302 (-10)	6.692 (-2)		5.764 (-4)	
138-Cs	3.588 (-4)	5.454 (-2)		2.380 (-8)	
139-Cs	1.242 (-3)	5.187 (-2)		6.538 (-9)	
Total			30%	1.847 (-3)	246
134-Ba	Stable	3.310 (-6)		9.700 (-10)	
135m-Ba	6.709 (-6)	2.880 (-8)		2.240 (-14)	
135-Ba	Stable	7.473 (-2)		2.190 (-5)	
136-Ba	Stable	1.056 (-3)		3.095 (-7)	
137-Ba	Stable	6.695 (-2)		1.962 (-5)	
138-Ba	Stable	5.662 (-2)		1.659 (-5)	
139-Ba	1.387 (-4)	5.642 (-2)		2.123 (-9)	
140-Ba	6.273 (-7)	5.571 (-2)		4.634 (-7)	
141-Ba	6.313 (-4)	5.326 (-2)		4.402 (-10)	
142-Ba	1.080 (-3)	4.841 (-2)		2.339 (-10)	
Total			1%	5.889 (-5)	8.1
137-La	3.663 (-13)	4.720 (-9)		1.383 (-12)	
138-La	2.099 (-19)	1.210 (-7)		3.008 (-11)	
139-La	Stable	5.642 (-2)		1.653 (-5)	
140-La	4.786 (-6)	5.582 (-2)		6.086 (-8)	
141-La	4.975 (-5)	5.360 (-2)		5.622 (-9)	
142-La	1.250 (-4)	4.999 (-2)		2.087 (-9)	
Total			1%	1.660 (-5)	2.3

TABLE IV-1
BASIS FOR FISSION-PRODUCT MATRIX SOLUTION
PAGE 2

Fission Product	Radioactive Decay Constant, Sec^{-1} (1)	^{239}Pu Fission Yield, Atom/Fis. (1)	Percent Release	Calculated Moles per Liter (2)	Calculated ppm (3)
138-Ce	Stable	3.630 (-8)		1.064 (-11)	
139-Ce	5.835 (-8)	4.860 (-10)		4.182 (-14)	
140-Ce	Stable	5.582 (-2)		1.636 (-5)	
141-Ce	2.466 (-7)	5.360 (-2)		1.134 (-6)	
142-Ce	4.396 (-25)	5.001 (-2)		1.466 (-5)	
143-Ce	5.835 (-6)	4.558 (-2)		4.076 (-8)	
144-Ce	2.821 (-8)	3.833 (-2)		5.636 (-6)	
145-Ce	3.501 (-4)	3.075 (-2)		4.583 (-11)	
146-Ce	8.136 (-4)	2.524 (-2)		1.619 (-10)	
Total			1%	3.783 (-5)	5.3

NOTES:

(1) M. E. Meek and B. F. Rider, Compilation of Fission Product Yields. Pleasanton, California: General Electric Company, Vallecitos Nuclear Center, January 1974, NEDO-12154-1

(2) Based on chain fission yields at 650 days of operation for a 3391 Mw(t) core with a coolant volume of 11,892 ft^3 (no formation or removal via activation considered).

(3) Based on natural isotope.

TABLE IV-2

PLANT PARAMETERS USED IN ACCIDENT EVALUATION FOR MATRIX EFFECTS

Parameter		Value Used
Reactor Volume, $ft.^3$		11,892 ft^3
Additive During Accident:		
Type		30% NaOH
	Chloride Level	25-50 ppm[(a)]
	Volume, gal	4000
Water in Sump:		
	Source	RWST/Accumulators
	Volume, gal	400,000
	Chloride Level	<1 ppm[(b)]
Core Thermal Power		3,391 $MW_{(t)}$
Time at Power		650 days

(a) This is the chloride level in the spray additive tank solution determined in a series of measurements made in two PWR reactor plants.

(b) Based on the chloride inventory available in the spray additive tank solution. This could increase to 10 ppm or more from leaching action on insulation and cement.

TABLE IV-3

POST-ACCIDENT SOLUTIONS USED TO VERIFY ANALYTICAL PROCEDURES - FINAL TESTING PROGRAM

Test Solution	Purpose	ppm B	ppm Li^+	N NaOH	ppm I^-	ppm Cs^+	ppm Ba^{++}	ppm Ce^{+4}	ppm La^{+4}	ppm Cl^-	ppm NO_3^-	ppm NH_4^+	ppm K^+
VEP-A	To determine effect of Li on low boron	500	1.98	0	0	0	0	0	0	0	0	0	0
VEP-A1	1:1,000 dilution of VEP-A	0.50	2.0(-3)	0	0	0	0	0	0	0	0	0	0
VEP-B	To verify RWST without spray additive	2500	0	0	0	0	0	0	0	0	0	0	0
VEP-B1	1:1,000 dilution of VEP-B	2.5	0	0	0	0	0	0	0	0	0	0	0
VEP-C	To determine effect of spray additive (4000 gal.) on sump (100,000 gallon)	2000	0	0.38	0	0	0	0	0	0	0	0	0
VEP-C1	1:1,000 dilution of VEP-C	2.0	0	3.8(-4)	0	0	0	0	0	0	0	0	0
VEP-D	To determine effect of fission product matrix on low boron	500	1.98	0	39	246	8.1	5.3	2.3	1.8	136	1.4	12
VEP-D1	1:1,000 dilution of VEP-D	0.50	2.0(-3)	0	3.9(-2)	0.25	8.1(-3)	5.3(-3)	2.3(-3)	1.8(-3)	0.14	1.4(-3)	1.2(-2)
VEP-E	To determine effect of fission product matrix on borated RCS	2000	1.98	0	39	246	8.1	5.3	2.3	1.8	136	1.4	12
VEP-E1	1:1,000 dilution of VEP-E	2.0	2.0(-3)	0	3.9(-2)	0.25	8.1(-3)	5.3(-3)	2.3(-3)	1.8(-3)	0.14	1.4(-3)	1.26(-2)
VEP-F	To determine effect of RWST (400,000 gallon) with spray additive (4000 gal.) in sump with chlorides	2000	0	0.098	0	0	0	0	0	100	0	0	0
VEP-F1	1:1,000 dilution of 2.0 VEP-F	2.0	0	9.8(-5)	0	0	0	0	0	0.10	0	0	0

TABLE IV-3
POST-ACCIDENT MATRIX SOLUTION USED TO VERIFY ANALYTICAL PROCEDURES
PAGE 2

Test Solution	Purpose	ppm B	ppm Li^+	N NaOH	ppm I^-	ppm Cs^+	ppm Ba^{++}	ppm Ce^{+4}	ppm La^{+4}	ppm Cl^-	ppm NO_3^-	ppm NH_4^+	ppm K^+
VEP-G	To determine effect of RWST (400,000 gal.) with spray additive (4000 gal.) in sump with chlorides mixed with RCS (89,000 gal.)	2000	0.36	0.080	7.0	44	1.5	1.0	0.42	82	25	0.25	2.2
VEP-G1	1:1,000 dilution of VEP-G	2.0	3.6(-4)	8.0(-5)	7.0(-3)	4.4(-2)	1.5(-3)	1.0(-3)	4.2(-4)	8.2(-2)	2.5(-2)	2.5(-4)	2.2(-3)

TABLE IV-4

REACTOR COOLANT MATRIX SAMPLES ANALYZED FOR BORON USING THE FLUOROBORATE SELECTIVE ION ELECTRODE - INITIAL TESTING PROGRAM

		Concentration in Parts Per Million (ppm) By Weight						
Simulation	**Solution**	**B**	**$^{7}Li^{+}$**	**NaOH**	**I^{-}**	**Ba^{++}**	**Cs^{+}**	**Ce^{+4}**
1:1000 Dilution of Reactor Coolant	B	2.0(a)	2.0E-3	0	1.2E-3	1.8E-4	6.3E-3	1.6E-4
	D	2.0(a)	2.0E-3	0	1.2E-3	1.8E-4	6.3E-3	1.6E-4
	F	2.0(a)	2.0E-3	0	1.2E-3	1.8E-4	6.3E-3	1.6E-4
	H	2.0(a)	2.0E-3	0	1.2E-3	1.8E-4	6.3E-3	1.6E-4
1:1000 Dilution of 400,000 Gal. RWST + 4,000 Gal. 30% NaOH Mixed with Reactor Coolant in Sump	J	2.0(a)	0	3.92	0	0	0	0
	L	2.0(a)	2.7E-4	3.38	1.6E-4	2.5E-5	8.7E-4	2.2E-5
	N	2.0(a)	2.7E-4	3.38	1.6E-4	2.5E-5	8.7E-4	2.2E-5
	P	2.0(a)	2.7E-4	3.38	1.6E-4	2.5E-5	8.7E-4	2.2E-5
1:200 Dilution of BWR Reactor Water	X	0.46(b)	0	0	0	0	0	0
	Z	0.46(b)	0	0	8.7(E-4)	1.3(E-4)	4.6(E-3)	1.2(E-4)
	BB	0.46(b)	0	0	8.7(E-4)	1.3(E-4)	4.6(E-3)	1.2(E-4)
	DD	0.46(b)	0	0	8.7(E-4)	1.3(E-4)	4.6(E-3)	1.2(E-4)
	FF	0.46(b)	0	0	8.7(E-4)	1.3(E-4)	4.6(E-3)	1.2(E-4)

(a) As H_3BO_3
(b) As $Na_2B_{10}O_{16} \cdot 10H_2O$

TABLE IV-5

MILLIVOLT RESPONSES FOR ORION 93-05
FLUOROBORATE SELECTIVE ION ELECTRODE TO STANDARD BORON SOLUTION

(All responses recorded after 10.0 minutes after acid addition.)

Test		Reference Probe	0	Δ_5	0.5	Δ_5	1.0	Δ_5	2.0	Δ_5	3.0	Δ_5	5.0	Date
5.0 ml sample, 1.0 ml Sat. NaF		IAN Gel	212.3	-18.6	215.1	-21.4	211.9	-8.2	206.3	-12.6	202.1	-8.4	193.7	5-30-80
0.5 ml 12 $\underline{N}$ HCl		Orion Double Junct.	136.2	-13.1	137.3	-14.2	137.3	-14.2	134.0	-10.9	130.3	-7.2	123.1	5-30-80
		Orion Single Junct.	256.2	-35.1	250.1	-29.0	245.2	-24.1	236.6	-15.5	229.9	-8.8	221.1	5-30-80
5.0 ml sample, 1.0 ml Sat. NaF, 0.5 ml 10 $\underline{N}$ H_2SO_4		IAN Gel	260.0	-50.8	262.7	-45.5	252.8	-35.6	239.2	-22.0	230.9	-13.7	217.2	5-30-80
			271.6	-56.9	257.6	-42.9	246.5	-31.8	234.2	-19.5	225.1	-10.4	214.7	6-02-80
		Orion Double Junct.	215.3	-60.6	204.9	-50.2	189.0	-34.3	177.1	-22.4	167.5	-12.8	154.7	5-30-80
			195.6	-46.4	188.5	-39.3	180.8	-31.6	168.3	-19.1	161.4	-12.2	149.2	6-02-80
(Operator 1)	1	Orion Single Junct., A	292.1	-56.1	285.1	-49.1	274.2	-38.2	258.7	-22.7	248.7	-12.7	236.0	5-30-80
	2		302.5	-65.7	289.0	-52.2	275.4	-38.6	259.1	-22.3	248.0	-10.2	236.8	6-02-80
	3		294.6	-58.5	286.2	-50.1	274.7	-38.6	258.8	-22.7	249.4	-13.3	236.1	6-02-80
	4		296.6	-57.9	286.2	-49.6	275.1	-38.5	259.6-23.0248.7-12.1236.66-02-80					
(Operator 2)	5	Orion Single Junct., A	297.1	-55.4	290.1	-48.4	280.2	-38.5	266.1	-24.4	255.3	-13.6	241.7	6-09-80
	6		297.9	-59.3	285.2	-46.6	274.0	-35.4	259.9	-21.3	251.2	-12.6	239.6	6-09-80
	7		296.5	-58.3	285.8	-47.6	277.1	-38.9	260.3	-22.1	250.7	-12.5	238.2	6-09-80
	8		302.5	-62.0	286.6	-46.1	276.6	-36.1	260.8	-20.3	251.4	-10.9	240.5	6-10-80
	9		295.7	-56.8	286.1	-47.2	273.9	-35.0	260.4	-21.5	251.5	-12.6	238.9	6-10-80
(Operator 2)	10	Orion Single Junct., B	-	-	291.0	-48.4	281.3	-39.1	263.2	-21.0	253.1	-10.9	242.2	6-06-80
$\bar{X}$*, mV			297.1	-58.9	287.1	-48.5	276.3	-37.7	260.7	-22.1	250.8	-12.2	238.6	
Std. Dev.*, mV			±3.5	±3.2	±2.1	±1.8	±2.6	±1.6	±2.3	±1.2	±2.2	±1.0	±2.3	
% for Indicated Boron Level at 95%			-	-	-	+34,-24		+18,-14		+15,-5.0		+13,-3.3		

---

* For 10 data sets with the Orion single junction reference cell with sulfuric acid catalyst.

TABLE IV-6

ANALYSIS RESULTS FOR DILUTIONS OF REACTOR WATER FOR DIFFERENT MATRIX CONDITIONS (DETERMINED DURING CALIBRATIONS)

Date	Standard Curve Used	Sample	ppm Boron	Measured mV	Measured ppm Boron	Comment
May 30, 1980	1	B	2.00	259.0	1.98	
June 9, 1980	5	B	2.00	259.0	2.62	Electrode used after being dry for about a week - drift noted.
		F	2.00	260.6	2.48	
		H	2.00	264.7	2.01	
June 9, 1980	6	H	2.00	259.2	2.10	
		J	2.00	259.1	2.12	
		L	2.00	259.3	2.08	
June 9, 1980	7	BB	0.46	282.1	0.62	Run after 5 ppm standard.
		DD	0.46	285.0	0.52	
		FF	0.46	284.9	0.53	
		Z	0.46	285.7	0.50	
June 10, 1980	8	BB	0.46	284.4	0.66	
		DD	0.46	285.4	0.63	
		FF	0.46	284.8	0.65	
		Z	0.46	286.8	0.58	
		B	2.00	259.7	2.18	
		F	2.00	260.3	2.10	
June 10, 1980	9	B	2.00	258.7	2.20	
		F	2.00	259.7	2.10	
		H	2.00	259.9	2.09	
		BB	0.46	286.2	0.49	
		DD	0.46	287.5	0.45	
		H	0.46	261.3	1.95	
Avg. (S.D.)			2.00	260.0 (±1.6)	2.15 (±.19)	
Avg. (S.D.)			0.46	285.3 (±1.5)	0.56 (±0.07)	

TABLE IV-7

ANALYSIS RESULTS FOR DILUTIONS OF POST-ACCIDENT MATRIX SOLUTIONS USING RECOMMENDED ANALYSIS PROCEDURE

Sample	Actual ppm Boron	Standard Used to Adjust Meter to Calibration Curve	Measured mV	Measured ppm Boron
VEP-A1	0.50	0.50 (287.1 mV)	(a) 286.9	0.51
			(b) 284.9	0.59
VEP-B1	2.5	3.0 (251.4 mV)	(a) 256.2	2.48
			(b) 255.0	2.60
VEP-C1	2.0	2.0 (261.3 mV)	(a) 260.2	2.10
			(b) 262.6	1.90
VEP-D1	0.50	0.50 (287.1 mV)	(a) 288.7	0.44
			(b) 286.1	0.54
VEP-E1	2.0	2.0 (261.3 mV)	(a) 261.5	2.00
			(b) 260.5	2.06
VEP-F1	2.0	2.0 (261.3 mV)	(a) 262.4	1.91
			(b) 261.5	1.98
VEP-G1	2.0	2.0 (261.3 mV)	(a) 262.1	1.94
			(b) 262.0	1.95

TABLE IV-8

BORON ANALYSIS RESULTS IONICS STANDARDS

Sample Type	ppm Boron	Analysis Results	ppm Error		% Error	
			Avg	Max	Avg	Max
Boric Acid	5000	4953,4956,4941	-50	-59	-1.0	-1.18
Boric Acid	3243	3174,3178,3177,3176	-67	-69	-2.06	-2.12
Boric Acid	1000	1011,993,986,1023, 1019,1000,1003,1001 1009,1012,1009	6	19	0.6	1.9
Basic Boron	500	515,515,513	14	15	2.8	3.0
Boric Acid	200	203,202,202	2	3	1.0	1.5
Boric Acid	50	50,49,49	- 1	- 1	-2.0	-2.0

*A 20 ppm blank is subtracted from results.

TABLE IV-9

BORON REPRODUCIBILITY RESULTS
2000 ppm IONICS STANDARD

Analysis Results	ppm DEV	% Error	Analysis Results	ppm DEV	% Error
1975	-25	-1.25	1975	-25	-1.25
1977	-23	-1.15	1975	-25	-1.25
1973	-27	-1.35	1975	-25	-1.25
1974	-26	-1.3	1975	-25	-1.25
1974	-26	-1.3	1974	-26	-1.3
1977	-23	-1.15	1975	-25	-1.25
1977	- 3	- .15	1977	-23	-1.15
1975	-25	-1.25	1977	-23	-1.15
1975	-25	-1.25	1998	- 2	-0.1
1973	-27	-1.35	2000	0	0
1973	-27	-1.35	1974	-26	-1.3
1973	-27	-1.35	1978	-22	-1.1
1979	-21	-1.05	1981	-19	-0.95
1976	- 4	- .2	1977	-23	-1.15
1973	-27	-1.35	1977	-23	-1.15
1974	-26	-1.3	1977	-23	-1.15
1973	-27	-1.35	1978	-22	-1.1
1973	-27	-1.35	1981	-19	-0.95
1974	-26	-1.3	1982	-18	-0.9
1975	-25	-1.25	1977	-23	-1.15
1974	-26	-1.3	1978	-22	-1.1
1974	-26	-1.3	1978	-22	-1.1
2002	2	0.1	1977	-23	-1.15
1974	-26	-1.3	1981	-19	-0.95
			1974	-26	-1.3

Average error = -1.05%
Maximum error = -1.35%

TABLE IV-10

BORON ANALYSIS RESULTS
NUS POST-ACCIDENT MATRICES

Sample Type	ppm Boron	Analysis Results*	ppm Error		% Error	
			Avg	Max	Avg	Max
Boric acid VEP-A	500	508,512	10	12	2.0	2.4
Basic boron VEP-C	2000	1973,2001,1996	-10	-27	-0.5	-1.35
Basic boron VEP-F	2000	2013,2015	14	15	0.7	0.7
Boric acid - Matrix VEP-D	500	526,518	22	26	4.4	5.2
Boric acid - Matrix VEP-E	2000	2001,2007	4	7	0.2	0.35
Boric acid - Matrix VEP-B	2000	2012,2011	12	12	0.6	0.6
Boric acid	5000	4925,4933,4938	-68	-75	-1.36	-1.5
Boric acid VEP-B	2500	2456,2462	-41	-44	-1.64	-1.76
Boric acid	1000	1034,1028	31	34	3.1	3.4
Boric acid	100	99,97	- 2	- 3	-2.0	-3.0

*A 20 ppm blank is subtracted from results.

Note: See Table IV-3 for composition of matrix solutions.

FIGURE IV - 1

FLUOROBORATE ELECTRODE RESPONSES: 5.0 ml SAMPLE, 1.0 SATURATED SODIUM FLUORIDE, 0.5 ml 12 N HYDROCHLORIC ACID; RESPONSES RECORDED AT 10.0 MINUTES (5/30/80)

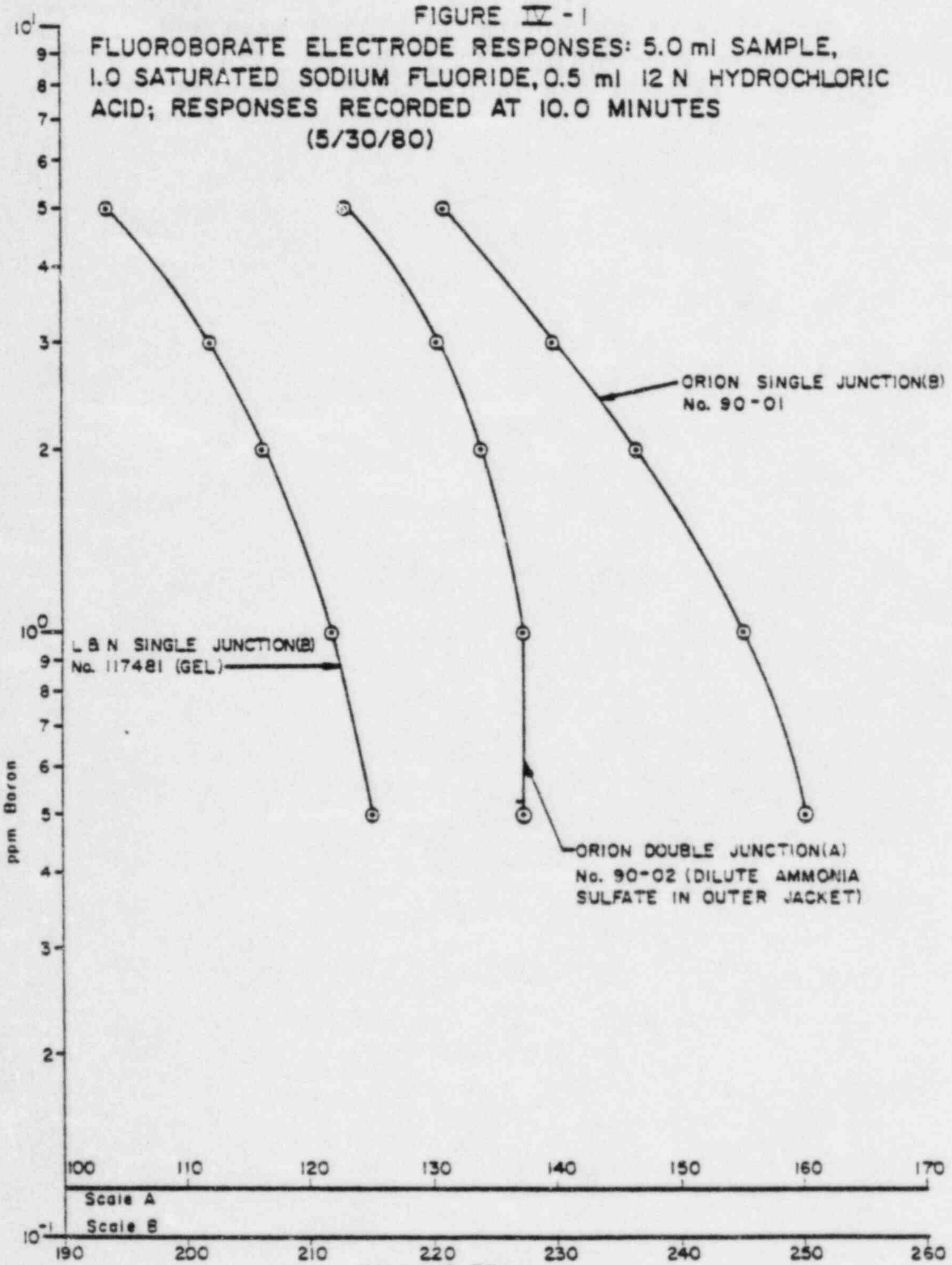


FIGURE IV-2

FLUOROBORATE ELECTRODE RESPONSES: 5.0 ml SAMPLE, 1.0 ml SATURATED SODIUM FLUORIDE, 0.5 ml 10 N SULFURIC ACID; RESPONSES RECORDED AT 10.0 MINUTES (5-30-80)

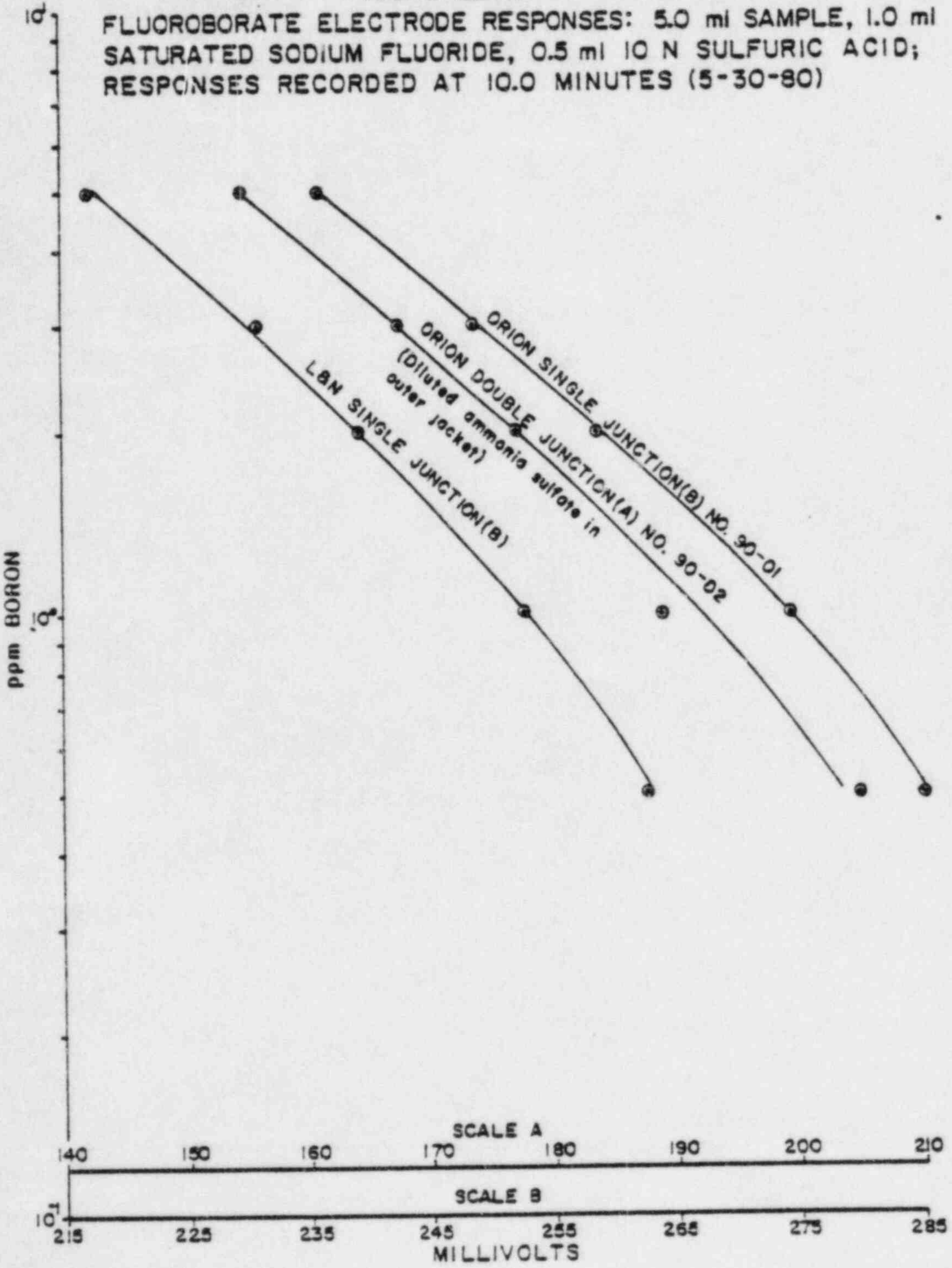
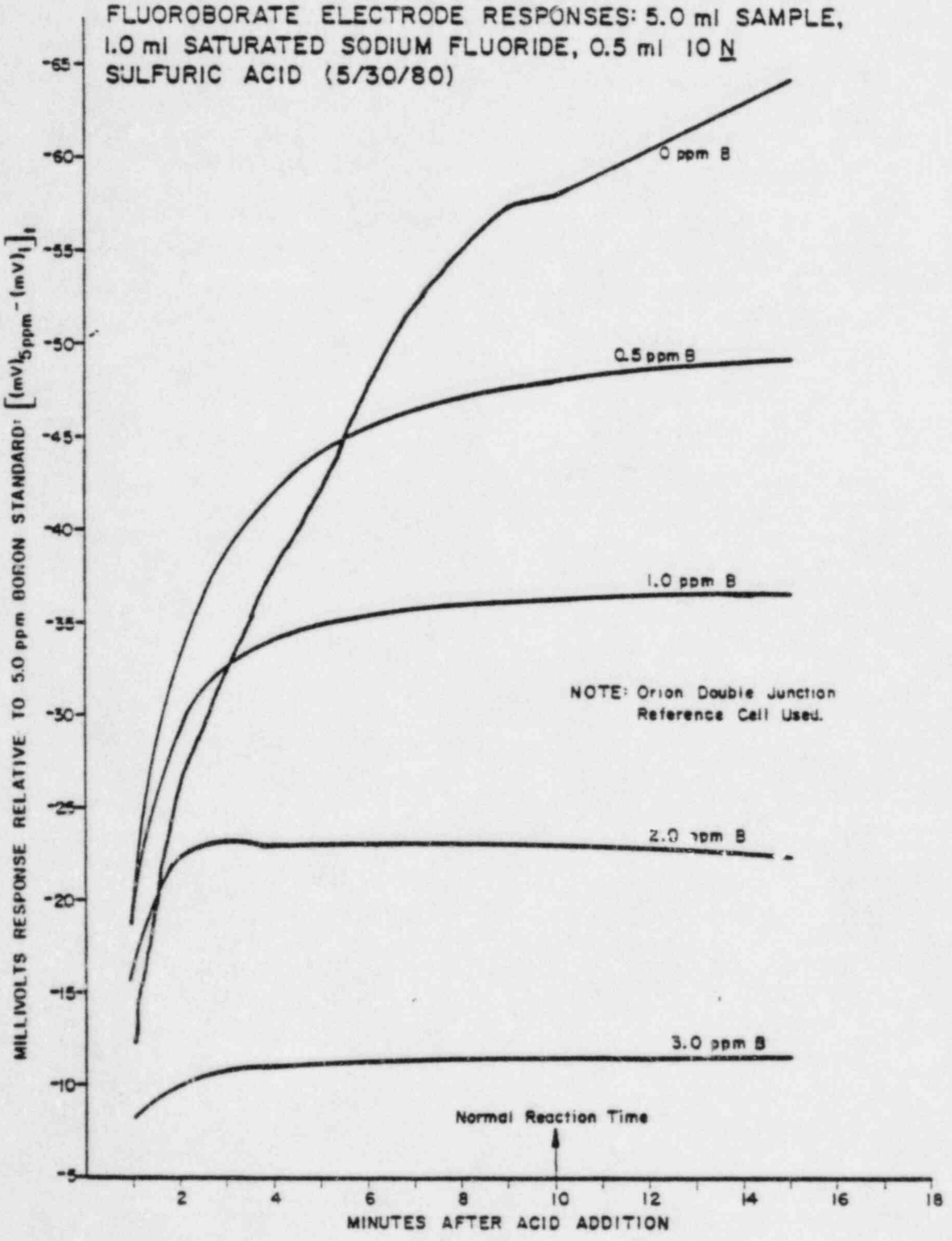


FIGURE IV-3
FLUOROBORATE ELECTRODE RESPONSES: 5.0 ml SAMPLE, 1.0 ml SATURATED SODIUM FLUORIDE, 0.5 ml 10 N SULFURIC ACID (5/30/80)



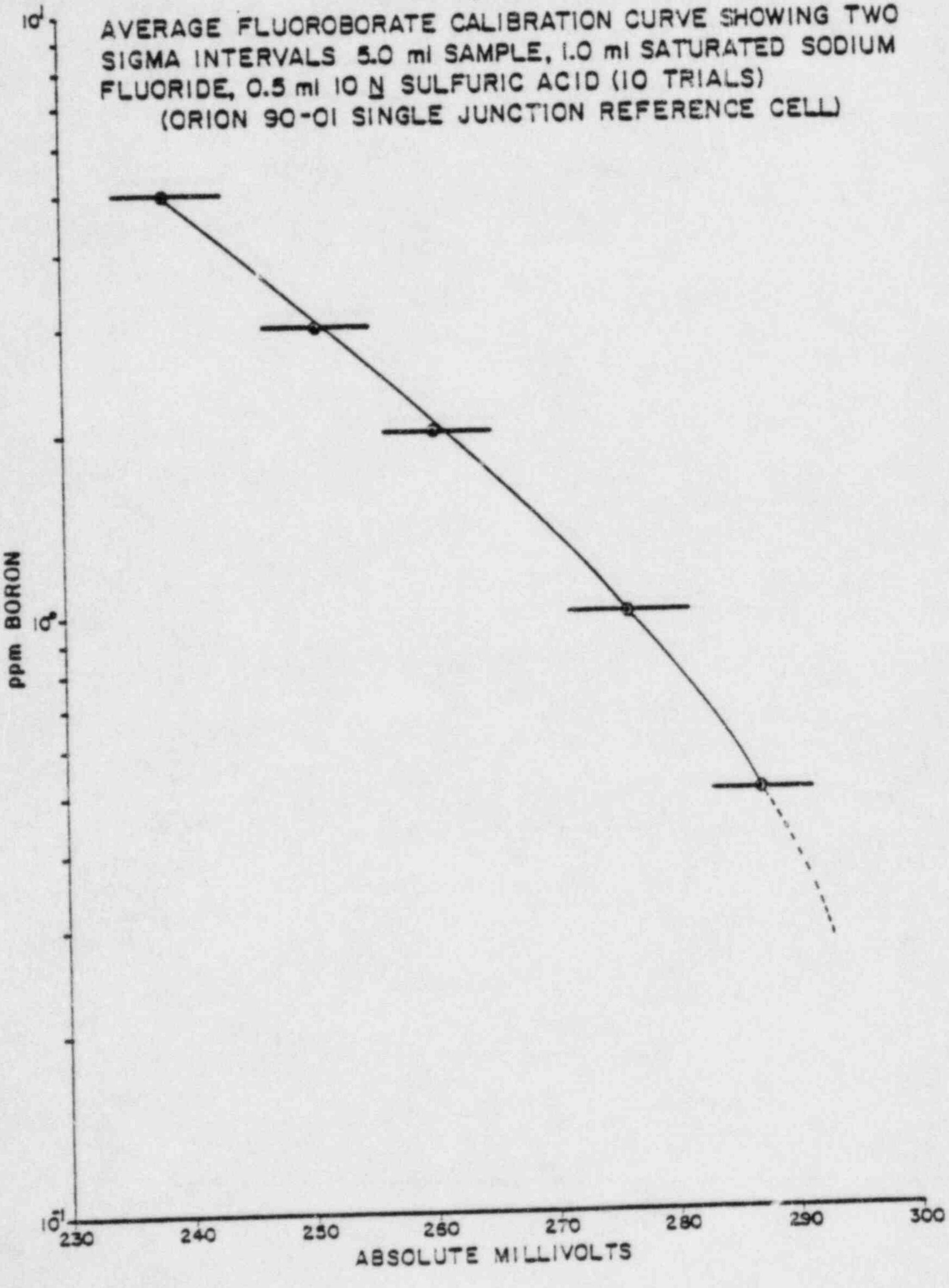
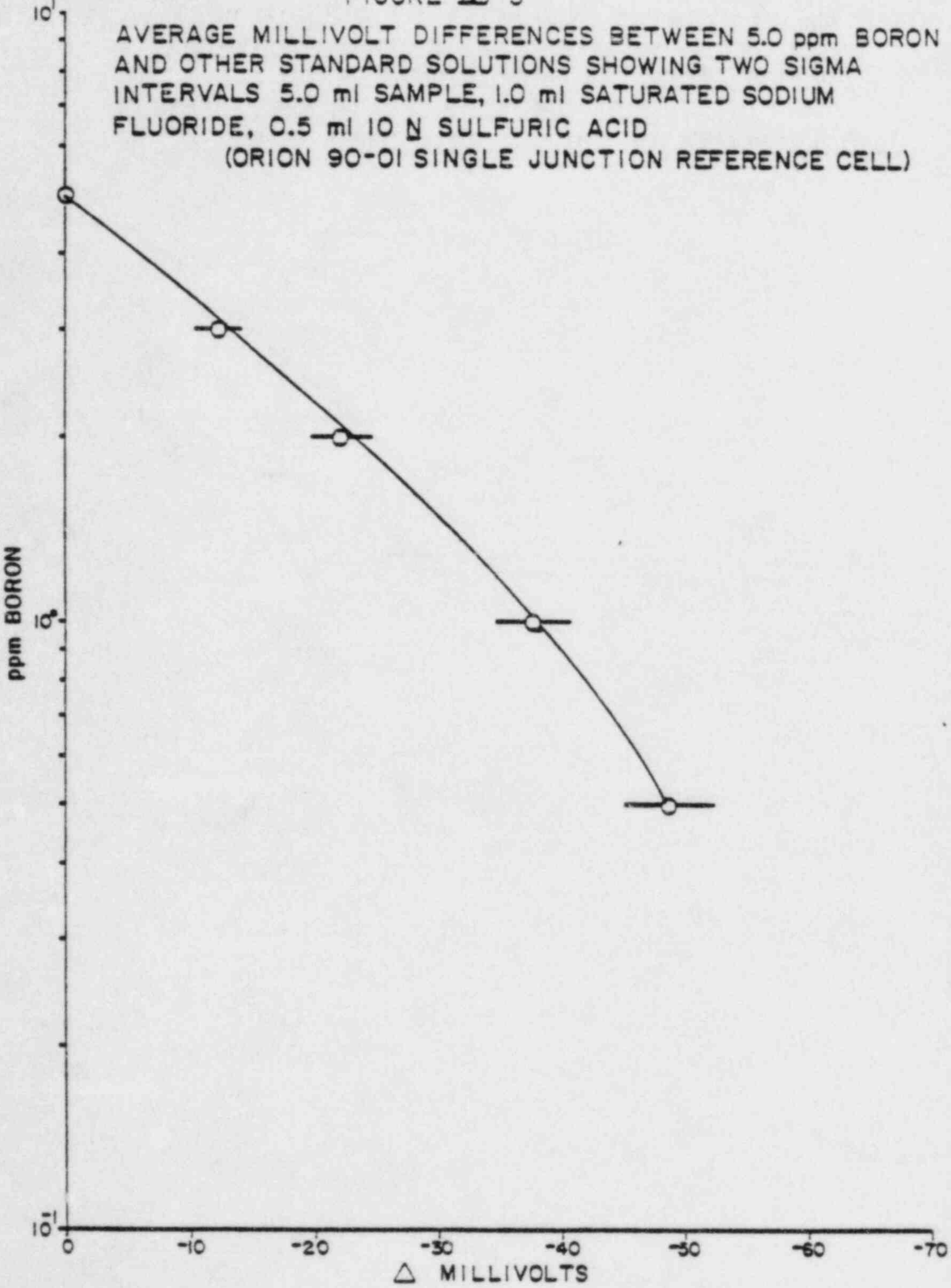
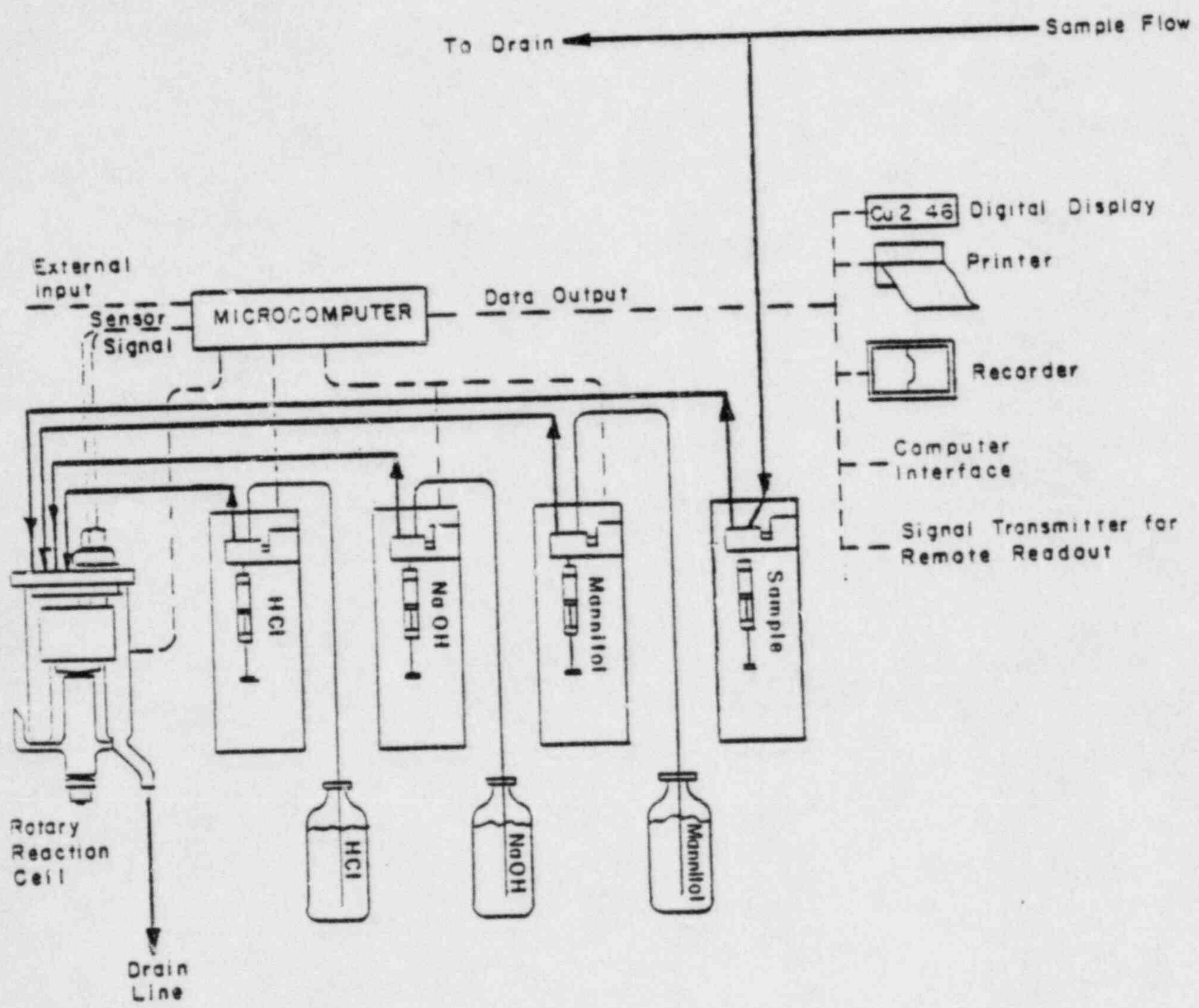


FIGURE IV-4
AVERAGE FLUOROBORATE CALIBRATION CURVE SHOWING TWO SIGMA INTERVALS 5.0 ml SAMPLE, 1.0 ml SATURATED SODIUM FLUORIDE, 0.5 ml 10 N SULFURIC ACID (10 TRIALS)
(ORION 90-01 SINGLE JUNCTION REFERENCE CELL)

FIGURE IV-5

AVERAGE MILLIVOLT DIFFERENCES BETWEEN 5.0 ppm BORON AND OTHER STANDARD SOLUTIONS SHOWING TWO SIGMA INTERVALS 5.0 ml SAMPLE, 1.0 ml SATURATED SODIUM FLUORIDE, 0.5 ml 10 N SULFURIC ACID (ORION 90-01 SINGLE JUNCTION REFERENCE CELL)





Simplified Flow Diagram of the Digi Chem Analyzer
FIGURE IV-6

V. CHLORIDE ANALYSIS DEVELOPMENT

A. ION CHROMATOGRAPH ANALYSES

Ion chromatograph (IC) analysis is based on ion exchange separation of the anions causing the sample anions of different species to split into distinct bands. The retention time of each anion species is governed by the affinity of that ion for the active site, the eluent used, the length of column, and the eluent flow rate. The effluent from the separator column is then fed to the suppressor column. The suppressor column resin (a strong acid resin in hydrogen form) removes Li^+, Na^+ and all other cations except hydrogen ion. Then, all the sample anions exit sequentially in wave form from the suppressor column as an acid since the sample cations are exchanged for H^+ in the suppressor.

$$Na^+X^- + R\text{-}H \rightarrow R\text{-}Na + H^+X^-$$

Solution from the suppressor column is passed through a conductivity cell and the resulting conductivity changes are recorded as peaks on a recorder. Peak height is proportional to the anion concentration present.

Both anion and cation analyses can be performed by IC. Only anion analyses are performed in this application since chloride is the item of concern. All anions which form relatively strong acids (e.g., Cl, F, SO_4, PO_4, etc.) can be determined quantitatively with IC. Typically, anion analysis are performed with an eluent containing 0.003M sodium bicarbonate/0.0024 molar sodium carbonate. This eluent could not be used in this application because it did not separate the borate and chloride peaks.

1. Model 10 Dionex Ion Chromatograph

It was determined that this instrument, combined with an externally attached strip chart recorder, can be used for in-line chloride analysis under normal or post-accident conditions. The IC contains eluents, regeneration solution, demineralized water, an eluent pump, a regenerant pump, a sample injector, an anion separator column, anion suppressor column, a conductimetric detector and meter, and an instrument control panel. Air operated valves are used for liquid control. The flow scheme is shown in Figure V-1.

The suppressor column is regenerated twice per day when used continually in this application. An automated system pumps regenerant solution (1<u>N</u> H_2SO_4) through the resin followed by rinse water. Regeneration flow is opposite to normal flow.

2. <u>Initial Developmental Effort</u>

Test solutions used simulated actual solutions expected during post-accident conditions (e.g., up to 2000 ppm B as boric acid in acid and basic matrices with the addition of simulated fission products). Various concentrations of chloride from 0.1 ppm to 10.0 ppm were added to these solutions for subsequent analysis. A list of solutions prepared and subsequently analyzed is given in Table V-1.

Initial testing was performed using a standard three-column system and a sodium carbonate/bicarbonate eluent. This approach proved unsuccessful because of overlapping between the boron and chloride peaks. Both peaks occurred at approximately three minutes after injection. The problem was corrected after an intensive investigative effort resulting in the following system changes:

a. The 3 x 150 mm precolumn was removed

b. The 3 x 500 mm anion separator column was changed to a 3 x 250 mm anion separator column.

c. The eluent was changed to 0.005<u>M</u> sodium tetraborate ($Na_2B_4O_7$).

3. Test Results

With the modified system, the borate peak occurs at about two minutes and the chloride peak at six minutes. Reasonable linearity and duplication of results were initially achieved as shown in Tables V-2 through V-5; however, problems developed with continued operation of the system. Chloride concentration determinations deviated from linearity (Tables V-2 and V-3), and the time required for the chloride peak to develop progressively decreased. The problem was corrected with installation of new columns. Subsequent information developed as discussed below indicate that the problem could have been prevented in its entirety.

The sodium tetraborate solution used for elution is very weakly ionized, and consequently does not easily displace the more tightly held anions (e.g., iodide) from the separator column. As a consequence, the availability of ion-exchange sites of the separator column decreases with time in operation. Poor retention qualities result and the time required for anions to move through the bed is decreased. Also, as ion-exchange capacity decreases, there is intermittent bleed-through of the tightly held ions. This bleed-through results in an erratic base line. Correction of this problem was achieved by addition of a strong base eluent to the system to clean the columns on a daily base. A 0.006 molar sodium carbonate solution is now flushed through the system prior to regeneration at the end of the day. The carbonate ion will displace anions such as iodide. Using this treatment followed by regeneration of the suppressor with sulfuric acid returns the columns to a like-new condition. Conductivity baseline conditions have substantially improved with this mode of operation.

The columns that had been replaced were reinstalled and treated with sodium carbonate eluent followed by regeneration. Complete recovery of the columns was achieved with respect to linearity and reproducibility of results using this treatment. However, absolute values for peak heights for standard solutions were diminished from new column values.

In the work performed with the two sets of columns it was noted that a slightly different response was observed with respect to peak height and retention time when the columns were changed. The consequence of this development is that new calibration curves will need to be developed when resin columns are replaced. The resin columns should be replaced every year.

The calibration curves obtained with the new (Curve 1) versus old columns (Curve 2) are shown in Figure V-2. Excellent linearity was obtained with both sets of columns; however; it is noted that the slopes are different with the two sets of columns. Figures V-3 and V-4 show the chromatograms obtained for two points on Curve No. 2 in Figure V-2.

The results indicate that in matrices up to 2,000 ppm boron (acidic or basic solutions) with fission products present, good chloride analyses are obtained. Evaluation of this data is based on calibration Curve No. 1 in Figure V-2. Deviation of actual sample chloride concentration from analysis results varies about ±15 percent in the range of 0.1 - 1.0 ppm chloride ion and 20-25 percent for higher chloride concentrations. Variability increases at the higher chloride concentration because peak height is not linear with change in attenuation. However, variability can be reduced if calibration operations are performed at the same attenuation as used for the analyses.

Similar sample data were obtained for samples analyzed with the old, reconditioned columns. These data are listed in Table V-5. Although the slope of the calibration curve differs from that obtained for new columns (Figure V-2), accuracy of results was the same as that obtained with the new columns.

4. Other Ion Chromatograph Test Work

During post-accident conditions involving primary coolant release many contaminants can exist in the coolant through recirculation with sump water. Species which could conceivably be found in this water include the following:

Morpholine
Hydrazine
Ammonia
Natural and synthetic oils

Testing was performed to determine if these contaminants would affect chloride determinations with the ion chromatograph. In addition to this, testing was also performed to determine if the ion-chromatograph can be used to perform low-level fluoride analyses on a routine basis. Results of this work are reported below.

a. Morpholine, Hydrazine and Ammonia

A 5 ppm morpholine standard and a 200 ppm hydrazine standard were analyzed by ion chromatography. Figures V-5 and V-6 show the chromatograms obtained from these samples. No chloride peak was noted in either sample. It was also determined that the presence of hydrazine will not affect results where chloride is present. A test solution containing 2000 ppm B plus 1 ppm Cl and fission products was analyzed alone and after adding 3 ml of a 1,000 ppm hydrazine standard to 10 ml of the chloride standard. Results shown in Figure V-7 indicate that the reduction in peak height noted with the hydrazine is directly proportional to dilution effect occurring from addition of the hydrazine solution.

One sample of water containing ammonia was tested. As expected, no change in baseline conductivity was noted at any time after injection. Ammonia is removed in the strong cation suppressor column with the resulting formation of pure water.

b. Oil

Two oils were tested for their effects on chloride analysis, (1) a natural oil (Gulf Pride 10W40) and (2) a synthetic oil (Mobil 1). In this work, oil was added to a basic boron solution containing a known amount of chloride and agitated vigorously for 15 minutes. After standing for 30 minutes, the solution was briefly agitated again, and a sample was drawn off the bottom for analyses after the solution was allowed to stand for five minutes. Only basic solutions were evaluated because oil contamination could only be present when there is release of reactor coolant to the containment. Under these conditions, the coolant will be basic because of the release of caustic spray to the containment. The following information was obtained from these tests:

(1) The addition of both oils increases the chloride results for standard solutions obtained by about 10 - 30 percent. This result could well be due to chlorides present in the oils; however, this was not verified by independent test.

(2) The time for the chloride peak to emerge is progressively reduced indicating adverse effect to the columns. Organics, and in particular oils, are known to be harmful to resins and it can be assumed that the presence of oil contamination will shorten column life.

(3) At least 10 to 15 oil contaminated samples could be analyzed under post-accident conditions without significantly affecting results.

Table V-6 lists the data obtained by analyzing Solution 1 (basic boron containing 1 ppm Cl and simulated fission products) with and without both types of oils. Chromatograms of Solution 1 alone and Solution 1 with the addition of the synthetic oil are shown in Figures V-8 and V-9 respectively. Inspection of the tables and figures show the higher value for chloride obtained after oil addition. Subsequent oil-free chloride standards analyzed also showed higher peak heights indicating that there is a memory effect associated with oil contamination.

Regeneration of the columns after analyses of the oil-contaminated samples was performed by first injecting two, 3-ml acetone rinses to the system, followed by a 15 minute sodium carbonate flush, and then normal regeneration. Regeneration after the natural oil runs resulted in a return of the calibration curve to the same slope that was obtained prior to the sample runs. Regeneration did not result in complete recovery of original calibration results after the synthetic oil samples. However, good linearity with different curve slope and reproducible results were achieved after regeneration. Samples analyzed prior to regeneration indicate that there was more of a memory effect with the synthetic oil than with the natural oil. Apparently, synthetic oils are more damaging to resins than are natural oils.

c. Fluoride

Chromatograms obtained from analyzing pure NaF standards of 25, 50, 100, and 200 ppb F are shown in Figure V-10. The fluoride peak occurs at 1.5 minutes (almost a single line). The peak initiates at the negative dip in the baseline when only water passes through the conductivity cell. The presence of this negative dip prevents accurate determination of fluoride levels below 25 ppb. Good linearity was obtained as indicated in the calibration curve shown in Figure V-11.

Samples were also prepared with various F^- concentrations (25-200 ppb F) in 100 ppm and 1 ppm B matrices. The F^- concentrations were determined by ion chromatography using the calibration curve shown in Figure V-11 as the reference standard. Table V-7 lists the data obtained. Good agreement was achieved between indicated and known values of standards. These data indicate that it is feasible to perform F^- analysis in boron matrices containing up to 100 ppm boron. Lower limits of detection for F^- are about 25 ppb. Accuracy of analyses is about ±10 percent. Typical chromatograms for F^- in a low level boron matrix are shown in Figure V-12.

Attempts made to analyze F^- concentrations in solutions containing high level boron concentrations were unsuccessful. There is overlap between the F^- and boron peaks. No problem was noted at low level boron concentrations because the 100 ppm boron solution does not yield a significant peak height.

Results of this work indicate that ion chromatography could be used to analyze for F^- concentrations in a BWR under routine conditions down to perhaps 25-50 ppb levels. No apparent application for F^- determination is evident for PWR's.

d. Iodide

An interest had been expressed by Commonwealth Edison concerning the feasibility of ion chromatograph analyses of primary coolant for radioactive iodine determinations. This holds some promise in theory, since the iodine is released at a later time from the columns than is chloride. Iodine can be present at concentrations in the range of 20-40 ppm under reference accident conditions; therefore it should be in the detectable range with ion chromatograph.

A series of tests were performed using standard solutions containing 0.5 to 100 ppm iodide. No iodide peak could be detected at the low end of the range. There was some release of iodide at the high end of the range, but it was not in peak form as required to obtain an iodide determination.

5. Summary of the Chloride Analysis Development Effort

a. The ion chromatograph columns required for chloride analyses in the presence of boron are:

   3 x 250 mm anion separator column
   6 x 250 mm anion suppressor column

b. A 0.005 molar sodium tetraborate solution is required as an eluent.

c. Regeneration is required about once every four hours during continuous operation of the system.

d. During continuous operation of the system, the columns must be cleaned on a daily basis or every other regeneration by pumping 0.006 molar sodium carbonate solution through the columns for a 15-20 minute period. This is done prior to regeneration of the suppressor column.

e. The calibration curve should be checked once every four samples by analyzing a chloride standard.

f. New calibration curves are required when columns are changed, since each set of columns will show slightly different results with respect to peak height and possibly retention time.

g. Calibration should be checked after making up new eluent. Results will differ if the concentration of the new eluent differs from the old.

h. Retention time for any ionic species will vary with pump stroke setting. Pump stroke should remain constant for routine analytical use.

i. The system is not linear between ranges. Deviation from linearity results because of the inherent limitations associated with using one conductivity cell constant for measuring dilute and concentrated solutions. Accuracy can be improved if calibration and analyses are performed in the same range.

j. There is a memory effect resulting in higher chloride peak levels associated with analyses of oil contaminated samples. This memory effect is more pronounced with synthetic oils. Cleaning of the columns with a sodium carbonate flush followed by regeneration is required to return the columns to their original condition.

B. SELECTIVE ION ELECTRODE (SIE)

The selective ion electrode (SIE) can provide for rapid and accurate determinations of chloride levels under certain conditions. Essentially, the method involves adjusting the pH to approximately 2 to 4 and measuring the SIE response relative to a reference cell. The response in millivolts is related to the chloride level (i.e., for every decade change in chloride concentration the response should change by about -59 millivolts under ideal conditions).

In the investigative work performed, NUS selected Graphic Controls Model PHI 91100 Ultra-Sensitive Solid State Chloride Electrode for this study. A double-junction reference cell, Graphic Controls No. GC 54473, was used in place of the conventional silver/silver chloride reference cell to eliminate chloride contamination from the reference cell fill solution (4 M potassium chloride saturated with silver chloride). This particular electrode system will distinguish 10 ppb chloride from pure water, and has a working range up to about 1.0 M chloride.

To use the system, about 1.0 ml of 2.0 M nitric acid is added to 100 ml of sample to adjust the pH and ionic strength and the electrode system response is recorded after it has stabilized. Moderate stirring is required. The response in millivolts is related to the chloride concentration.

Because the post-accident reactor water will contain iodide at a significant level, direct measurement of chloride is not feasible. The following sections discuss removal of this interference and analysis of the matrix solutions.

1. Iodide Oxidation by Hydrogen Peroxide

Table V-8 shows the Graphic Controls electrode response to iodide levels. Table V-9 gives the response to standard chloride solutions and the response to these solutions with 0.99 ppm iodide. Note that as the chloride level increases, the interference from 0.99 ppm iodide is less significant. Other calibration data are given in Table V-10. One method of minimizing the iodide interference is to oxidize iodide to iodate. In acidic solutions, hydrogen peroxide will effect the desired oxidation. Figure V-13 shows that 4.0 ml of 30 percent hydrogen peroxide will result in a stable electrode response within eight minutes. Tests showed that lower peroxide additions result in much longer reaction times.

Table V-9 also gives the apparent chloride levels of the standards after iodide oxidation. The data shows that in the presence of 0.99 ppm iodide, chloride levels cannot be accurately measured after hydrogen peroxide treatment. These measurements are illustrated in Figure V-14.

Figure V-15 shows the electrode system response to the chloride standards with and without peroxide addition. When compared to the Figure V-14 data in Table V-9, the Figure V-15 data shows the net response is a function of the original iodide level. Thus, variable response should be expected for a single chloride level with different iodide levels upon peroxide treatment.

Table V-11 gives the analysis results of the PWR post-accident matrix samples. The millivolts readings were related to three calibration curves:

a. The pure chloride standards.

b. The pure chloride standards to which iodide was added to 0.99 ppm, and then the iodide was oxidized with 4.0 ml of 30 percent hydrogen peroxide.

c. The pure chloride standards with 4.0 ml of 30 percent hydrogen peroxide.

The results are biased low relative to the first two calibration curves. However, the results are acceptable for high chloride levels (i.e., greater than about 1700 ppb) when the calibration curve for the chloride standards with the peroxide and no iodide addition are used (last column of Table V-11).

Samples with caustic may not have been acidic enough, even though the pH was about 4 to 5 which is within the manufacturer's specifications. This may explain the low results for these samples.

Various techniques were used to eliminate residual hydrogen peroxide after the reaction with iodide, including hydrazine and ferrous compound additions. Results were unacceptable. Heating will destroy the residual peroxide, but this is not plausible with the volatile radioactivities, plus the electrode response is sensitive to temperature.

Thus, evaluating chloride levels in post-accident reactor waters by using SIE measurements after peroxide additions is unacceptable with the electrode tested.

2. Iodide Oxidation by Sodium Nitrite with Subsequent Solvent Extraction

A common radiochemical procedure for radioiodine uses solvent extraction techniques. After oxidation-reduction steps to effect exchange of carrier iodine with various radioactive species, iodide in an acidic environment is oxidized to free iodine with sodium nitrite and extracted into 1,1,1-trichloroethane. Other steps follow.

The same technique can be used to remove iodide from the matrix solutions. However, 1,1,1-trichloroethane should not be used with highly radioactive samples, as the gamma activity levels may be sufficient to effect iodine reaction with the solvent (i.e., possible substitution for chlorine). The author has had experience with this problem, and used carbon tetrachloride or cyclohexane for the extraction. However, OSHA requirements may limit the use of carbon tetrachloride, and cyclohexane is unacceptable because it is lighter than water.

Figure V-16 shows the Graphic Controls electrode system response to pure chloride standards, pure chloride standards with sodium nitrite, and the standards spiked with 0.99 ppm iodine, which was removed after sodium nitrite addition and solvent extraction before measurement. As with the hydrogen peroxide additions, the sensitivity of the system is decreased.

Before these measurements were performed, the chloride SIE tip was polished with alumina per manufacturer's directions. The effect is shown in Table V-10 which gives various calibration data.

The procedure is performed as follows: First, 100 ml of sample is adjusted for pH and ionic strength with 2.0 M nitric acid. The pH should be between 2 and 4. About 4 ml of carbon tetrachloride was next added, and finally 1.0 ml of 1.0 M sodium nitrite solution was added. The mixture is rapidly stirred for three to five minutes and allowed to separate for about two minutes. The top layer (aqueous) is poured off (alternately, the bottom layer of organic could be drained). The solution is moderately stirred and the millivolts reading is taken after a stable reading is obtained. The temperature is also noted. The millivolts is related to the chloride level.

Table V-12 gives the results for the PWR matrix solutions. Two sets of measurements were made - one per procedure outlined above and a second set to which an additional iodide addition to 0.99 ppm was added. The results were compared to calibration data with pure chloride standards to which 1.0 ml of 1.0 M sodium nitrite was added, and also to chloride standards which contained 0.99 ppm iodide extracted with carbon tetrachloride after nitrite addition. The results show acceptable results when the former calibration data are used, giving an average percent error of about 15 percent for chloride levels between 176 ppb and 6294 ppb.

Table V-13 gives the results for the BWR matrix solutions. No additional iodine spike was added to these solutions. The average error for this set was 28 percent, which does not include a control sample from the previous set.

These results show that chloride analysis after iodine removal is feasible, but results for less than about 200 ppb chloride are marginal because of the decreased sensitivity, Figure V-16. Other negative features include:

a. A relatively large sample is required. As little as about 10 ml may be required with an appropriately designed container.

b. pH adjustment is required. For samples with sodium hydroxide (PWR) or sodium pentaboratate decahydrate (BWR), several adjustments may be required before the optimum range is reached.

c. The organic phase should be removed before the electrodes are immersed, as moderate stirring is required and organics will foul the electrodes.

d. Organics will present a problem for subsequent cleanup of waste solutions by ion exchange resin.

e. Using carbon tetrachloride may present safety problems because of OSHA requirements.

The most promising SIE technique NUS used was to oxidize iodide to higher oxidizable states. Higher oxidizable states affect the chloride SIE to a much lesser extent than iodide. The electrode sensitivity was decreased under these conditions, and erratic responses were noted. While some indication of chloride concentration can be obtained from this approach the method does not have the degree of reliability that is desirable for post-accident analyses. In addition, the technique requires large volumes of samples and extensive handling by the analyst resulting in excessive radiation exposure. For these reasons, the SIE methods were ruled unacceptable for post-accident analyses.

C. OTHER METHODS CONSIDERED

1. Mercuric Nitrate Titration

The mercuric nitrate titration procedure is a standard method for chloride. First, diphenylcarbozone-bromophenol blue indicator is added to 100 ml of sample and the pH is adjusted. The sample is titrated with standardized mercuric nitrate solution using a microburet. The volume of titrant is related to the chloride level. The accuracy is about ±0.1 ppm for chloride values less than 0.5 and ±20 percent for higher concentrations.

This method is not suitable for post-accident analysis requirements because of the following considerations.

a. The 100 ml sample volume is prohibitive because of the radiation level.

b. pH adjustment may be difficult for sump samples containing the sodium hydroxide from the spray additive tank.

c. End point color changes are difficult to perceive for many analysts using this procedure. Relatively close contact to the sample is required to detect the end point and this would result in excessive radiation exposure.

2. Spectrophotometric Techniques

A common spectrophotometric method for chloride is performed on waters containing 0.02 to 10 ppm chlorides. Solutions of ferric ammonium sulfate and mercuric thiocyanate are added to 25 ml of sample. An orange color will develop if chlorides are present. The intensity of the color is determined with a spectrophotometer and related to the chloride concentration.

This simple method is not suitable for post-accident monitoring requirements for the following reasons:

a. Handling 25 ml of undiluted sample for a spectrophotometric method will result in very high radiation exposure.

b. Iodides interfere with the method.

3. Turbidimetric/Nephelometric Chloride Techniques

Turbidimetric and nephelometric chloride techniques involve the formation of a chloride precipitate. The turbidimetric method measures the sample turbidity, whereas the nephelometric techniques compare the sample turbidity to standards assigned empirical values. Chloride levels from about 0.1 to 10 ppm could be determined by these methods.

These techniques are unacceptable for post-accident monitoring requirements for the following reasons:

a. Greater than about 25 ml of undiluted sample is required for these techniques. This will result in very high radiation exposure.

b. Too many matrix variables affect the sample turbidity -pH, suspended matter, temperature, ionic environment, and time for development.

c. The fission product iodide would cause an interference.

ANALYTICAL PROCEDURE FOR CHLORIDE ANALYSES BY ION CHROMATOGRAPHY

1.0 PURPOSE

This procedure is to be used for measuring chloride concentration for the range of 0.1 to 20 ppm in primary coolant water samples. The estimated precision is about ±15 percent for the range of 0.1 to 1 ppm and ±20 percent for the range of 1 to 20 ppm. Accuracy of analysis for the higher range can be improved to about ±10 percent by calibration in that range. A chloride determination can be obtained within 15 minutes after primary coolant is charged to the ion chromatograph.

2.0 PROCEDURE

2.1 Initial Conditions

2.1.1 The operator shall be familiar with the operating instructions of the ion chromatograph.

2.1.2 Check that 80-100 psi air or nitrogen pressure is available to actuate the valves in the ion chromatograph.

2.1.3 Check and vent pump if air bubbles are visible in sight glass. Venting is normally required when the eluent containers are filled.

2.1.4 The ion-exchange columns have been recently regenerated.

2.1.5 The following reagents must be available or prepared. Preparation of these reagents will probably be required every 2-3 months under normal operating conditions.

2.1.5.1 0.005 M Sodium Tetraborate ($Na_2B_4O_7 \cdot 10H_2O$)

Dissolve 7.63 grams of $Na_2B_4O_7 \cdot 10H_2O$ in 4 liters of deionized water. Transfer the solution to a four liter collapsable container provided by the ion chromatograph vendor. Remove excess air from the container by opening the top valves and squeezing the container till overflow occurs. Label the container and connect to line E-2 in the reagent storage facility of the ion chromatograph. Open the container valve and vent feed line as indicated in the instrument manual.

2.1.5.2 0.006 M Sodium Carbonate ($Na_2CO_3 \cdot 10H_2O$)

Dissolve 6.87 grams of sodium carbonate in four liters of deionized water. Transfer the solution to a four liter collapsable container, remove excess air, and label the container. Connect to line E-1 in the reagent storage facility of the ion chromatograph. Open the container valve and vent feed lines.

2.1.5.3 1N H_2SO_4

Add 120 ml of concentrated sulfuric acid to four liters of deionized water. Transfer the solution to a four liter collapsable container, remove excess air, and label the container. Connect it to line REGEN SYSTEM-1 in the reagent storage facility of the ion chromatograph. Open the container valve and vent feed line.

2.1.5.4 Deionized Water Rinse

Fill a four liter collapsable container with deionized water. Remove excess air from the bottle and label. Connect it to the waterline in the reagent storage facility. Open the container valve and vent feed lines.

2.1.5.5 For PWR plants, check that the chloride calibration solution tank is over half full with standard solution containing 2000 ppm B (as boric acid) and 1 ppm chloride. Use a 1 ppm standard without boron for BWR plants. A chloride standard should be analyzed after every four unknown samples.

2.2 System Startup

2.2.1 Place the POWER and AIR switches on.

2.2.2 Check that the INJECT switch is in the load position (down) and the E-2 switch to the on position (up).

2.2.3 Place the SEPARATOR switch on (up position) and the suppressed column switch to the on position (up).

2.2.4 Turn the pump switch to the on position and operate the system for about 30 minutes or until the baseline on the recorder stabilizes with the UMHOS switch in the 1 position. Leave the UMHOS switch in the 1 position for subsequent calibration and analyzer operations.

2.3 Analyzing Standards and Samples

Refer to the attached Chemical Analysis Panel drawing (Figure III-1) when analyzing standards and samples.

2.3.1 Perform the following valve lineups for chloride analyzer calibration.

2.3.1.1 Check shut valves 8, 9 and 10.

2.3.1.2 Open valve 9 to pressurize the chloride calibration solution tank to 50 psig.

2.3.1.3 Align valve 7 to the chloride analyzer (line L-25).

2.3.1.4 Place the INJECT switch on the analyzer to the LOAD position.

2.3.1.5 Open valve 8 and allow the standard to flush through the analyzer through lines L-25 and L-26 for a period of five minutes. Check the flow indicator to assure that there is flow through the line.

2.3.1.6 After five minutes, place the INJECT switch to the INJECT position and press the events recorder. This will inject 0.2 ml of the solution to be analyzed and mark the time of injection on the strip chart recorder. The chloride peak will occur at six minutes after injection. This serves as a reference point to determine the chloride concentration in the subsequent unknown samples.

2.3.1.7 The solution will be automatically flushed from the analyzer and anion column. Allow approximately 30 minutes to complete this operation. Place the inject switch on the ion chromatograph in the load position.

2.3.1.8 Shut valves 8 and 9. Then align valve 7 to rinse the lines-25 and L-26 with deionized water (through line L-24) for a period of five minutes. Secure the flush water rinse.

2.3.2 To analyze reactor coolant:

2.3.2.1 Align valve 7 to the chloride analyzer and open the shutoff valve on the primary coolant inlet line. Allow reactor coolant to flow to waste for a period of five minutes. Check the flow meter installed in line L-25 for flow indication.

2.3.2.2 Repeat steps 2.3.1.6 and 2.3.1.7.

2.3.2.3 If the chloride peak goes off scale the chloride peak is above 1.5 ppm. Another determination will be required, repeating steps 2.3.2.1 through 2.3.2.3. Set the conductivity meter on the ion chromatograph at 3x or perhaps 10x for the duplicate run. Rinsing of the lines is not required between repeat determinations.

2.3.2.4 Isolate the primary coolant flow and align valve 7 with line L-24 to rinse the lines L-25 and L-26 with deionized water for a period of five minutes. The inject switch on the ion chromatograph must be in the load position during rinse operations. Secure the flush water rinse.

2.4 Column Regeneration

2.4.1 Under post-accident conditions, column regeneration is performed as soon as practicable after completing the chloride analyses. Regeneration will significantly reduce or virtually eliminate the resin columns as a radiation source.

2.4.2 Column regeneration is performed twice/shift if the ion chromatograph is in continuous use. The need for column regeneration under other conditions is indicated by a high baseline conductivity, or a significant change in the time for the chloride peak to occur, or change in peak height when running the chloride standard. A sodium carbonate flush is performed prior to every other regeneration. Go to step 2.4.5 if only regeneration is required.

2.4.3 The following valve lineup is initially required for flushing of the resin columns.

Mode Switch	Zero
E1 Switch	Up (on)
E2 Switch	Down (off)
Separator Switch	Up (on)
Suppression Switch	Up (on)
Pump Switch	Up (on)

2.4.4 This valve lineup will provide for sodium carbonate flushing of both columns. Operate for 15-20 minutes, then turn the E1 switch to the water position (down) and flush for 10 minutes.

2.4.5 Turn the Suppressor Switch to Bypass/Regeneration (Down).

2.4.6 Depress the regeneration start button. The system timer is set to provide for a 15 minute acid regeneration followed by a 45 minute water rinse, do not change the setting. After one hour the system will shut off automatically and the red ready light will be activated.

TABLE V-1

SOLUTIONS USED IN Cl^- ANALYSIS PROGRAM

	Conc. ppm							
	Boron	Iodide	Cesium	Lithium	Chloride	NaOH	Cerium	Barium
Soln 1	2000	2	10	1	1	500	-	-
Soln 2	500	0.5	2.5	0.25	0.25	12.5	-	-
Soln 3	250	0.25	1.25	0.125	0.125	6.25	-	-
Soln 4	2000	2	10	2	1	-	-	-
Soln 5	1000	1	5	1	0.5	-	-	-
Soln 6	500	0.5	2.5	0.5	0.25	-	-	-
Soln 7	250	0.25	1.25	0.25	0.125	-	-	-
Soln 8	-	1.19	6.28	-	0.05	-	0.16	0.16
Soln 9	2000	1.19	6.28	1.98	0.15	-	0.16	0.16
Soln 10	2000	1.19	6.28	1.98	0.50	-	0.16	0.16
Soln 11	2000	1.19	6.28	1.98	10.0	500	-	-
Soln 12	2000	1.19	6.28	1.98	10.0	-	-	-
Soln 13	-	-	-	-	0.2	-	-	-
Soln 14	-	-	-	-	0.5	-	-	-
Soln 15	-	-	-	-	1.0	-	-	-
Soln 16	-	-	-	-	5.0	-	-	-
Soln 17	-	-	-	-	10.0	-	-	-

TABLE V-2

ANALYSES OF STANDARD SOLUTIONS
(NEW COLUMNS EARLY IN LIFE)

Solution No. in Table V-1	ppb Cl	Scale	Peak Height	Conc., ppb Cl^- As Analyzed
10	500	3	50.4	511
10	500	3	50.1	514
1	1,000*	3	96.3	988
16	5,000	10	523	5,364
13	200	1	20.1	206
5	500	1	48.4	496
5	500	1	50.8	521
4	1,000*	3	98.7	1,012
16	5,000	10	542	5,559
11	10,000	30	1086	11,138
14	500	3	59.1	606
10	500	3	57.0	585

*An average peak height of 97.5 was obtained for the 1000 ppb standards.

TABLE V-3

CHLORIDE ANALYSES RESULTS
(NEW COLUMNS LATER IN LIFE)

Solution No. in Table V-1	ppb Cl-	Scale	Peak Height	Conc., ppb Cl$^-$ As Analyzed
4	1000	1	60*	922
1	1000	1	61*	1008
2	250	1	17	281
3	125	1	9	149
11	10,000	10	770	12,727
12	10,000	10	770	12,727
14	500	1	36	595
2	250	1	16	264

*An average peak height of 60.5 was obtained for the 1.0 ppm standard. Note in Table V-2 that a peak height of 97.5 was obtained for a 1.0 ppm standard earlier in life for these same columns.

TABLE V-4

SAMPLE AND STANDARD SOLUTIONS
CALIBRATION CURVE 1
(REPLACEMENT COLUMNS)

Solution No. in Table V-1	Peak Height	Conc. - ppm Cl^- Actual	Conc. - ppm Cl^- As Analyzed
Standard*	34.0	1.0	0.98
10	14.0	0.50	0.41
9	4.0	0.15	0.13
9	5.0	0.15	0.15
Standard*	34.0	1.0	0.98
Standard*	34.0	1.0	0.98
5	17.0	0.50	0.50
6	9.0	0.25	0.26
7	4.5	0.12	0.14
Standard*	35.0	1.0	1.0
2	12.0	0.25	0.38
3	4.5	0.125	0.14
5	18.0	0.50	0.52
Standard*	35.0	1.0	1.0
Standard*	35.0	1.0	1.0
5	17.5	0.50	0.50
Standard*	32.0	1.0	0.92
5	18.0	0.50	0.52
2	9.5	0.25	0.29
7	4.0	0.125	0.12

*1 ppm Cl in a 2000 ppm boron solution.

TABLE V-5

SAMPLE AND STANDARD SOLUTIONS
CALIBRATION CURVE 2
(RECONDITIONED COLUMNS)

Solution No. in Table V-2	Peak Height	Conc. - ppb Cl^-	
		Actual	As Analyzed
5	24.0	500	500
2	13.0	250	270
4	44.0	1000	930
1000 ppb Cl*	50.0	1000	1040
500 ppb Cl*	24.0	500	500
6	12.0	250	260
3	6.0	120	130
5	26.5	500	560
2	13.0	250	270
1000 ppb Cl*	48.5	1000	1020
10	26.0	500	550
9	8.0	1500	180
8	3.0	50	70
1	52.0	1000	1100

*As NaCl

TABLE V-6

PEAK HEIGHT BEFORE AND AFTER ADDING OIL TO SOLUTION 1

4-4-80
Scale 1
Pump Setting 45
Eluent - 0.005 M $Na_2B_4O_7$
Oil: Gulf Pride 10W40 Super Premium

Basic Boron and 1 ppm Cl^- (Soln 1)	Chloride Peak Height
Soln 1 + Oil	56.0
Soln 1 + Oil	58.0
Soln 1 + Oil	58.0
Soln 1 + Oil	59.0
Soln 1 + Oil	59.0

*Peak height of initial oil free 1 ppm standard = 52.0.

4-18-80
Scale 1
Pump Setting 40
Eluent - 0.005 M $Na_2B_4O_7$
Oil: Mobil 1

Soln 1	Peak Height 62.0*
Soln 1 + Oil	83.0
Soln 1 + Oil	83.0
Soln 1 + Oil	85.5
Soln 1 + Oil	88.5
Soln 1 + Oil	90.0

*This standard was run after analysis of the oil-contaminated samples. The peak height observed here (62 vs. 52 for 1/4/80 results) indicate that there is a memory effect associated with the analyses of oil-contaminated water with ion-chromatography.

TABLE V-7

SAMPLE AND STANDARD SOLUTIONS FLUORIDE STANDARD CURVE

Solution	Peak Height	Analysis Results ppb F
25 ppb F	5.5	22
50 ppb F	13.0	48
100 ppb F	27.0	98
200 ppb F	60.0	216
150 ppb F	42.0	152
50 ppb F + 100 ppm B	12.0	45
100 ppb F + 100 ppm B	26.0	95
200 ppb F + 100 ppm B	58.5	211
50 ppb F + 1 ppm B	10.5	40
100 ppb F + 1 ppm B	26.5	96
25 ppb F + 1 ppm B	6.0	23

TABLE V-8

EFFECT OF IODIDE ON GRAPHIC CONTROLS CHLORIDE ELECTRODE

(11/2/79)

ppm I^-	°C	Absolute Millivolts*
0.10	24.0	365.8
1.0	23.6	336.6
10	25.5	234.0
100.3	25.4	157.9
1003	25.1	56.3

*The response to iodide was sluggish and not reproducible. The readings were taken after 1.0 ml of 2.0 M HNO_3 was added with moderate stirring.

TABLE V-9

RESPONSE OF GRAPHIC CONTROLS CHLORIDE ELECTRODE TO SOLUTIONS WITH CHLORIDE AND IODIDE

(11/5/79)

		Solution Adjusted to 0.99 ppm I^-			I^- Oxidized with 4.0 ml 30% H_2O_2		
ppb Cl^-	mV @ 25°C	mV @ 25°C	Apparent ppm Cl^- [a]	ΔmV	mV @ 25°C	Apparent ppm Cl^- [b]	% Error [c]
10	385.0	326.1	554	-58.9	382.6	17	+78
25	378.2	322.8	632	-55.4	373.0	59	+148
50	357.6	320.7	687	-54.9	370.9	67	+41
100	364.3	317.0	797	-47.3	357.8	145	+52
200	351.1	315.0	864	-36.1	347.8	232	+22
500	329.2	297.7	1727	-31.5	328.1	511	+7.3
1000	311.3	288.8	2466	-22.5	312.7	947	-0.6
5000	271.3	253.7	10,056	-17.6	273.1	4624	-2.9
10,000	253.6	239.1	18,044	-14.5	256.5	8989	-5.7

---

a. A volume of 102 ml relative to a calibration volume for 101 ml.

b. These values must be corrected for dilution, 1.0 ml for iodide addition and 4.0 ml for peroxide addition: $\frac{106}{101}$ is the dilution correction

c. Dilution taken into account.

TABLE V-10

CALIBRATION DATA FOR GRAPHIC CONTROLS CHLORIDE ELECTRODE (ABSOLUTE MILLIVOLT RESPONSE AT 25.0°C)

Date	Condition	Parts per Billion (PPB) Chloride								
		10	25	50	100	200	500	1000	5000	10000
11-2-79	No stirring	390.6	380.5	375.5	363.2	352.1	331.7	313.6	275.6	2573
11-2-79	Moderate stirring	386.5	383.2	377.7	366.4	352.3	329.8	312.5	273.2	255.8
11-5-79	Moderate stirring	385.0	378.2	375.6	364.3	351.1	329.2	311.3	271.3	253.6
11-6-79	Moderate stirring	384.2	380.5	371.2	361.8	348.3	327.4	311.3	272.2	254.9
11-9-79	Electrode cleaned; moderate stirring	404.6	400.1	395.3	382.6	367.6	347.8	330.8	291.0	272.6
11-19-79	Electrode cleaned; moderate stirring	403.4	400.8	392.5	381.7	369.2	348.0	330.9	290.7	272.6
11-6-79	4.0 ml of 30% H_2O_2 added, moderate stirring (readings at ∿8 min.)	426.3	423.6	420.9	406.3	387.4	356.0	336.5	293.4	274.5
11-9-79	Electrode cleaned; moderate stirring; 1.0 ml of 1.0M $NaNO_2$ added	389.4	388.0	385.8	385.6	378.9	374.9	360.3	314.8	295.5
11-19-79	Electrode cleaned; moderate stirring; 1.0 ml of 1.0M $NaNO_2$ added	387.2	386.8	385.2	386.1	380.7	371.3	362.7	316.8	296.8
11-9-79	Electrode cleaned; moderate stirring; 1.0 ml of 1.0M $NaNO_2$ added - then solution adjusted to 0.99 ppm iodide and free iodine extracted with CCl_4 and poured off	381.5	383.3	381.4	379.9	375.9	363.8	349.2	311.9	293.2

TABLE V-11

ANALYSIS RESULTS OF CHLORIDES IN PWR MATRIX SAMPLES BY IODIDE OXIDIZATION WITH 30% HYDROGEN PEROXIDE

		Original Sample			Original Sample Plus 4.0 ml of 30% H_2O_2[b]							
Solution	Actual ppb Chloride[a]	OC	MV	ml 2.0N HNO_3 Add.	OC	MV	ppb Cl^-[c]	% Error[c]	ppb Cl^-[d]	% Error[d]	ppb Cl^-[e]	% Error[e]
A	176	23.6	322.7	1.0	25.0	379.2	$34\times\frac{105}{101}$	-80	$13\times\frac{105}{106}$	-93	$240\times\frac{105}{105}$	+36
B	0.176	23.5	383.3	1.0	25.0	409.4	(f)		(f)		$83\times\frac{105}{105}$	(g)
C	226	23.5	318.4	1.0	25.0	369.7	$71\times\frac{105}{101}$	-67	$40\times\frac{105}{106}$	-82	$335\times\frac{105}{105}$	+48
D	0.226	23.5	383.4	1.0	25.0	410.9	(f)		(f)		$80\times\frac{105}{105}$	(g)
E	326	23.5	308.9	1.0	25.0	353.0	$195\times\frac{105}{101}$	-38	$140\times\frac{105}{106}$	-57	$604\times\frac{105}{105}$	+85
F	0.326	23.5	387.1	1.0	24.0	433.7	(f)		(f)		(f)	
G	676	23.5	292.9	1.0	24.4	327.0	$534\times\frac{105}{101}$	-18	$535\times\frac{105}{106}$	-22	$1510\times\frac{105}{105}$	+123
H	0.676	23.5	383.8	1.0	24.5	424.2	(f)		(f)		$29\times\frac{105}{105}$	(g)
I	6294	24.5	286.0[h]	5.0	25.3	294.8	$1940\times\frac{109}{101}$	-67	$2040\times\frac{109}{106}$	-67	$4700\times\frac{109}{105}$	-22
J	6.29	24.5	386.1	1.0	25.0	427.1	(f)		(f)		$15\times\frac{105}{105}$	(g)
K	5451	24.0	280.5[h]	5.0	25.3	292.4	$2130\times\frac{109}{101}$	-58	$2250\times\frac{109}{106}$	-58	$5110\times\frac{109}{105}$	-2.7
L	5.45	24.1	380.9	1.0	25.5	423.8	(f)		(f)		$33\times\frac{105}{105}$	(g)
M	2991	24.5	293.6[h]	5.0	25.6	311.5	$994\times\frac{109}{101}$	-64	$1020\times\frac{109}{106}$	-65	$2610\times\frac{109}{105}$	-9.4
N	2.99	24.0	381.0	1.0	25.4	426.3	(f)		(f)		$18\times\frac{105}{105}$	(g)
O	1741	24.1	312.5[h]	5.0	25.4	331.2	$451\times\frac{109}{101}$	-72	4[illegible]9$\times\frac{109}{106}$	-73	$1300\times\frac{109}{105}$	-22
P	1.74	24.0	381.4	1.0	25.6	429.4	(f)		(f)		$10\times\frac{105}{105}$	(g)

(a) Includes estimated chlorides from reagents
(b) Readings taken after approximately 8 minutes
(c) Relative to standard calibration curve
(d) Relative to standard calibration curve; standards adjusted to 0.99 ppm iodide and 4.0 ml of 30% H_2O_2 added
(e) Relative to standard calibration curve; standards adjusted with 4.0 ml of 30% H_2O_2
(f) Less than blank
(g) Not evaluated
(h) This indicates that the untreated samples indicated less chloride than actually in the samples. This is thought to be a result of the pH being too high for the conditions, even though it was within the manufacturer's specifications. See Table 9 which gives the results for a different technique at a lower pH.

TABLE V-12

ANALYSIS RESULTS OF CHLORIDES IN PWR
MATRIX SAMPLES AFTER IODINE EXTRACTED WITH CARBON TETRACHLORIDE

		Iodide Oxidized to Iodine with $NaNO_2$, Extracted with CCl_4					0.99 ppm Iodide Added, Iodide Oxidized to Iodine with $NaNO_2$, Extracted with CCl_4					
Sample	Actual ppb Chloride[a]	ml 2.0N HNO_3 Add.	mV @ 25.0°C	ppb Cl^-[b]	% Error[b]	ppb Cl^-[c]	% Error[c]	ml 2.0N HNO_3 Add.	mV @ 25.0°C	ppb Cl^-[b]	% Error[b]	ppb Cl^-[c]	% Error[c]
A	176	1.0	383.8	$130\times\frac{102}{102}$	-26	$10\times\frac{102}{103}$	-94	1.0	380.0	$255\times\frac{103}{102}$	+46	$82\times\frac{103}{103}$	-53
C	226	1.0	379.7	$270\times\frac{102}{102}$	+19	$90\times\frac{102}{103}$	-61	1.0	376.7	$390\times\frac{103}{102}$	+74	$175\times\frac{103}{103}$	-23
E	326	2.0	381.7	$190\times\frac{103}{102}$	-41	$44\times\frac{103}{103}$	-87	1.0	374.5	$480\times\frac{103}{102}$	+49	$225\times\frac{103}{103}$	-31
G	676	1.0	367.3	$740\times\frac{102}{102}$	+9.5	$402\times\frac{102}{103}$	-41	1.0	360.4	$980\times\frac{103}{102}$	+46	$490\times\frac{103}{103}$	-28
I	6294	6.0	311.3	$5680\times\frac{108}{103}$	-4.4	$4860\times\frac{108}{103}$	-19	4.0	331.8[d]	$2650\times\frac{100}{34}$ $\times\frac{106}{102}$	+29	$2030\times\frac{100}{34}$ $\times\frac{106}{103}$	-2.4
K	5451	6.0	313.6	$5210\times\frac{108}{102}$	+1.2	$4410\times\frac{108}{103}$	-15	7.0	312.6	$5410\times\frac{109}{102}$	+6.1	$4600\times\frac{109}{103}$	-11
M	2991	7.0	330.3	$2800\times\frac{109}{102}$	0	$2160\times\frac{109}{103}$	-24	7.0	330.5	$2780\times\frac{109}{102}$	-0.7	$2150\times\frac{109}{103}$	-24
O	1741	6.0	351.0	$1300\times\frac{108}{102}$	-21	$896\times\frac{108}{103}$	-46	7.0	349.5	$1370\times\frac{109}{102}$	-16	$955\times\frac{109}{103}$	-42

(a) Includes estimated chloride from reagents
(b) Based on calibrations with chloride standards with 1.0 ml of 1.0M $NaNO_2$ (pH adjusted with 1.0 ml of 2.0N HNO_3)
(c) Based on calibrations with chloride standards adjusted to 0.99 ppm iodide, 1.0 ml of 1.0M $NaNO_2$ added, and free iodide extracted with CCl_4 (pH adjusted with 1.0 ml of 2.0M HNO_3)
(d) 34.0 ml diluted to 100.0 ml

TABLE V-13

ANALYSIS RESULTS OF CHLORIDES IN BWR MATRIX SAMPLES AFTER IODINE EXTRACTED WITH CARBON TETRACHLORIDE

Actual ppb Chloride[(a)]	ml 2.0N HNO$_3$ Add.	°C	mV		°C	mV	ppb Cl^{-}[(b)]	% Error[(b)]
80	1.0	25.2	338.3	790	25.0	385.3	$55\times\frac{101}{101}$	-31
130	1.0	25.0	336.1	790	25.3	385.0	$64\times\frac{101}{101}$	-51
280	1.0	25.0	330.0	1010	25.5	376.2	$380\times\frac{101}{101}$	+36
280	1.0	25.2	327.0	1170	25.1	377.7	$310\times\frac{101}{101}$	+11
1080	1.0	25.0	301.5	3200	25.5	358.2	$1180\times\frac{101}{101}$	+9.3
1080	1.0	25.0	298.6	3650	25.2	354.7	$1320\times\frac{101}{101}$	+22
2	1.0	25.5	395.4	41	25.7	385.1	$60\times\frac{101}{101}$	(d)
12	1.0	25.3	392.7	50	25.9	385.4	$55\times\frac{101}{101}$	(d)
19	1.0	25.3	394.0	45	25.3	385.0	$63\times\frac{101}{101}$	(d)
41	1.0	25.0	388.3	70	25.5	381.3	$170\times\frac{101}{101}$	(d)
41	1.0	25.3	386.6	78	26.0	383.0	$117\times\frac{101}{101}$	(d)
158	1.0	25.0	380.7	117	25.0	383.0	$117\times\frac{101}{101}$	-26
158	1.0	25.1	378.7	124	25.6	379.7	$220\times\frac{101}{101}$	+39
2991[(c)]	5.0	24.0	308.5	2400	25.2	336.0	$2550\times\frac{100}{97.5}\times\frac{105}{101}$	-9.1

(a) Includes estimated chlorides from reagents

(b) Based on calibrations with chloride standards with 1.0 ml of 1.0 M NaNO$_2$ (pH adjusted with 1.0 ml of 2.0 M HNO$_3$)

(c) Control from previous set: 97.5 ml diluted to 100.0 ml

(d) Electrode reading low by approximately 2 mV per check of standards, which resulted in high results

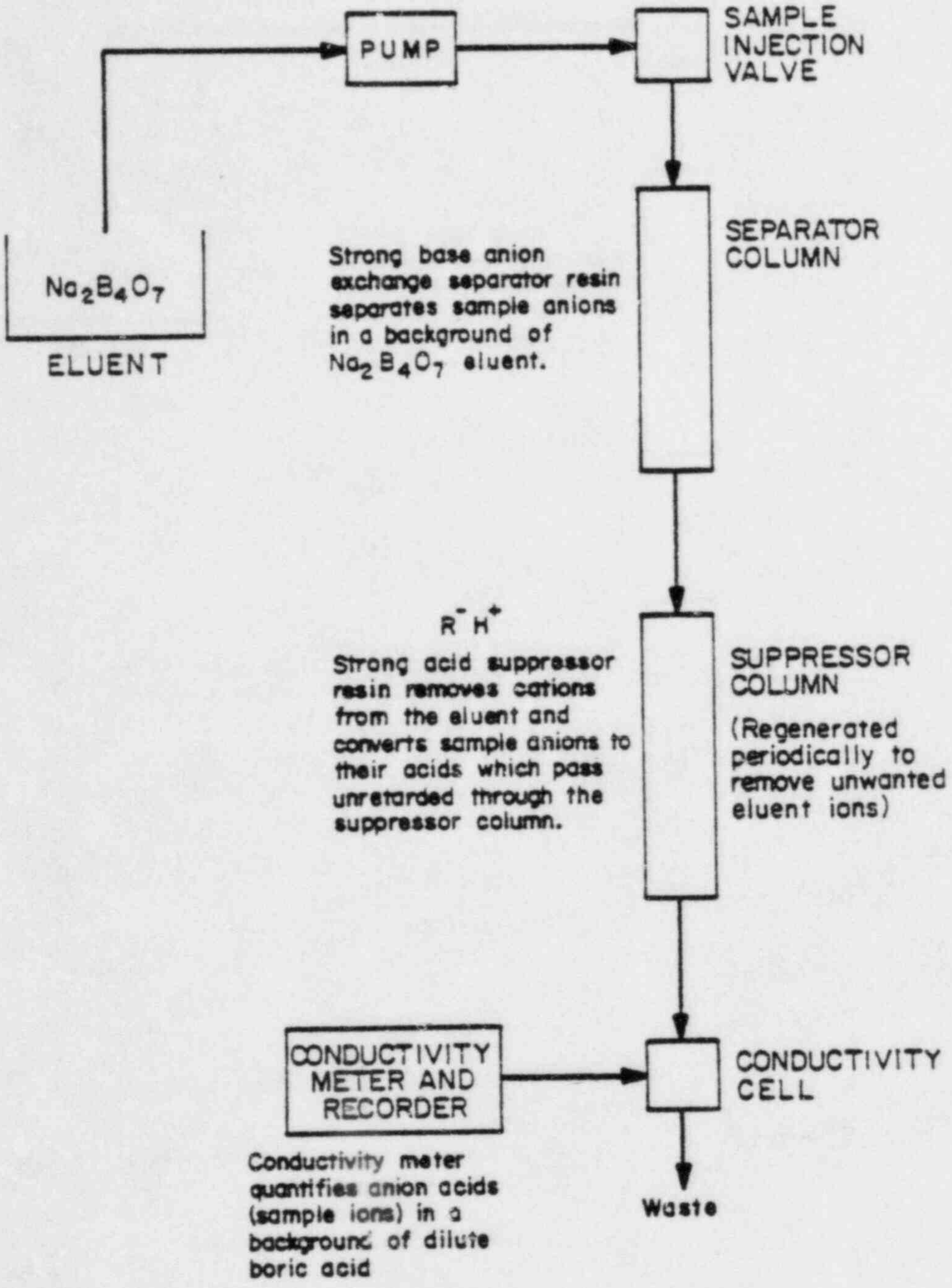
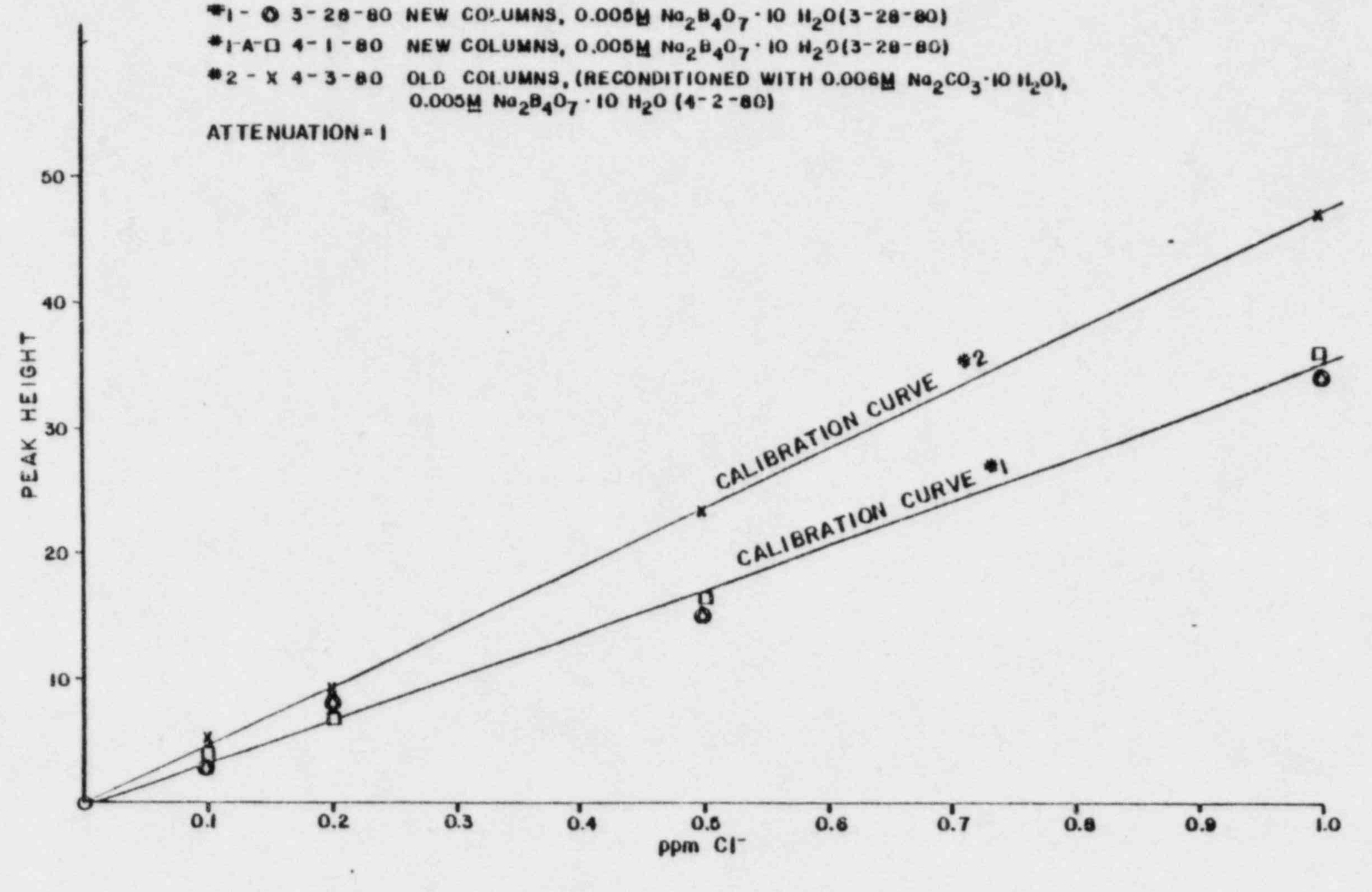


FIGURE V-1

ANION ANALYSIS ION CHROMATOGRAPHY FLOW SCHEME

FIGURE V-2 CHLORIDE CALIBRATION CURVES



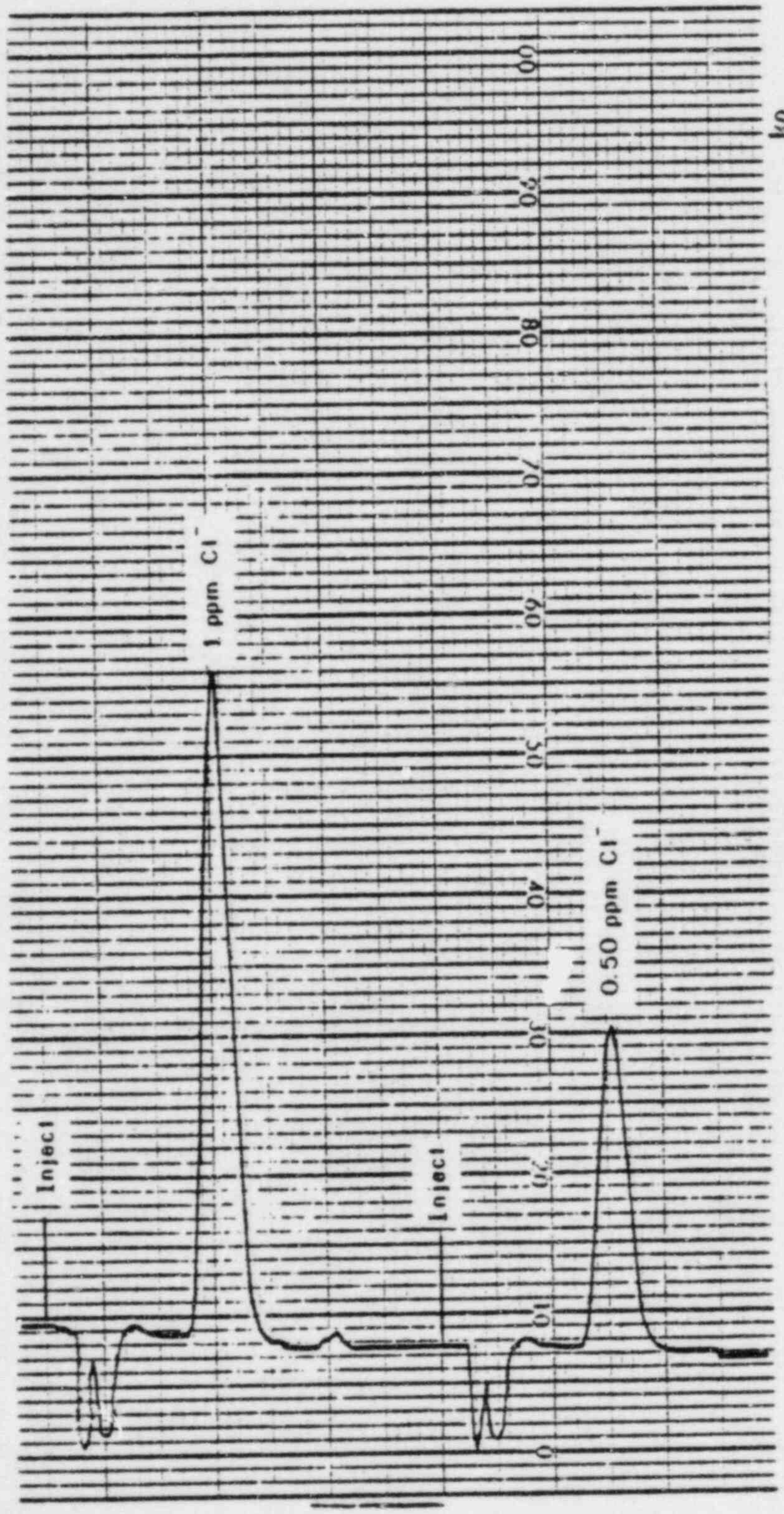


FIGURE V-3
CHROMATOGRAM
STANDARD Cl^- CURVE #2

Scale - 1
Pump Setting - 40
Eluent - 0.005 M $Na_2B_4O_7 \cdot H_2O$ (4/2/80)
Sample Size - 0.20 ml
Cl^- Peak Occurs - 6 min

Peak Heights
1 ppm Cl^- = 48
0.50 ppm Cl^- = 23

Recorder Settings
Span - 1000
Chart Speed - 0.5 cm/sec

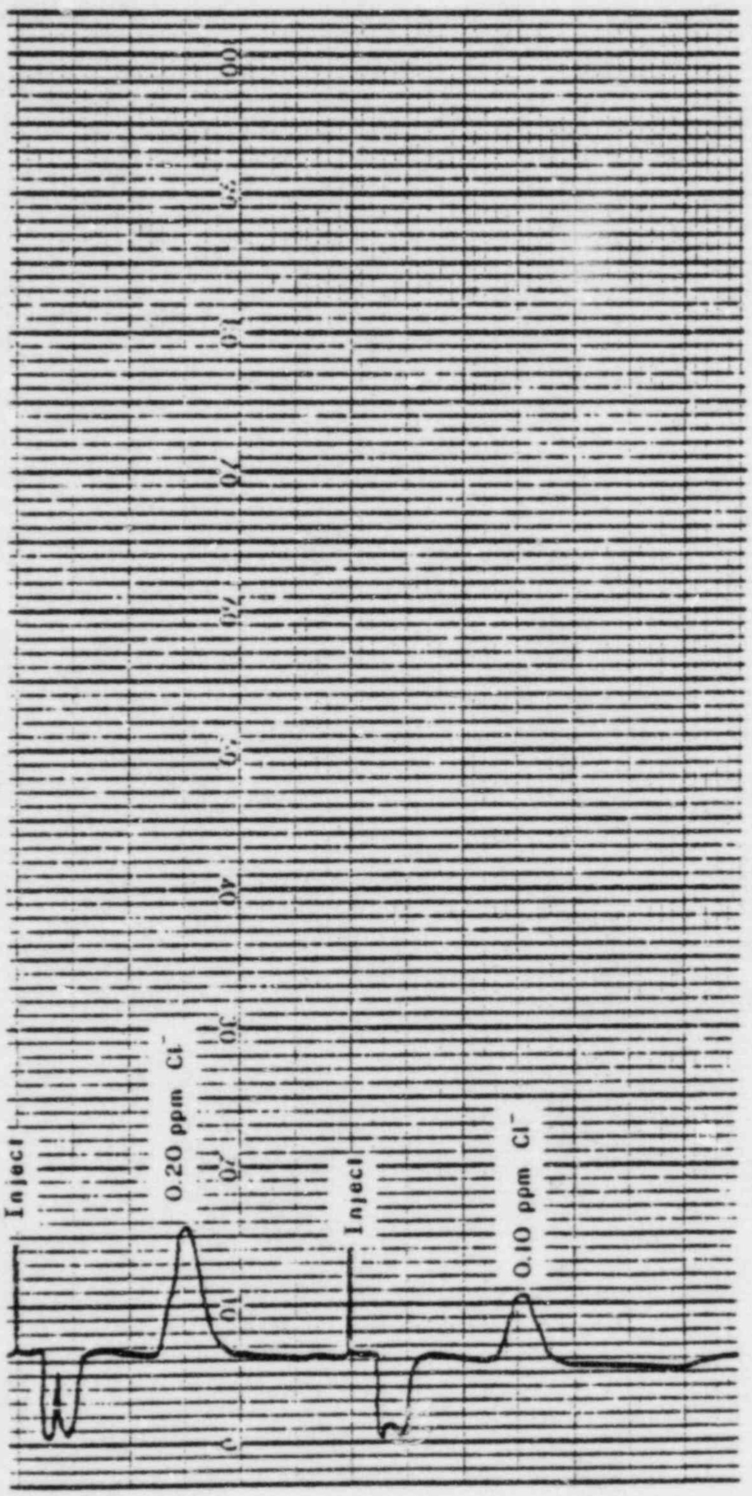


FIGURE V-4
CHROMATOGRAM
STANDARD Cl⁻ CURVE # 2

Scale - 1
Pump Setting - 40
Eluent - 0.005 M $Na_2B_4O_7 \cdot 10$
H_2O (4/2/80)
Sample Size - 0.20 ml
Cl⁻ Peak Occurs - 6 min.

Peak Heights
0.20 ppm Cl⁻ = 9.5
0.10 ppm Cl⁻ = 5.0

Recorder Settings
Span - 1000
Chart Speed - 0.5 cm/min.

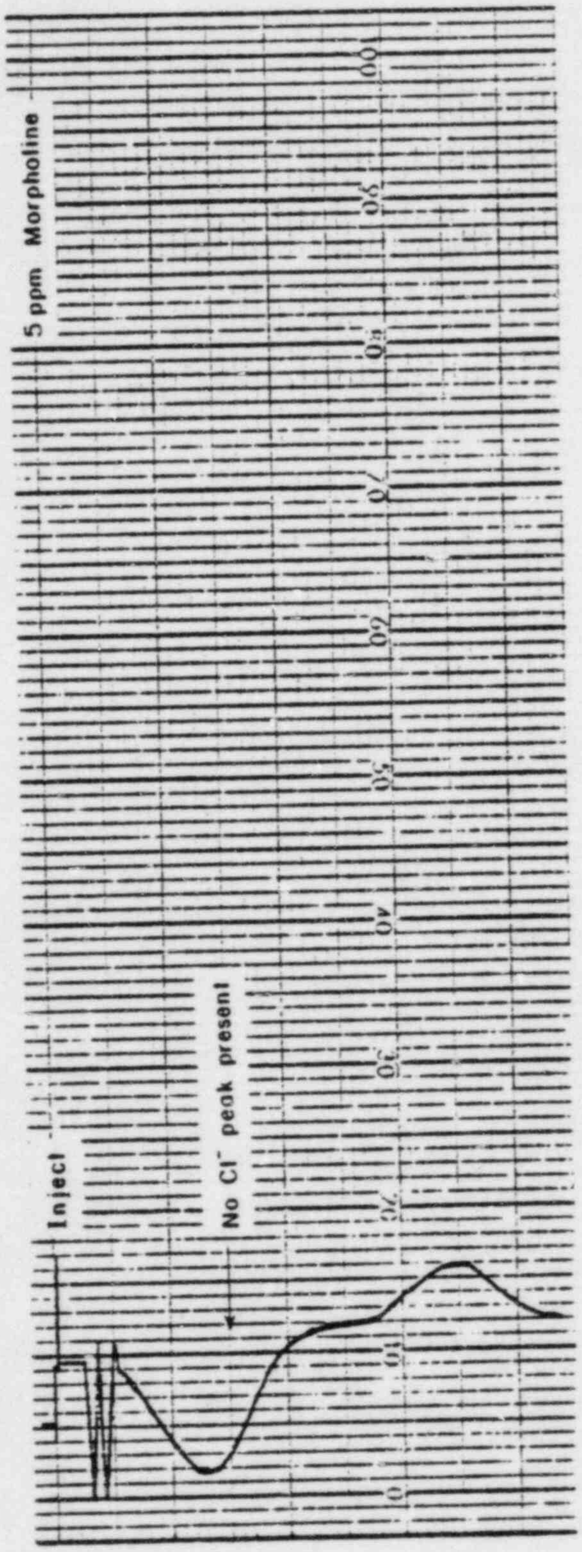


FIGURE V-5

5ppm MORPHOLINE CHROMATOGRAM

3/28/80

Calibration Curve #1

Scale - 1

Pump Setting - 50

Eluent - 0.005 M $Na_2B_4O_7$ (3/28/80)

Sample Size - 0.20 ml

Peak Heights

This shows the absence of of a Cl$^-$ peak at 6 min.

This sample was run three times with the same results.

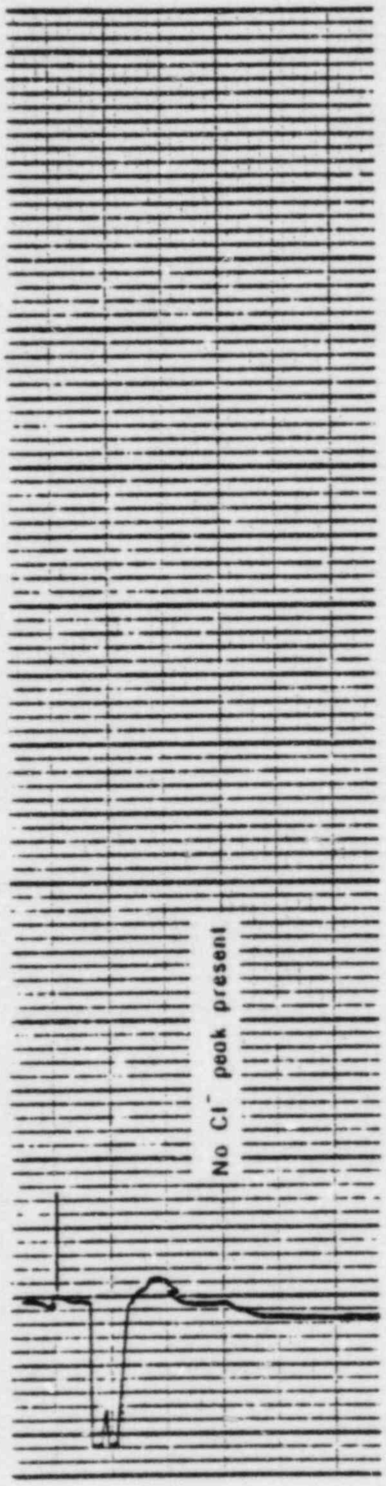


FIGURE V-6
200 ppm HYDRAZINE
3/25/80

Run on earlier calibration curve.
Scale - 1
Pump Setting - 40
Eluent - 0.005 M $Na_2B_4O_7 \cdot 10\ H_2O$
Sample Size - 0.20 ml

Peak Height

This shows an absence of a Cl^- peak at 6 min.

Hydrazine was used to spike Solution 10. First Solution 10 was run by itself; Then a mixture (27mls Solution 10   3 ml of 1000 ppm hydrazine) was run. There was no effect other than that caused by dilution. See Figure 7 .

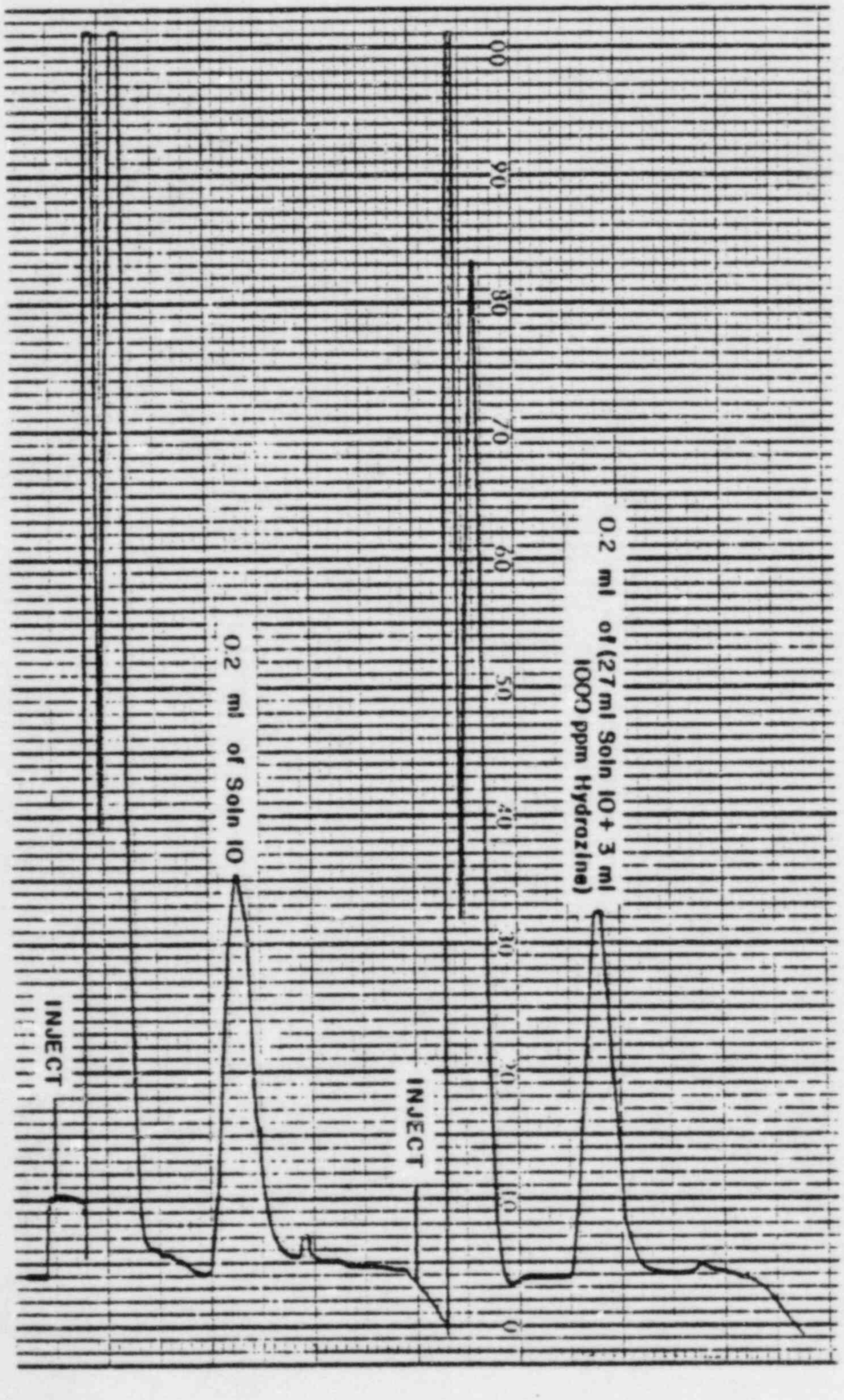


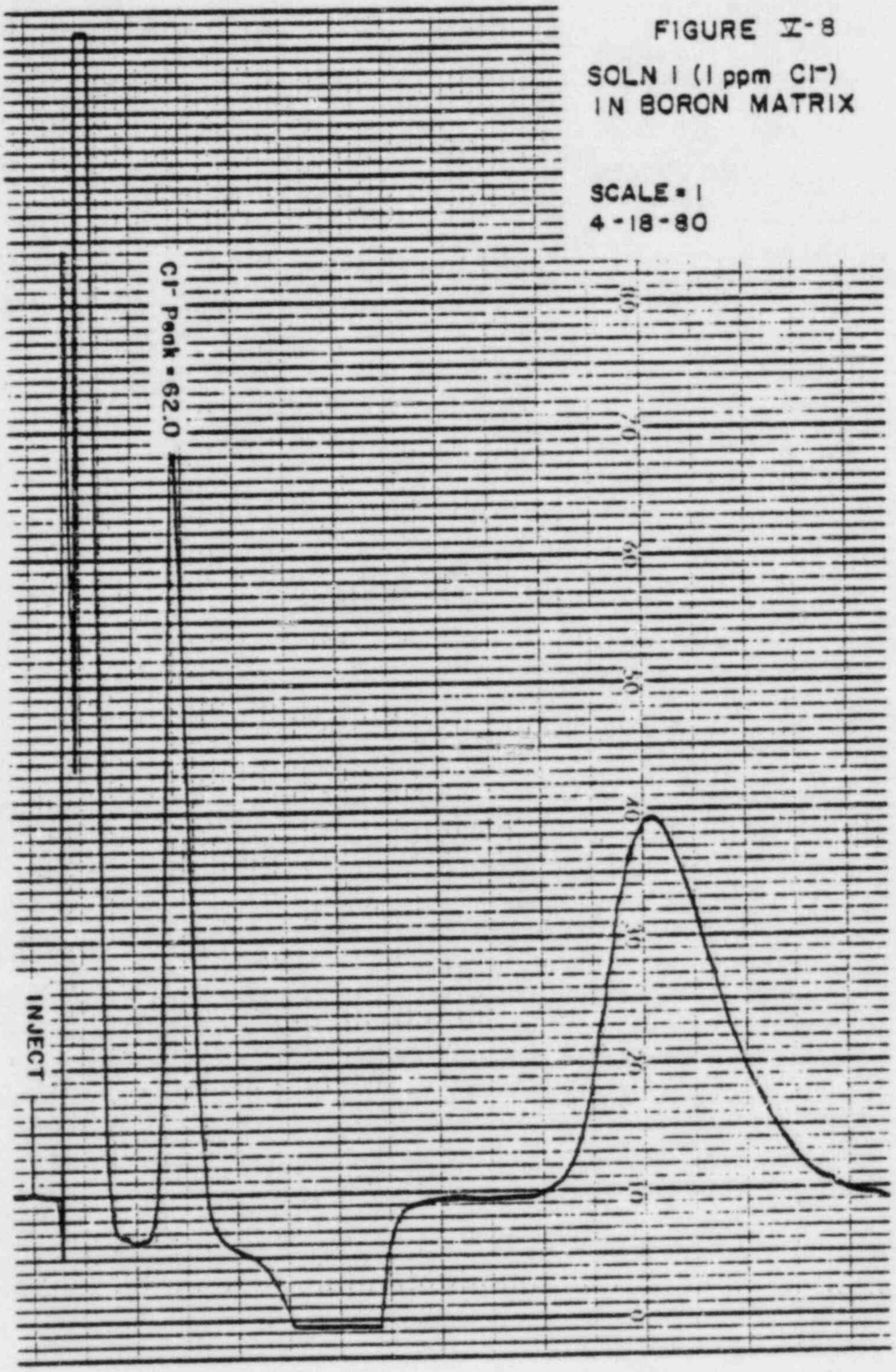
FIGURE V-7

CHLORIDE SOLUTION WITH HYDRAZINE ADDED

FIGURE X-8

SOLN I (I ppm Cl$^-$)
IN BORON MATRIX

SCALE = I
4-18-80



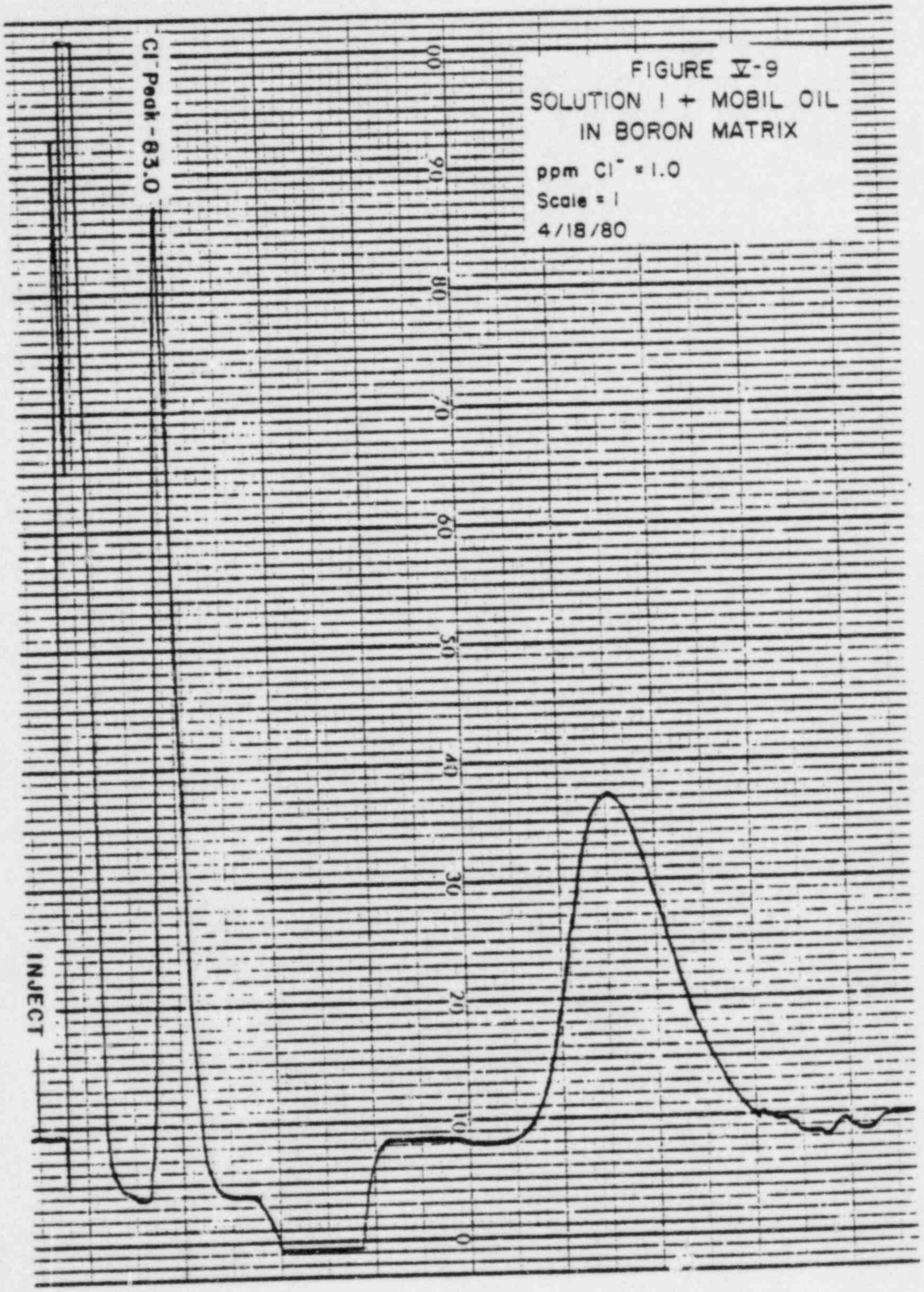


FIGURE V-9
SOLUTION 1 + MOBIL OIL
IN BORON MATRIX

ppm Cl⁻ = 1.0
Scale = 1
4/18/80

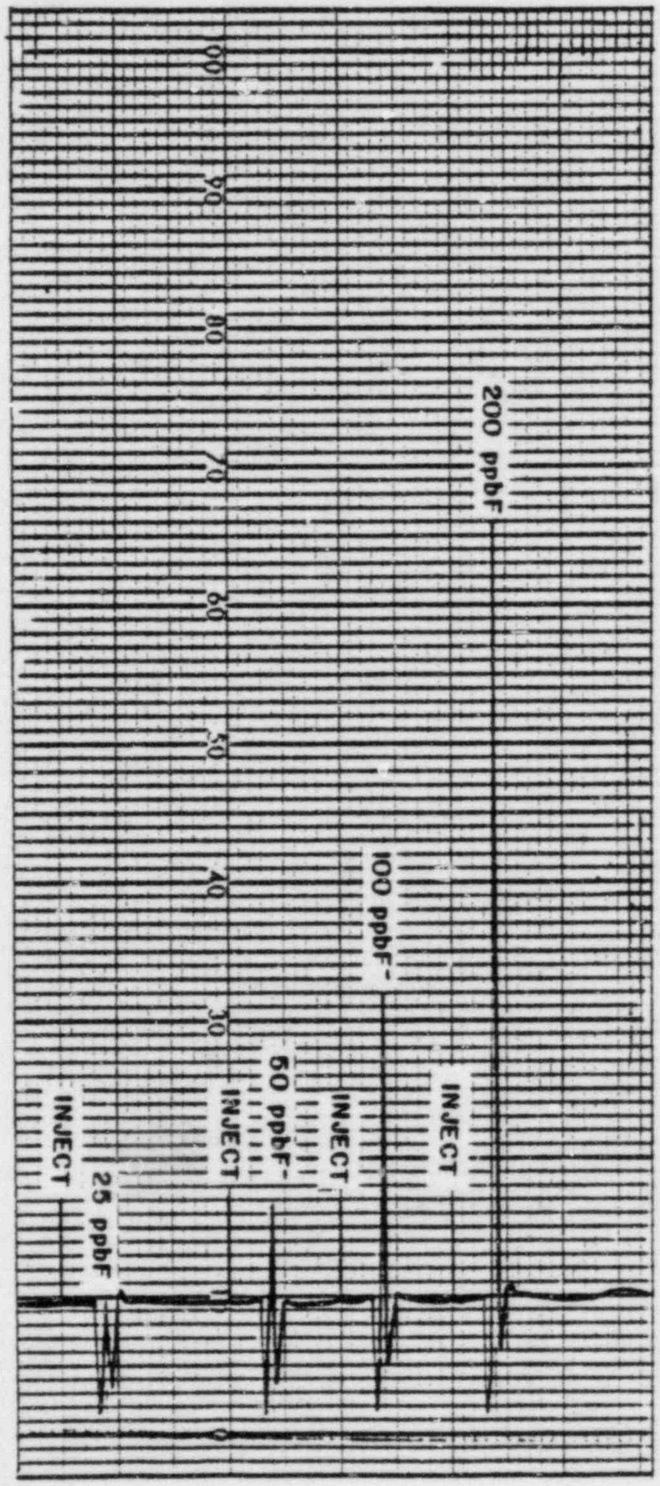


FIGURE V-10
CHROMATOGRAM

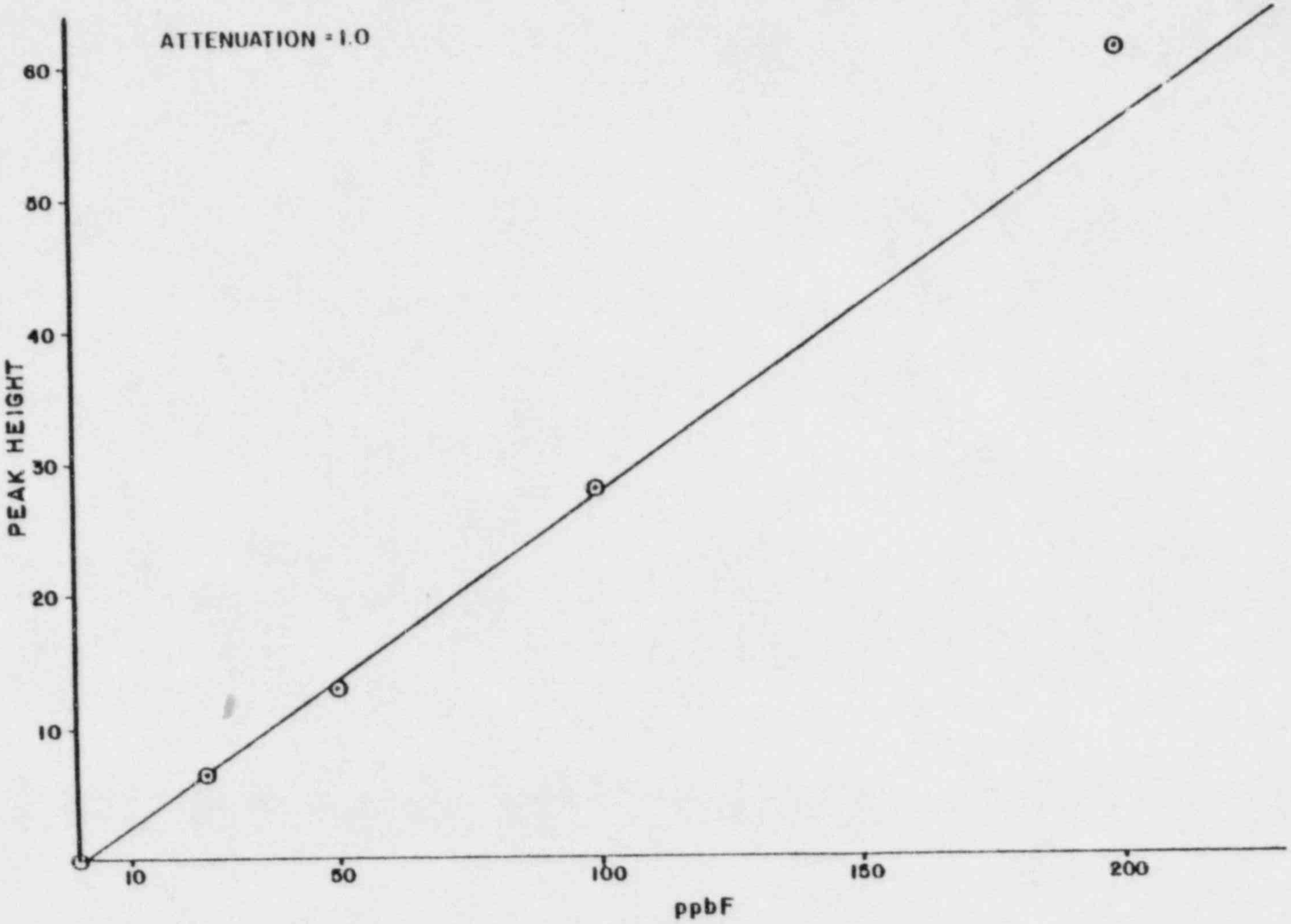
FLUORIDE STANDARD CURVE
4-17-80

SCALE 3
PUMP SETTING 40′
ELUENT 0.005 $\underline{M}$ $Na_2B_4O_7 \cdot 10$
(4-17-80)
SAMPLE SIZE 0.20 ml
F^- PEAK OCCURS - 1.5 MIN.

PEAK HEIGHTS-
25 ppbF$^-$ -6.5
50 ppb - 13.0
100 ppb - 28.0
200 ppb - 61.0

RECORDER SETTINGS
SPAN - 1000
CHART SPEED - 0.5 cm/min

FIGURE V-11 FLOURIDE CALIBRATION CURVE



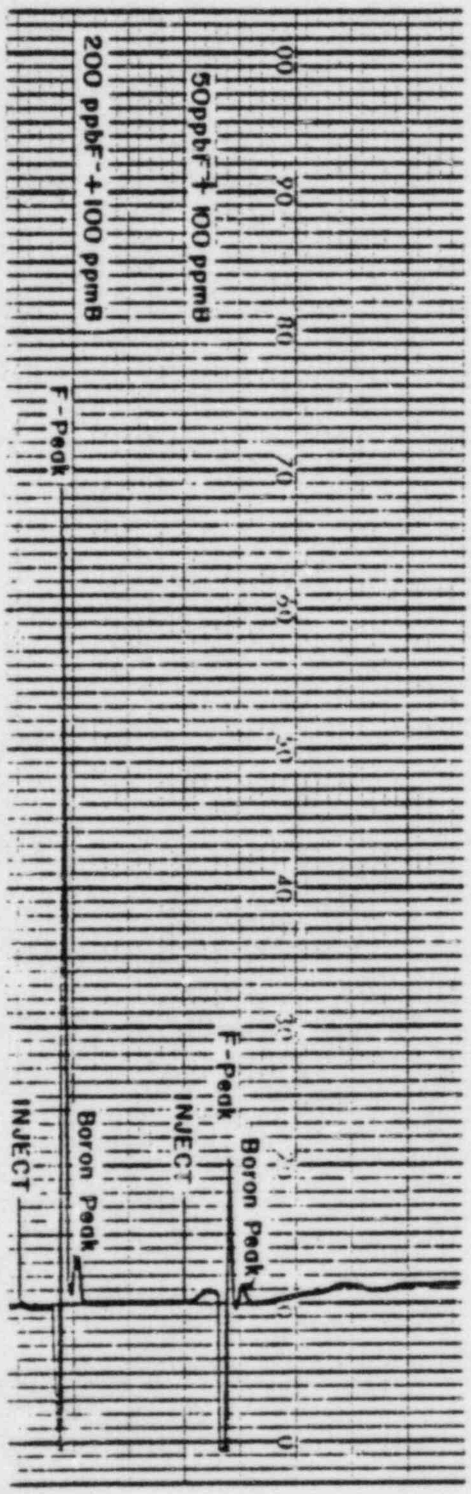


FIGURE V-12
CHROMATOGRAM

FLUORIDE IN THE PRESENCE OF BORON

PUMP SETTING 40
ELUENT 0.005M $Na_2B_4O_7 \cdot 10\ H_2O$

SAMPLE SIZE -0.20 ml
F-PEAK OCCURS 1.5 MIN.
B PEAK OCCURS 2 MIN.

PEAK HEIGHTS FOR F⁻
200 ppbF⁻ - 58.5
50 ppbF - 10.5

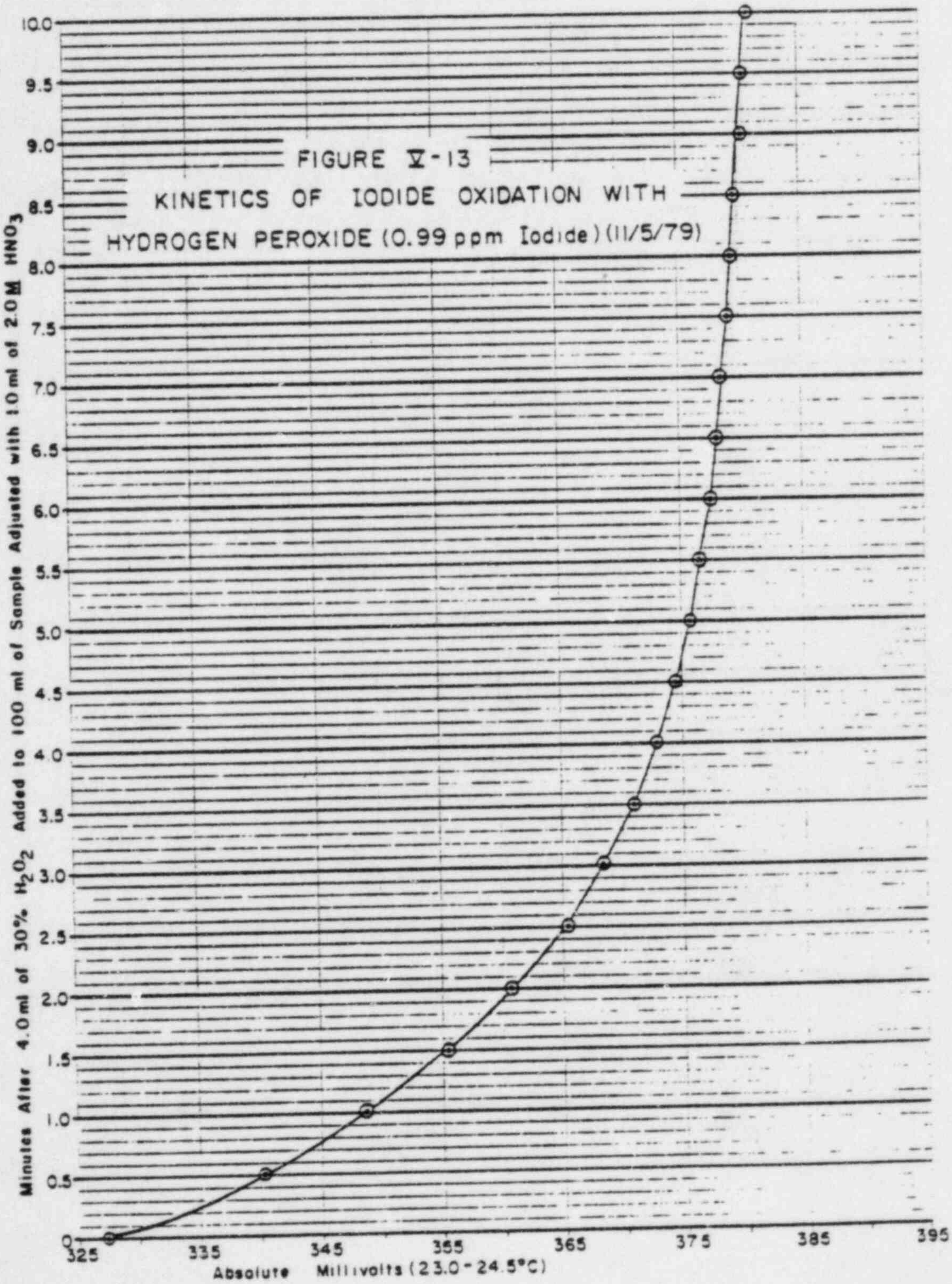


FIGURE V-13

KINETICS OF IODIDE OXIDATION WITH HYDROGEN PEROXIDE (0.99 ppm Iodide) (11/5/79)

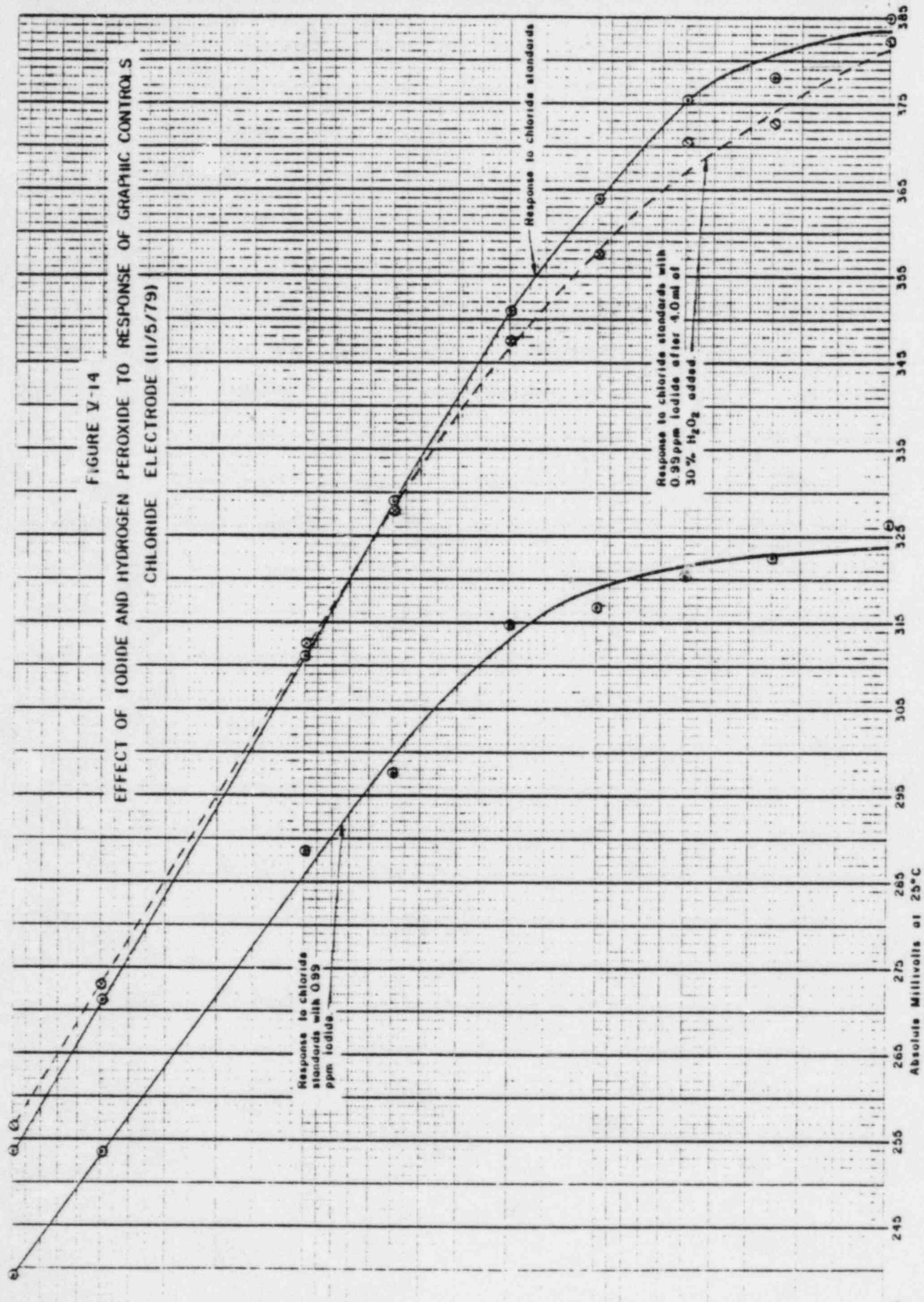


FIGURE V-14

EFFECT OF IODIDE AND HYDROGEN PEROXIDE TO RESPONSE OF GRAPHIC CONTROLS CHLORIDE ELECTRODE (11/5/79)

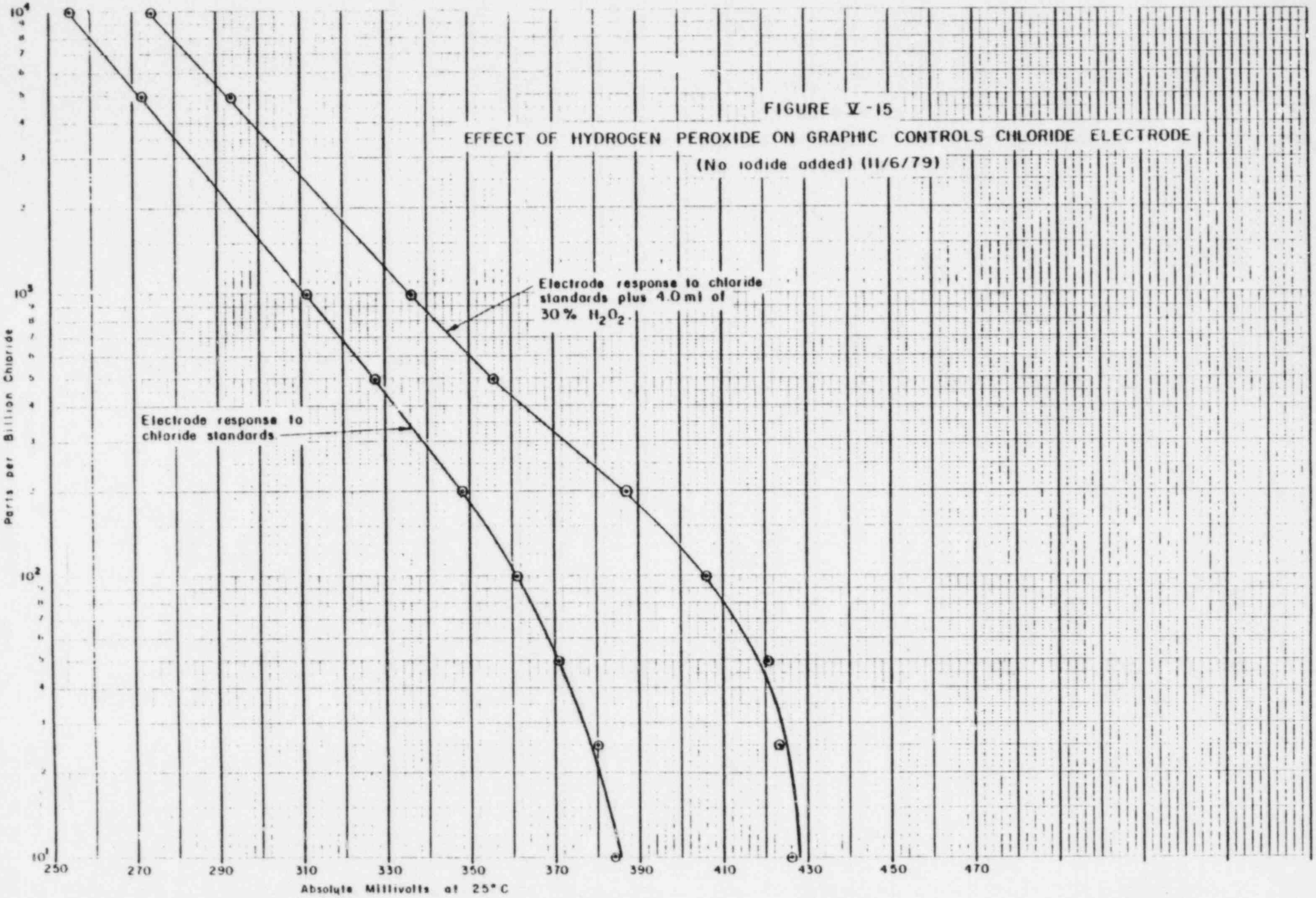


FIGURE V-15

EFFECT OF HYDROGEN PEROXIDE ON GRAPHIC CONTROLS CHLORIDE ELECTRODE

(No iodide added) (11/6/79)

Electrode response to chloride standards plus 4.0 ml of 30% H_2O_2.

Electrode response to chloride standards

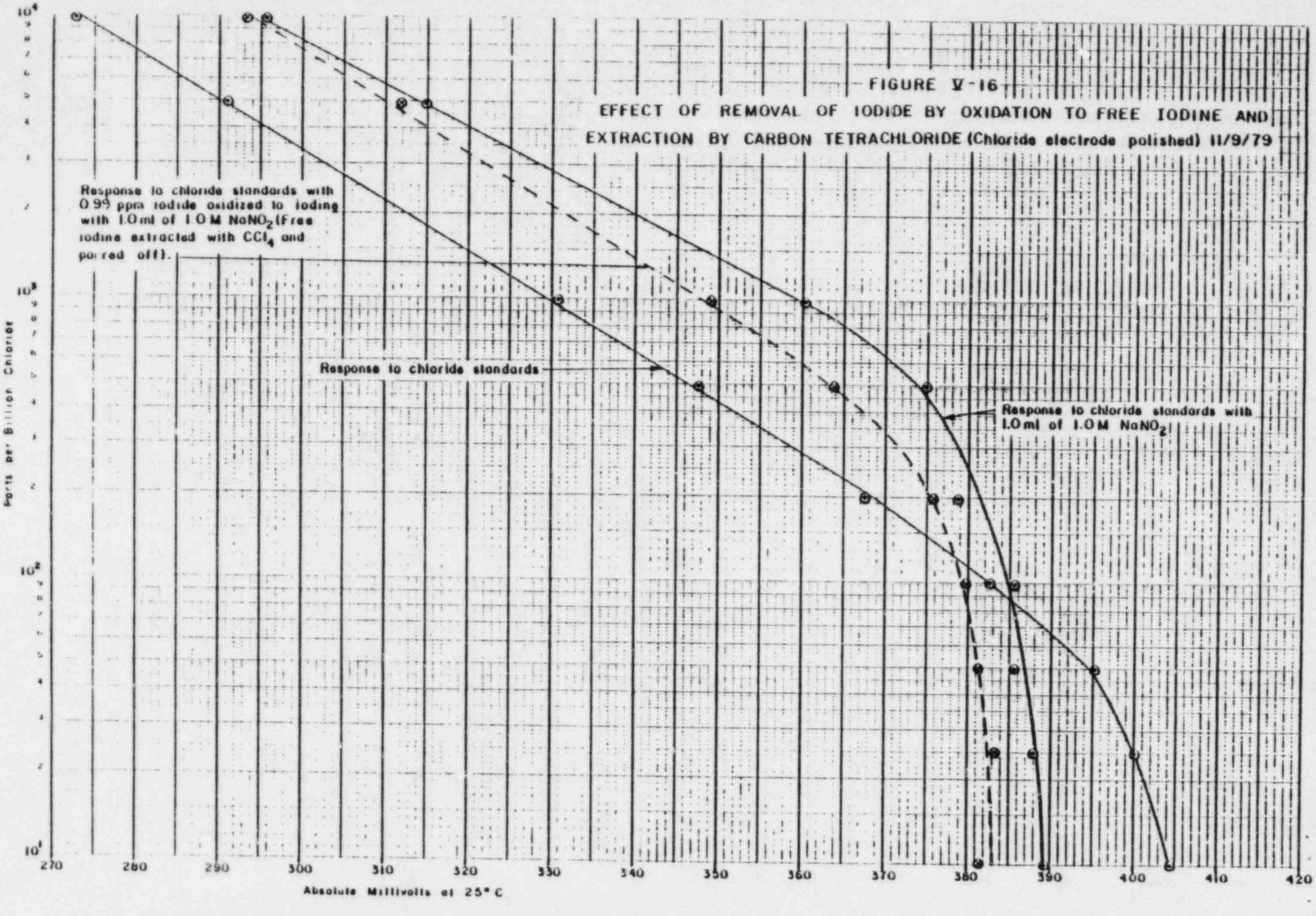


FIGURE V-16

EFFECT OF REMOVAL OF IODIDE BY OXIDATION TO FREE IODINE AND EXTRACTION BY CARBON TETRACHLORIDE (Chloride electrode polished) 11/9/79

VI. DEVELOPMENT OF DISSOLVED HYDROGEN ANALYSIS PROCEDURES

A. BACKGROUND

The gas analysis system shown in Figure III-2 and discussed in Section III, provides for the analysis of dissolved hydrogen concentration in the primary coolant. The gas is stripped from a 30 ml liquid sample with argon gas to yield a final gas volume of 600 cc at STP conditions. The resulting gas mixture is collected in a 300 cc container. Hydrogen concentration of the gas mixture as determined by gas chromatograph is related to dissolved hydrogen concentration in the primary coolant.

Prior to discussing the work performed on this topic, a brief explanation is offered concerning the terminology used in describing gas-mixtures and gas-water systems. Gas-mixtures are referred to as ppm by volume in this report. This is consistent with conventional terminology. For example, a 200 ppm hydrogen standard would contain 0.02 percent or 200 cc's of hydrogen in a total volume of 1,000,000 cc's of gas. It is convenient to use a volume basis when referring to the concentration of an individual gas in a mixture of gases because gas is normally processed, stored and sold on a volume basis.

In referring to dissolved gas concentration in water, conventional terminology is to use the term cc of gas/kg of water. However, it is not uncommon to use the term ppm which represents the standard term to indicate concentration of gas present by weight. There is a significant difference between ppm and cc/kg particularly with respect to hydrogen. Conversion factors for converting cc/kg to ppm for hydrogen, nitrogen and oxygen are indicated below:

Gas	cc/kg	x	Factor	=	ppm Gas In Solution
H_2	1	x	0.0893	=	0.0893
N_2	1	x	1.25	=	1.25
O_2	1	x	1.428	=	1.428
Ar	1	x			
Xe	1	x			

→ 2.23 ft^3

Reactor coolant contains 25-35 cc/kg of hydrogen under normal operating conditions. This could increase to around 1320 cc/kg under post-accident conditions as indicated by calculations presented in Appendix A. Also, there would be significant concentrations of fission product gases in solution as is indicated in Table VI-1. With 25 cc/kg of hydrogen in the reactor coolant, and assuming a 30 ml sample, 0.75 cc of hydrogen will be present in the sample to be analyzed. Stripping a 30 ml sample with 600 cc of argon will result in 0.75 cc/600 cc = 0.125 percent (or 1250 ppm) of hydrogen by volume in the gas sample to be analyzed. This assumes 100 percent scrubbing efficiency which apparently can be achieved with the proper system design. Similarly, if 2000 cc/kg of hydrogen is present in the reactor coolant, stripping a 30 ml sample with a 600 cc end volume will result in 60 cc/600 cc = 10 percent (or 100,000 ppm) of hydrogen by volume in the gas sample to be analyzed.

NUS performed testing to determine:

1. The range of hydrogen concentrations that could be analyzed using a gas chromatograph,
2. The accuracy of analysis that can be achieved under these conditions,
3. The effect of wet gas on analysis results,
4. Other problems that might be encountered during the hydrogen analyses.

B. PRIMARY COOLANT GAS CONCENTRATIONS UNDER ACCIDENT CONDITIONS

During accident conditions there will be a significant release of fission product gases to the primary coolant. Calculated and concentrations for gases in solution based on NRC guidelines for core damage are indicated in Table VI-1. The concentrations listed in this table are sufficient to give a peak height indication on the gas chromatograph over a wide range on the attenuation scale. However, fission product gases will be held up in the gas chromatograph columns for a longer period of time than is hydrogen, consequently will not interfere with the hydrogen determination.

The assumptions used in developing Table VI-1 are as follows:

1. Radioactive Gas

    a. Sargeant and Lundy source term

    b. Reactor coolant volume of 12,700 ft^3 at 2300 psia and 540 °F

    c. Decay for one hour

2. Nonradioactive Gas

    a. 3300 MW(t)

    b. 239 Pμ fission yields

    c. 650 days at 100 percent power

    d. 1.5 x 10^{13} m/cm^2 - sec thermal flux for removal via neutron capture

Using the assumptions listed above, the maximum fission product gas concentrations in the gas stripped from a 30 ml sample of primary coolant into a 300 cc container (24.7 psia) will be as follows:

	Radioactive Gas		Nonradioactive Gas	
	cc/kg in Coolant	ppm in Gas*	cc/kg in Coolant	ppm in Gas*
Kr	2.32	138	11.90	1,184
Xe	1.32	78.6	192.14	19,100

*Gas in the 300 cc gas collection container at 24.7 psia. Sentry has indicated that the end pressure in their gas collection container will be 10 psig or 24.7 psia.

There will be essentially no dissolved nitrogen, oxygen or argon in the primary coolant for reasons as follows:

- Nitrogen will be stripped from solution during the boiling that occurs during a loss of coolant accident.
- Oxygen will be stripped from solution or will be consumed through gamma induced combination with hydrogen.
- Argon will be stripped from solution through boiling.

C. INSTRUMENT OPERATION

A Fisher Model 1200 Gas Chromatograph was used for the initial study. A Baseline chromatograph will be used in plant applications; however, this instrument was not available at the time testing was performed. Both gas chromatographs have similar characteristics concerning operational requirements and restrictions in use. The Baseline can analyze over a wider hydrogen concentration range than the Fisher instrument.

The Fisher gas chromatograph employs a dual column, dual detector chromatographic system to separate and measure hydrogen (and other gases). Argon is utilized as the carrier gas. Samples are introduced into the gas chromatograph through a constant temperature gas sampling valve or with a syringe through an injection port. The injected gas is swept through two chromatographic columns by a continuous flow of argon carrier gas. The gaseous components are absorbed on, and then released from the columns at specific time intervals characteristic of the gas.

As each component is eluted, a detector senses and indicates its presence by the difference in thermal conductivity of the gas of interest relative to that of the carrier gas.

The detection and measuring system is a thermal conductivity cell consisting of two matched pairs of hot wire filaments. The electrical resistance of these filaments changes marked with small changes of temperature. When exposed to pure carrier gas flow, the filaments reach temperature equilibrium and constant resistance, causing the bridge to be electrically balanced. When a component of the gas sample such as hydrogen is carried past the filaments, the increase in thermal conductivity causes the filament to lose heat. As the bridge becomes unbalanced, a signal is sent to the recorder. The result, after a complete sample has passed through the system, is a chromatogram with a peak for each separate component. The height or area of the peak is proportional to the concentration of the specific gaseous component. Concentration of an unknown sample is determined by comparison with a known standard.

D. INITIAL DRY H_2 STANDARD DETERMINATIONS

Initially, the peak heights and linearity of response of the instrument were determined for dry hydrogen standards (in nitrogen) using the 0.25 cc sample size collector originally installed with the instrument. A 1 cc sample loop will be used with the Baseline instrument. The following data shown in Table VI-2 were obtained for duplicate runs of each standard.

Chromatograms for each hydrogen standard are shown in Figures VI-1 through VI-4. The chromatograms are similar and peaks occur in the following order:

1. A positive peak at the time of injection.
2. This is followed almost immediately by a composite peak as the sample sweeps through the first column and enters the second column.
3. The hydrogen peak occurs at about 2.5 minutes.
4. A nitrogen peak (the standards are H_2 in N_2) occurs at about six minutes.

Inspection of the data shown in Table VI-2 indicates excellent linearity was obtained among standards.

Linearity checks were then made for each standard at different attenuation settings to determine the linearity characteristics between ranges. Obviously, it will be necessary to use different attenuations to accommodate the wide range of hydrogen concentrations that can occur in the primary coolant during an accident condition. The data obtained from this work is presented in Table VI-3.

Linearity of the hydrogen peak for different attenuation settings is good provided peak height is at some reasonable level over the baseline indication. Some variation in linearity results at low peak levels. These data indicate that the attenuation settings can be changed as necessary with good linear response in signal output.

E. VARYING SAMPLE LOOP SIZE

Optimizing sample loop size is necessary for maintaining the flexibility of analyzing for wide ranges of hydrogen concentration. Of greatest importance, however, for post-accident analysis application is reducing sample loop size to minimize shielding problems.

The 0.25 cc sample loop used in the initial work was replaced with a 1.0 cc sample sized loop. Hydrogen standards were analyzed with this larger sample volume. Data obtained for the 1.0 cc sample loop are compared to the expected peak heights based on the 0.25 cc sample volume data in Table VI-4.

There is some deviation from between sample loop sizes due to small variations in the indicated size of the sample loops. However, linearity was obtained for the standards within a consistant sample loop size. These results indicate that the 1.0 cc sample loop can be used for hydrogen sampling and may be advantageous if hydrogen concentrations in the end gas mixture are expected to be less than 100 ppm by volume. A 100 ppm hydrogen concentration in the 300 ml gas collection flask as determined with a 0.25 cc sample loop corresponds to a dissolved hydrogen concentration of about 2 cc H_2/kg in the primary coolant. The approximate minimal level of detection based on peak heights obtained for the 0.25 cc and 1.0 cc sample loops are about 100 ppm and 250 ppm respectively. Thus, with a 0.25 cc sample loop and assuming perfect stripping, it will not be possible to measure dissolved hydrogen concentration in the range below 2 cc H_2/kg. The 1 cc loop is recommended in this application since it covers a range below 2 cc H_2/kg to the maximum of 2000 cc/kg expected under post-accident conditions.

Chromatographs were also obtained with a 3.0 cc sample loop for hydrogen concentrations in nitrogen gas of 200 and 500 ppm. However, it was found that erratic recorder behavior occurred when low attenuation settings were used with this sample loop size. The recorder pen would sweep in the positive direction off scale and would not return to the original baseline without manually changing the zero baseline adjustment. The recorder worked normally at attenuation settings of 8 or above; however, sensitivity was lost at low hydrogen concentrations. Data obtained with the 3.0 cc sample loop volume are given in Table VI-5.

It is possible that the Baseline gas chromatograph will behave differently from the Fisher with use of a 3.0 cc sample loop. However, there is little incentive to investigate the 3.0 cc sample loop since the 1.0 cc sample loop that Baseline recommends will easily cover the range required.

The calibration curves obtained for the 0.25 cc, 1.0 cc, and 3.0 cc sample volumes are shown in Figure VI-5.

F. DRY VS. WET SAMPLES

The instrument provides for removal of moisture from the samples by passing the sample through a Drierite column prior to entering the chromatographic columns. In the Fisher system, the Drierite columns may become water saturated and it may not be possible to dry gaseous samples during post-accident conditions. Therefore, the effect of moisture on hydrogen analyses results was checked utilizing the 0.25 cc sample volume. Three separate methods were used for introducing the H_2 standards to the instrument as follows:

1. Dry standards were injected directly from the tank of gas.

2. Moisture saturated standards were introduced via the normal route passing through the installed Drierite column.

3. Moisture saturated samples were injected by-passing the Drierite column. The data from these tests are summarized in Table VI-6.

Figure VI-6 shows the dry vs. wet hydrogen standard calibration curves. The standard peak heights obtained with the wet standards are approximately 66 percent greater for the Fisher gas chromotagraph than those obtained with dry samples. In addition to the difference in readout, it is know that moisture will shorten the useful life of the columns by some appreciable, though unknown amount. If it is necessary to analyze wet samples, calibration curves should be checked more frequently (i.e., every 3-4 samples rather than once a day).

The vendor indicates that dry gas is also required with the Baseline gas chromotagraph; however, there is less potential for introducing a wet sample to the Baseline than to the Fisher gas chromotagraph.

G. EVALUATION OF HYDROGEN ANALYSIS SYSTEM DESIGN

1. Preparation of Standards

In the work performed with dissolved hydrogen concentrations of 125 cc H_2/kg and below, water samples containing known concentrations of hydrogen were prepared by circulating water through a reaction flask containing 99.9 percent pure hydrogen at various pressures. Water charged into the reaction flask was sprayed through the hydrogen atmosphere. The water used to prepare the samples was degassed prior to introduction to the reaction flask. At least three system volumes of hydrogen-saturated water from the reaction flask were then pumped into a previously evacuated 30 ml sample container. A throttling valve was used to maintain backpressure on the system to keep the hydrogen gas in solution.

The high pressure standards were prepared as indicated above except that the recirculation made to provide for hydrogen saturation of the water was eliminated. A rocking autoclave was used to provide the mixing required to achieve a saturated solution. Driving force to move the sample through the 30 ml liquid sample container was achieved by maintaining a constant hydrogen overpressure on the autoclave or reaction flask as the valving was opened to permit flow.

Work performed with hydrogen concentrations below that obtained at 14.7 psia (17cc H_2/kg) was performed at subatmospheric conditions. The hydrogen concentrations of the resulting solutions were determined by use of Henry's Law. The coefficients used in this work were taken from the values indicated in Table VI-7. Data concerning coefficients for hydrogen solubility are also shown in graphical form in Figure VI-7. This table and figure are reproduced from data presented in reference (f).

2. Evaluation of Initial Sentry System Design for Stripping Hydrogen Gas From Solution

a. Procedure

The operating procedures presented below are intended only to describe the general sequence of operations used to perform test operations. Operating procedures as will be used by the utilities will be issued by separate correspondence through Sentry.

The first sequence of testing was performed under operating conditions as follows: (Refer to Figure III-2 to follow flow path).

(1) Water samples with known hydrogen concentrations were introduced into the water sample container. (SF 1.2)

(2) About 300 cc of argon gas was slowly purged through SF 1.2 collecting the gas into a previously evacuated 300 cc sample container. (EF1)

(3) EF1 was then pressurized with argon from the top of the container to 30 psia to force all water back into SF 1.2.

(4) Gas in the sample container was then analyzed as follows:

   (a) Evacuate the systems from the vacuum source to valve V-10. The GC sampling valve is in the sample position during evacuation.

   (b) Turn valve V-2 to position 3-2. The pressure gauge immediately indicates 0 psia.

   (c) Turn valve V-2 to position 1-3.

   (d) Crack open valve V-10 and close when pressure gauge indicates 14.7 psia.

   (e) Move GC sample valve to inject position and perform hydrogen analysis on gas scrubbed from solution.

This procedure provides for purging all sample lines and filling the gas chromatograph sample loop to 14.7 psia. Approximately 60-70 cc of gas was consumed for each gas sample analyzed. This was with the use of 20 feet of 1/8 inch tubing from the gas sample container EF-1 to the gas chromatograph. Since the sample container EF-1 contains about 300 cc of gas above atmospheric pressure, sufficient gas was available for 3-4 repeat analyses.

The test procedure was subsequently modified to purge about 600 cc of argon gas through SF 1.2 collecting the gas in a previously evacuated EF-1. No attempt was made to force water from EF-1 to SF 1.2. Gas anaylses were then performed.

b. Results

Erratic results were obtained using the procedure where the gas collection container was pressurized from the top of the container to force water back into the water sample container. It became quickly obvious that improvement was in order. Accordingly, the procedure was changed to purge the 600 cc of argon gas used through SF 1.2. Water in varying amounts was transported from the SF 1.2 to EF-1 container using this approach. Despite the variation in water carryover between successive samples, far better results were obtained using this approach than the original approach. Results of these tests are shown in Table VI-8 and plotted in Figure VI-8.

The reason for the high hydrogen values and deviation from linearity with the initial procedure cannot be satisfactorily explained. Contamination between successive runs is ruled out because the gas collection container was nitrogen purged and evacuated between runs. The problem may have been caused by variation in water carryover during successive tests or by stratification in the gas mixture.

No correction could be made for the change in volume resulting in the gas collection container from carryover because volume of the water was not constant each time. In any event, deviation from theoretical values was greater than the ±15 percent indicated as a goal for determining dissolved hydrogen concentration by Commonwealth Edison.

3. Evaluation of Modified System Design

a. Modification

Other gas analyses tests performed by NUS indicate that better linearity can be achieved and recovery yields will be closer to theoretical if the gas saturated water is sprayed into an evacuated chamber. Also, it is obvious that it is easier to correct for the change in volume in the gas collection container if the water carryover is a constant. Changes to the existing system were made as follows to achieve these ends. The design used is shown in Figure VI-10.

(1) A 90 micron porous metal capped cylinder was installed in the inlet to the gas collection container (EF-1). A fine spray results when water from the sample container is forced through this porous metal. The porous metal cylinder consists of a Nupro sintered filter element (Cat. No. SS-2FE-90).

(2) Argon gas was introduced from the top of the water sample container to force all the water into the gas collection container. An alternate approach to this would be to replace the existing 30 ml sample container with an appropriate length of 1/4 inch tubing. The use of tubing is considered superior as a sample vessel since earlier work performed by NUS with transparent systems indicates that gas bubbles have a propensity to remain on walls in areas where flow velocity decreases. These gas bubbles lead to erratic results. Purge flow time must be increased to sweep the gas bubbles from the walls in these areas.

b. Procedure

Testing to evaluate the modified design was performed as indicated below in abbreviated form.

(1) Water samples with known hydrogen concentrations were introduced into the water sample container.

(2) The water sample container was isolated and the argon gas line leading to the top of the container was pressurized to 29.7 psia.

(3) The valve between the water sample container and the previously evacuated gas sample container was opened (V-9). Immediately thereafter, the valve to the argon gas line at the top of the water sample container was opened.

(4) Argon gas was purged through the system at a rate of about 200 cc/min until system pressure in the gas sample container (EF-1) was at 29.7 psia.

(5) Gas from the sample container was bled to the 40 ml accumulator through the gas chromatograph sampling valve. When system pressure was at atmospheric pressure, a bite sample of gas was taken with the gas sampling valve for analyses.

c. Results

Results of the tests performed with the modified design are shown in Tables VI-9 and VI-10 and plotted in Figure VI-9. Good linearity was achieved throughout the range investigated. The lowest level of hydrogen measured was 4.4 cc/kg. Extrapolation of data at the low end of the range indicates that it will be possible to measure dissolved hydrogen concentrations of about 1-2 cc H_2/kg or lower.

Four test runs were made with a hydrogen pressure of 1014.7 psia in a reaction flask. The resulting dissolved hydrogen concentration in water is about 1230 cc/kg at this pressure. End results after stripping and analysis were about 2-5 percent below theoretical. These data are presented in Table VI-10.

Considerable difficulty was initially involved in obtaining reproducible results at the high hydrogen concentration. It was finally established that the problem only occurred when the gas chromatograph was evacuated prior to admitting the gas to the sample loop. No problem developed when the gas chromatograph was operated at atmospheric pressure. The problem was eliminated by using a larger sample of gas to flush out the lines. It is believed that the problem stemming from evacuation is peculiar to the Fisher gas partitioner.

4. Evaluation of a Reduced Sample Volume

An investigation was made to determine if dissolved hydrogen analyses could be performed on a smaller sample volume. The equipment was modified for this work as follows:

a. A coiled loop of tubing with a 10 ml liquid volume was substituted for the 30 ml sample container, SF1.2.

b. A 150 ml gas sample container was substituted for the 300 ml container EF1.

c. Gas stripping was performed with the modified design shown in Figure VI-10.

Testing was performed for this work using the procedure outlined in Section VI-F-3. Results of the work presented in Figure VI-11, indicate that acceptable hydrogen analyses results can be obtained with a 10 ml sample. Howver, the existing design should remain as is, because it would be too expensive to change design at this stage of operations. Also, there is little incentive to reduce liquid sample volume now since shielding design has been fixed.

5. Problem Areas with Determining Dissolved Hydrogen Concentration

The work performed indicate that the following design and operating features are required to obtain consistent results with respect to determining dissolved hydrogen concentration.

a. Dead legs should be eliminated from the design of the primary coolant sample container. Elimination of dead legs requires the use of three-way valves at the inlet and outlet to the liquid sample container as shown in Figure VI-10.

b. The primary coolant sample container should be mounted vertically with flow inlet at the bottom. This is to prevent gas pocketing in the sample container.

c. While the data are not overwhelming in this respect, there is indication that reproducibility is improved using a sample container made of tubing rather than a 30 ml sample cylinder. The explanation offered is the higher velocity achieved in the tubing is more likely to sweep out all gas bubbles from the system.

d. Dead legs should be eliminated from the design of the gas collection cylinder. This requires the use of a shut-off valve at the outlet of the collection cylinder as shown in Figure VI-10. The valve is closed during gas stripping operations to confine all gas to the collection cylinder.

e. A 90 micron porous metal cap should be installed at the inlet to the gas collection cylinder. The purpose of this porous metal cap is to break up the water entering the gas collection cylinder into a fine spray. This increases surface area of the water and thus facilitates degasification.

f. Design of the system should provide for forcing all water from the primary coolant sample container through the porous metal cap into the gas collection cylinder.

g. The gas collection cylinder should be evacuated to a pressure of 1 psia or less prior to performing gas stripping operations.

h. A positive pressure of about 30 psig should be imposed on the primary coolant sample container prior to opening the valve between the primary coolant sample container and the gas collection cylinder. This results in a pressure differential of about 45 psi across the system. With this driving force, water is forced at a rapid rate through the porous metal cap to create a fine spray which facilitates degasification.

i. Best results with respect to gas stripping operations with argon were obtained when the inlet and outlet valve to the primary system coolant container were opened simultaneously.

j. When performing stripping operations on the primary coolant with argon gas, flow should be held relatively constant at about 100-200 cc/min. This requires opening of the argon gas throttling valve during the stripping operation to compensate for the change in pressure differential across the system as pressure increases in the gas collection cylinder.

k. About 2 or 3 minutes is required for the gas to mix after performing gas stripping operations. Gas samples taken immediately can, or probably will give erratic results.

TABLE VI-1

POTENTIAL PRIMARY COOLANT FISSION PRODUCT GAS CONCENTRATION UNDER ACCIDENT CONDITIONS

Isotope	Radioactive Gas cc/kg	Isotope	Non Radioactive Gas cc/kg
83 m Kr	3.015-4	78 Kr	-
85 m Kr	1.733-3	80 Kr	3.722-5
85 Kr	2.313+0	82 Kr	3.064-2
87 Kr	6.719-4	83 Kr	2.1518
88 Kr	2.946-3	84 Kr	3.7605
89 Kr	1.961-10	86 Kr	5.9590
Total Kr	2.3183 cc/kg		11.9020 cc/kg
131 m Xe	0.6852	128 Xe	9.061-4
133 m Xe	6.329-3	129 Xe	11.7816
133 Xe	0.6198	130 Xe	0.04754
135 m Xe	2.564-5	131 Xe	28.1340
135 Xe	8.827-3	132 Xe	41.4791
137 Xe	7.017-9	134 Xe	58.5753
138 Xe	5.065-5	136 Xe	52.1185
Total Xe	1.3202 cc/kg		192.1369 cc/kg

TABLE VI-2

DRY HYDROGEN STANDARD ANALYSES

H_2 Concentration in Nitrogen	Attenuation Setting	Peak Height	Attenuation X Peak Height
200 ppm	1	6	6
200 ppm	1	6	6
500 ppm	1	14	14
500 ppm	1	14	14
1000 ppm	1	28	28
1000 ppm	1	28	28
10,000 ppm	4	70	280
10,000 ppm	8	35	280

NOTE: ppm in gas mixtures is by volume.

TABLE VI-3

ATTENUATION LINEARITY DATA

H_2 Concentration in Nitrogen	Attenuation Setting	Peak Height	Attenuation X Peak Height
200 ppm	1	6	6
200 ppm	2	3	6
200 ppm	4	1.3	5.2
200 ppm	8	0.8	6.4
500 ppm	1	14	14
500 ppm	2	7	14
500 ppm	4	3.5	14
500 ppm	8	2.0	16
1000 ppm	1	28	28
1000 ppm	2	14	28
1000 ppm	4	7	28
1000 ppm	8	3.7	29.6
1000 ppm	16	2.0	32
10,000 ppm	4	70	280
10,000 ppm	8	35	280

NOTE: ppm in gas mixtures is by volume.

TABLE VI-4

1.0 cc SAMPLE VOLUME - HYDROGEN STANDARD DATA

H_2 Concentration in Nitrogen	Attenuation Setting	Peak Height	Attenuation X Peak Height	Expected Peak Height Based on 0.25 cc Sample Data
200 ppm	1	20	20	6x4 = 24
200 ppm	2	10	20	
200 ppm	4	5	20	
200 ppm	8	2.5	20	
200 ppm	16	1.3	20.8	
500 ppm	1	47	47	14x4 = 56
500 ppm	2	23	46	
500 ppm	4	12	48	
500 ppm	8	6	48	
500 ppm	16	3	48	
1000 ppm	2	43	86	28x4 = 112
1000 ppm	4	24	96	
1000 ppm	8	12	96	
1000 ppm	16	6	96	

NOTE: ppm in gas mixtures is by volume.

TABLE VI-5

3.0 cc SAMPLE VOLUME - HYDROGEN STANDARD DATA

H_2 Concentration in Nitrogen	Attenuation Setting	Peak Height	Attenuation X Peak Height	Comment
200 ppm	4	–	–	Recorder would return to the baseline only by manually changing course zero adjustment
200 ppm	8	–	–	Same as above
200 ppm	16	4	64	
200 ppm	32	2	64	
200 ppm	64	1.1	70	
500 ppm	8	–	–	Recorder would return to the baseline only by manually changing course zero adjusment
500 ppm	16	10	160	
500 ppm	32	4	128	

NOTE: ppm in gas mixtures is by volume.

TABLE VI-6

DRY VS WET HYDROGEN STANDARDS

H_2 Concentration in Nitrogen	Mode of Sample Entry	Attenuation Setting	Peak Height	Attenuation X Peak Height
1000 ppm (by volume)	a	1	28	28
1000 ppm (by volume)	a	1	28	28
1000 ppm (by volume)	b	1	29	29
1000 ppm (by volume)	b	1	28	28
1000 ppm (by volume)	c	2	21	42
1000 ppm (by volume)	c	2	21	42
500 ppm (by volume)	a	1	14	14
500 ppm (by volume)	a	1	15	15
500 ppm (by volume)	b	1	14	14
500 ppm (by volume)	b	1	16	16
500 ppm (by volume)	c	2	11	22
500 ppm (by volume)	c	2	10	20
200 ppm (by volume)	a	1	6	6
200 ppm (by volume)	a	1	6	6
200 ppm (by volume)	c	2	4.5	9.0
200 ppm (by volume)	c	2	4.8	9.6

---

* a - Dry gas from tank
b - Wet gas passed through Drierite column
c - Wet gas by passing Drierite column

TABLE VI-7

CALCULATED VALUES OF HENRY'S LAW COEFFICIENTS

$\frac{\text{psia}}{\text{cc/kg } H_2O}$

Temp (°F)	Correlating	99% Confidence Limits	
		Lower	Upper
32	0.7041	0.6804	0.7278
40	0.7307	0.7070	0.7544
60	0.7935	0.7699	0.8172
80	0.8517	0.8281	0.8754
100	0.9058	0.8821	0.9295
120	0.921	0.904	0.941
140	0.921	0.901	0.936
160	0.896	0.883	0.912
180	0.860	0.850	0.874
200	0.8091	0.7992	0.8189
212	0.7762	0.7668	0.7856
220	0.7549	0.7457	0.7640
240	0.7038	0.6953	0.7123
260	0.6556	0.6476	0.6635
280	0.6099	0.6025	0.6173
300	0.5667	0.5598	0.5735
320	0.5257	0.5193	0.5320
340	0.4867	0.4808	0.4925
360	0.4497	0.442	0.4550
380	0.4144	0.4094	0.4193
400	0.3807	0.3761	0.3852
420	0.3486	0.3444	0.3527
440	0.3179	0.3141	0.3216
460	0.2885	9.2851	0.2919
480	0.2604	0.2573	0.2635
500	0.2335	0.2307	0.2362
520	0.2076	0.2052	0.2100
540	0.1828	0.1807	0.1849
560	0.1590	0.1571	0.1608
580	0.1361	0.1345	0.1376
600	0.1140	0.1127	0.1153
620	0.0928	0.0918	0.0938
640	0.0723	0.0715	0.0731
660	0.0526	0.0521	0.0531
680	0.0336	0.0333	0.0338
700	0.0152	0.0151	0.0152
705.4	0.0103	0.0103	0.0103

TABLE VI-8
CECO GAS SCRUBBER H_2
ANALYSIS DATA HIGH PRESSURE RESULTS

Hydrogen Overpressure in Reaction Flask (psig)	ccH_2/kg	ppm H_2 in H_2O By Weight	Analysis Results, ppm H_2 in Gas Collection Container		Theoretical ppm by by Volume in Gas Collection Container**	% Deviation From Theoretical
			Volume ppm	Weight ppm*		
1014.7 psia	1230	109	51,077	2554	53,622	-4.7
1014.7 psia	1230	109	51,385	2569	53,622	-4.2
1014.7 psia	1230	109	52,308	2615	53,622	-2.5
1014.7 psia	1230	109	51,692	2585	53,622	-3.6

---

*Weight ppm hydrogen in argon gas.

**Based on the use of Henry's Law in calculating hydrogen solubility levels and a 100% scrubbing efficiency.

TABLE VI-9
CECO GAS SCRUBBER H_2 ANALYSIS (MODIFIED DESIGN)

Hydrogen Overpressure in Reaction Flask (psig)	ccH_2/kg	ppm H_2 in H_2O By Weight	Analysis Results, ppm H_2 in Gas Collection Container: Volume ppm	Analysis Results, ppm H_2 in Gas Collection Container: Weight ppm*	Theoretical ppm by by Volume in Gas Collection Container**	% Deviation From Theoretical
94.7	115.5	10.3	7000	350	6351	+10%
			7384	369	6351	+16%
84.7	103.3	9.2	6461	323	5681	+14%
			5692	285	5681	+0.2%
			5076	254	5681	+11%
			6000	300	5681	+6%
			6076	304	5684	+7%
74.7	91.1	8.1	4769	238	5010	-5%
			4769	238	5010	-5%
64.7	78.9	7.0	4307	215	4340	-0.8%
			4769	238	4340	+10%
			4461	223	4340	+3%
54.7	66.7	5.9	3846	192	3669	+5%
			3846	192	3669	+5%
44.7	54.5	4.9	3076	154	2998	+3%
			5320	266	2998	+77%
			3076	154	2998	+3%
34.7	42.3	3.8	2384	119	2327	+2%
			2615	131	2327	+12%
			2384	119	2327	+2%
			2692	135	2327	+10%
			2307	115	2327	-0.8%
			2307	115	2327	-0.8%
			2538	127	2327	+9%

TABLE VI-9
CECO GAS SCRUBBER H_2 ANALYSIS DATA (MODIFIED DESIGN)
PAGE 2

Hydrogen Overpressure in Reaction Flask (psig)	ccH_2/kg	ppm H_2 in H_2O By Weight	Analysis Results, ppm H_2 in Gas Collection Container		Theoretical ppm by by Volume in Gas Collection Container**	% Deviation From Theoretical
			Volume ppm	Weight ppm*		
24.7	30.1	2.7	1692	85	1657	+2%
			1538	77	1657	-7%
			1538	77	1657	-7%
			1615	81	1657	-2%
			1692	85	1657	+2%
14.7	17.9	1.6	1000	50	985	+2%
			1000	50	985	+2%
			1000	50	985	+2%
			1000	50	985	+2%
9.1	11.1	0.98	692	35	610	+13%
			692	35	610	+13%
3.6	4.4	0.39	250	12.5	241	+4%
			250	12.5	241	+4%

---

*Weight ppm hydrogen in argon gas.
**Based on the use of Henry's Law in calculating hydrogen solubility levels and a 100% scrubbing efficiency.

TABLE VI-10
CECO GAS SCRUBBER H_2 ANALYSIS (INITIAL DESIGN)

Hydrogen Overpressure in Reaction Flask (psig)	ccH_2/kg	ppm H_2 in H_2O By Weight	Analysis Results, ppm H_2 in Gas Collection Container		Theoretical ppm by by Volume in Gas Collection Container**	% Deviation From Theoretical
			Volume ppm	Weight ppm*		
104.7	127.7	11.4	8000	400	7200	+11%
			7600	380	7220	+5%
94.7	115.5	10.3	7428	371	6531	+14%
84.7	103.3	9.2	7000	350	5841	+20%
			6442	322	5841	+11%
74.7	91.1	8.1	6000	300	5151	+16%
64.7	78.9	7.0	5428	271	4462	+22%
			5142	257	4462	+16%
54.7	66.7	5.9	5035	252	3772	+35%
			4571	229	3772	+21%
			3928	196	3772	+5%
44.7	54.5	4.9	3857	193	3082	+25%
			4000	200	3082	+30%
34.7	42.3	3.8	3000	150	2393	+25%
			2857	143	2393	+19%
24.7	30.1	2.7	1741	87	1703	+2%
			1857	93	1703	+9%

---

*Weight ppm hydrogen in argon gas.

**Based or the use of Henry's Law in calculating hydrogen solubility levels and 100% scrubbing efficiency.

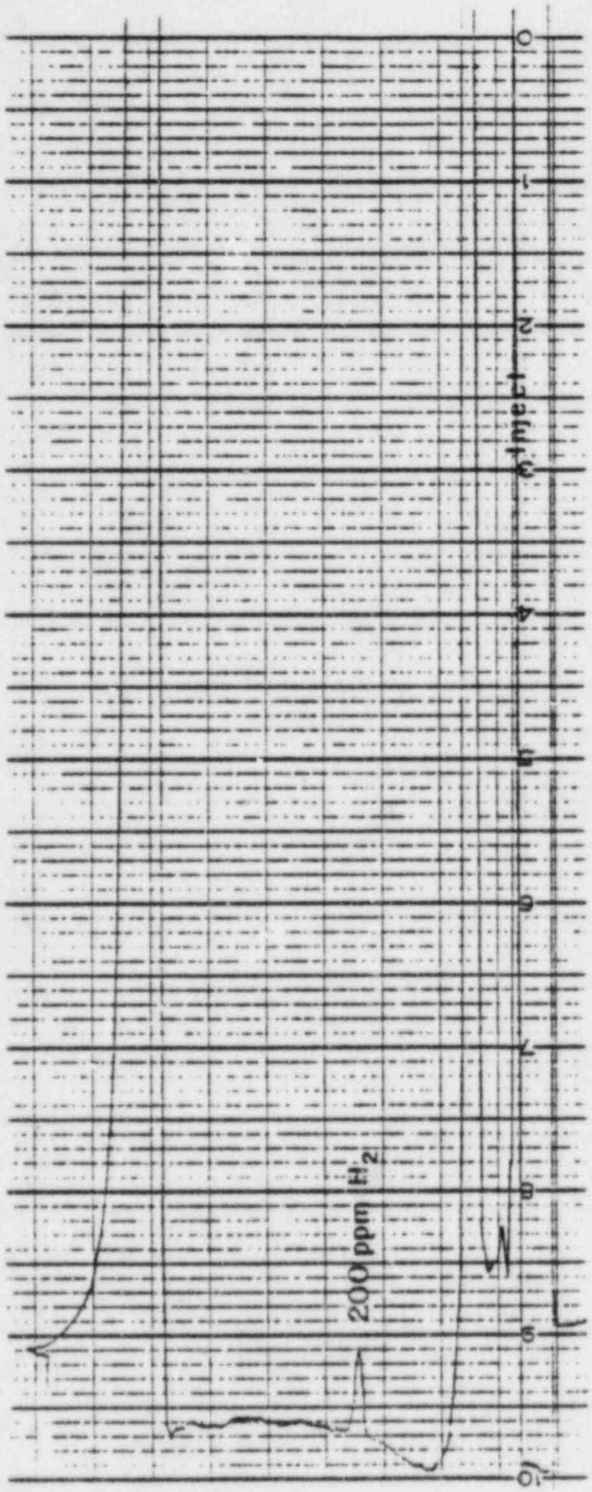


FIGURE VI-1
200 ppm H_2 CHROMATOGRAM

Carrier Gas - Argon
Oven Temp. - 50° C
Bridge Current - 125 mA
Sample Size - 0.25 cc
Attenuation - x 1
Carrier Gas Flow - 30cc/min
Chart Speed - 0.5"/min

Peak Height = 6
H_2 Peak Occurs 2.5 min. after Injection.

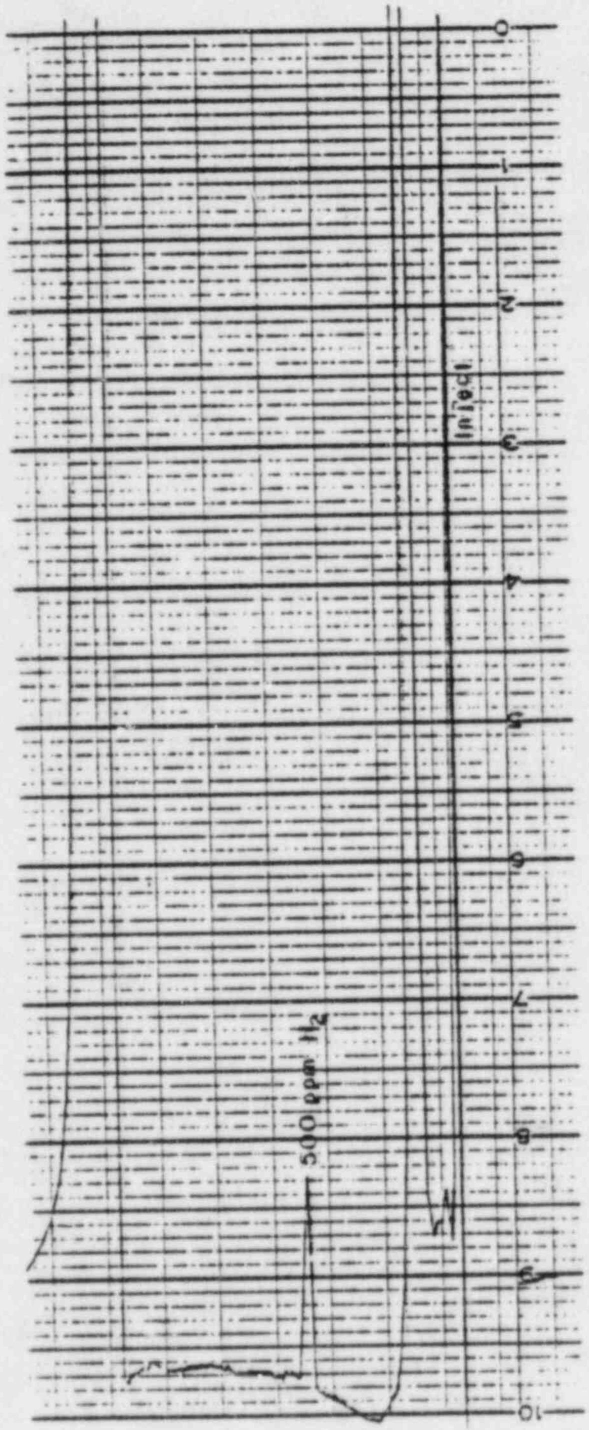


FIGURE VI-2
500 ppm H_2 CHROMATOGRAM

Carrier Gas - Argon
Oven Temp. - 50° C
Bridge Current - 125 mA
Sample Size - 0.25 cc
Attenuation - x 1
Carrier Gas Flow - 30cc/min.
Chart Speed - 0.5"/min.

Peak Height = 14
H_2 peak occurs 2.5 minutes after injection.

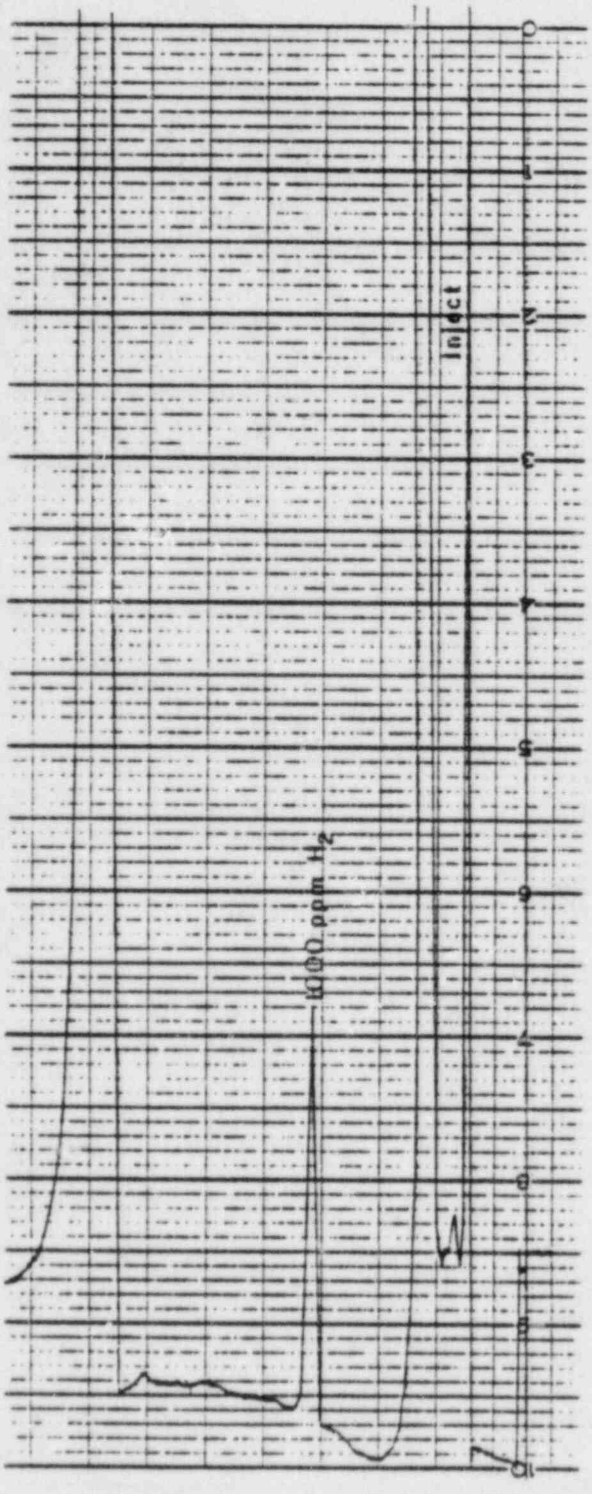


FIGURE VI-3

1000 ppm H_2 CHROMATOGRAM

Carrier Gas - Argon
Oven Temp. - 50° C
Bridge Current - 125 mA
Sample Size - 0.25 cc
Attenuation - x 1
Carrier Gas Flow - 30cc/min.
Chart Speed - 0.5"/min.

Peak Height - 28
H_2 peak occurs 2.5 minutes after injection.

FIGURE VI-4

1% H_2 CHROMATOGRAM

Carrier Gas - Argon
Oven Temp. - 50° C
Bridge Current - 125 mA
Sample Size - 0.25 cc
Attenuation - x 8
Carrier Gas Flow - 30 cc/min.
Chart Speed - 0.5"/min.

Peak Height = 280
H_2 peak occurs 2.5 minutes after injection.

FIGURE VI-5 - ppm H_2 VS PEAK HEIGHT (DRY H_2 STDs)

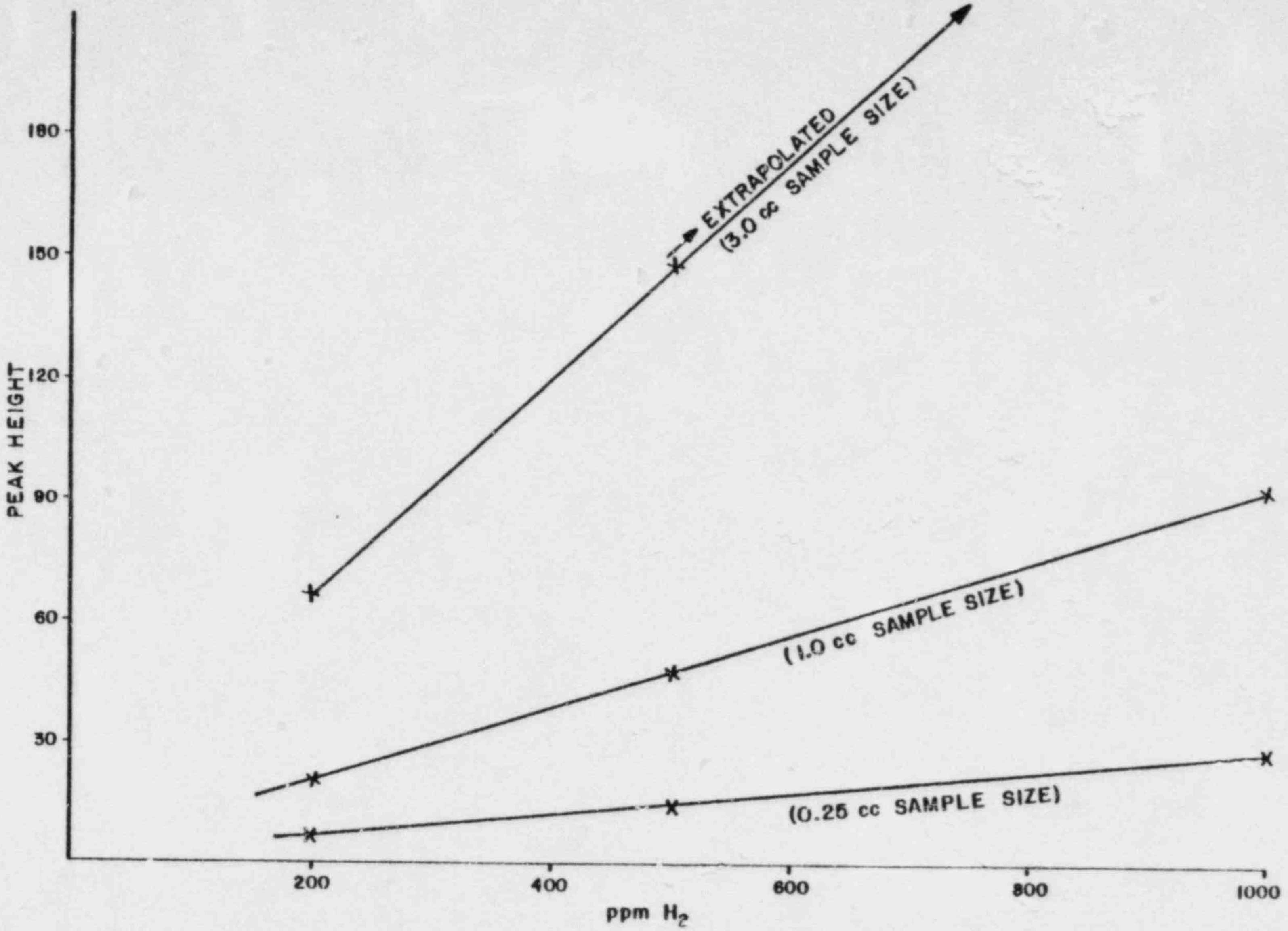


FIGURE VI-6-DRY vs WET H_2 STANDARD CALIBRATION

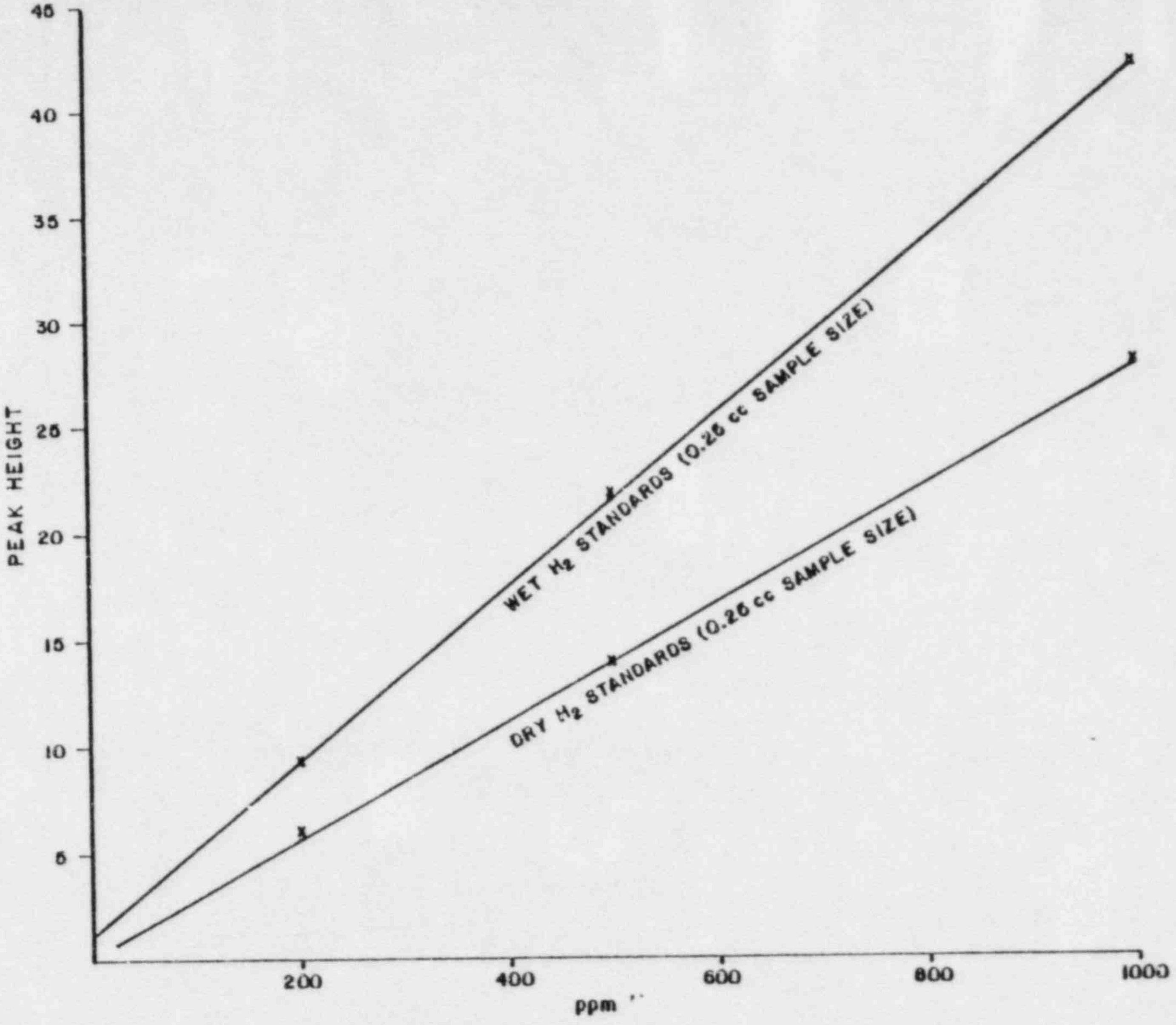


FIGURE VI-7

HENRY'S LAW COEFFICIENT FOR HYDROGEN IN WATER
(CORRELATION OF SOLUBILITY DATA FOR HYDROGEN AND NITROGEN IN WATER, WAPD-TM-633)

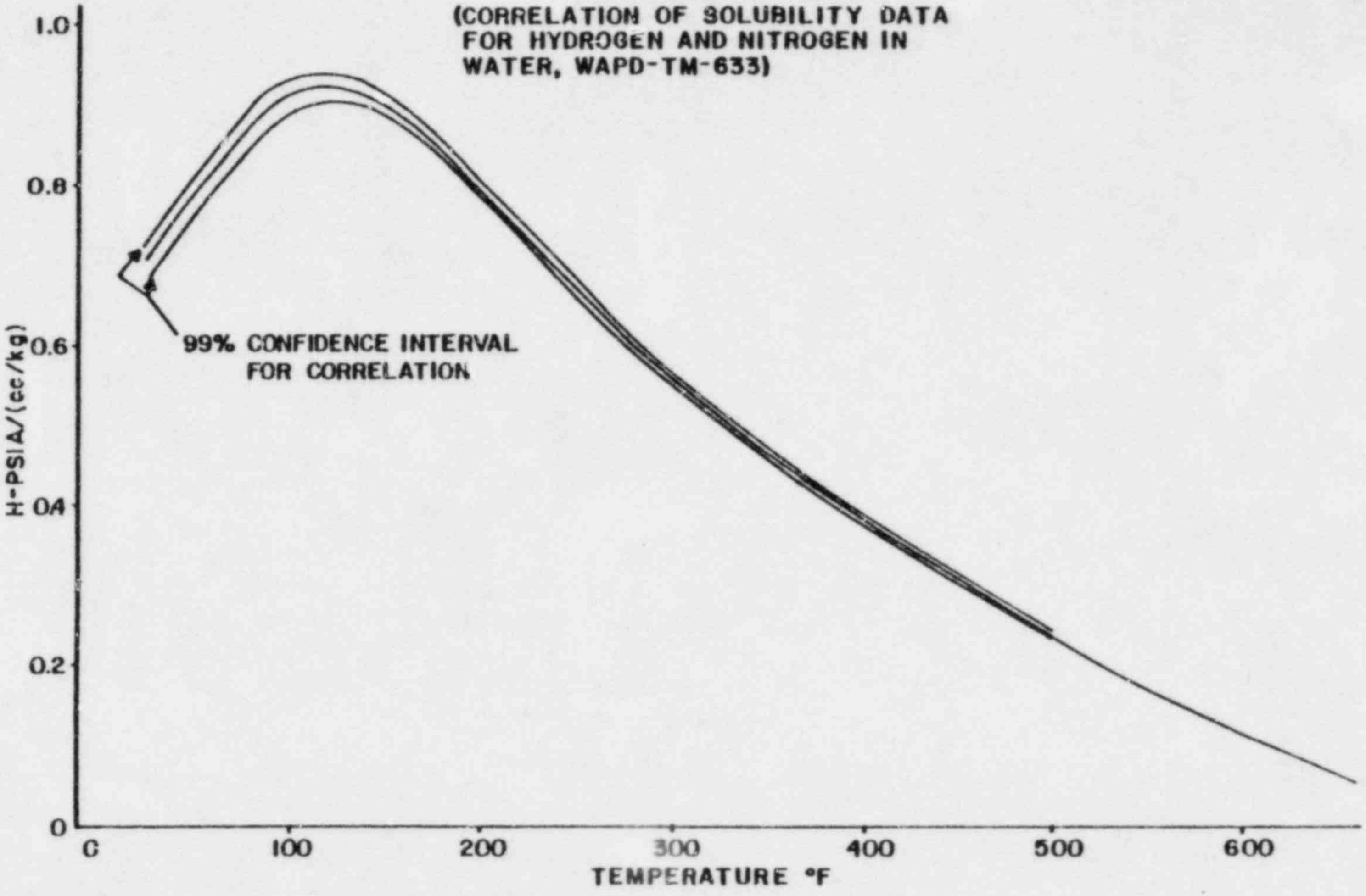


FIGURE VI-8

CECO GAS SCRUBBER
(INITIAL DESIGN)

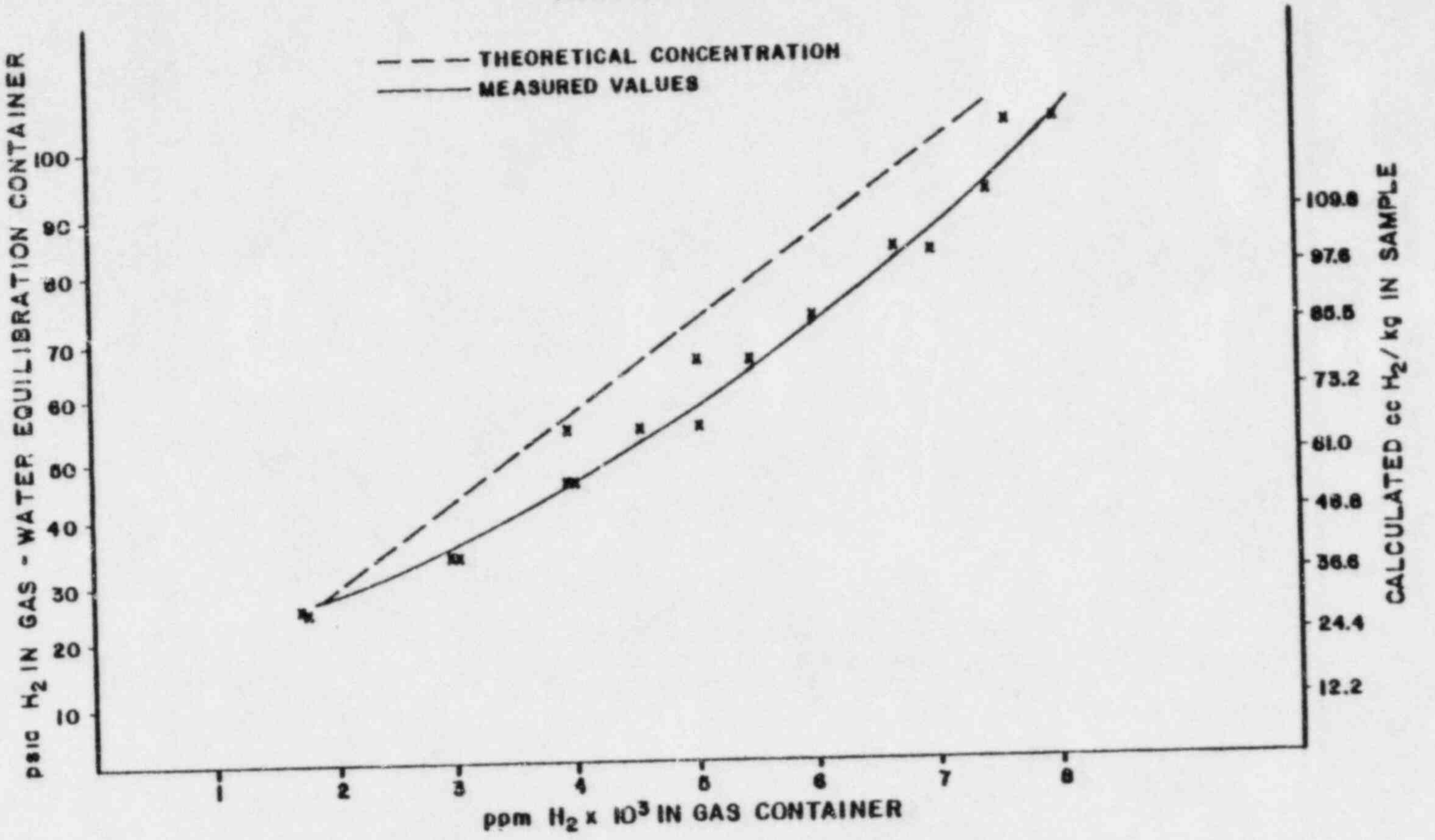
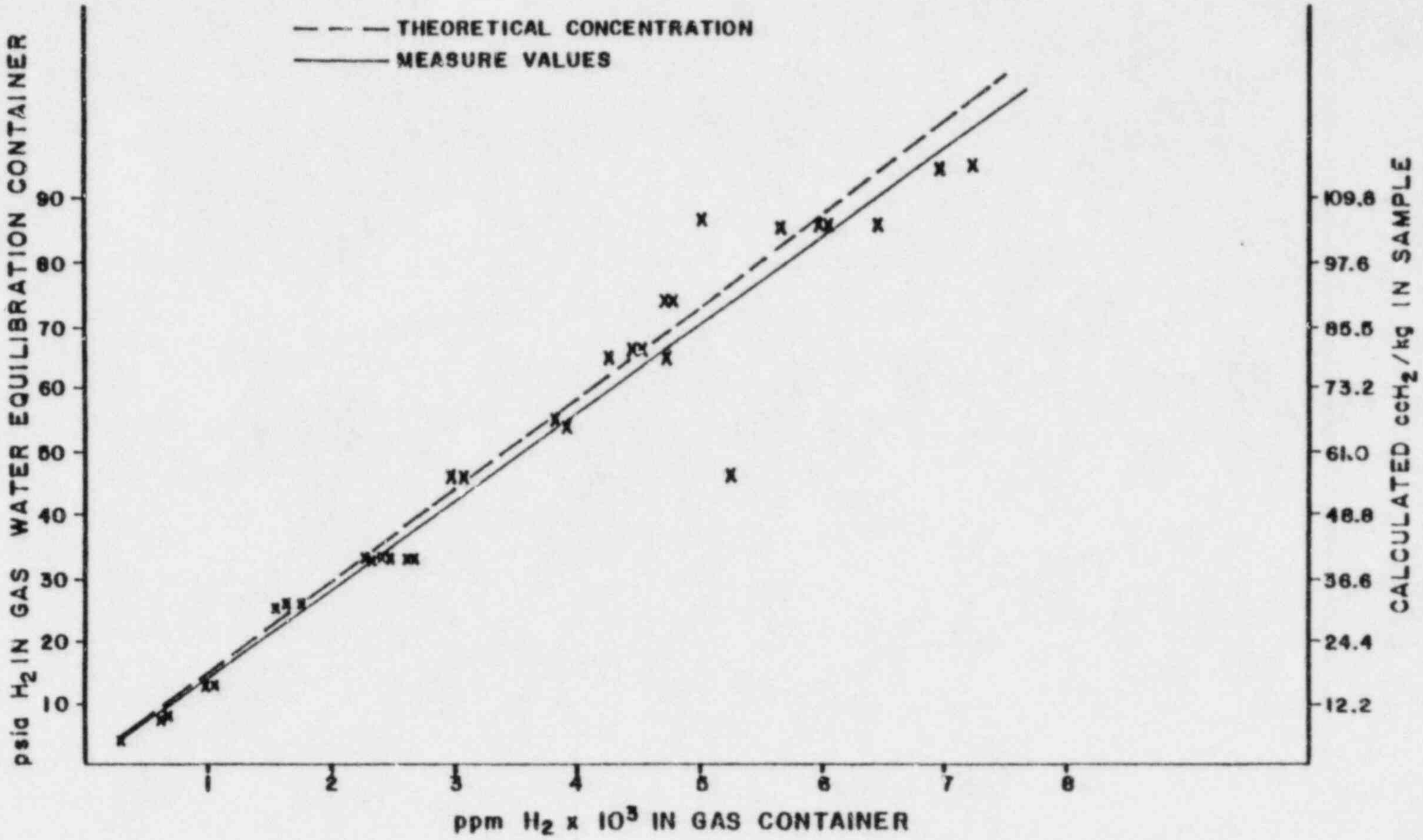


FIGURE VI-9
CECO GAS SCRUBBER
(MODIFIED DESIGN)



Recommended Primary Coolant Gas Stripping System

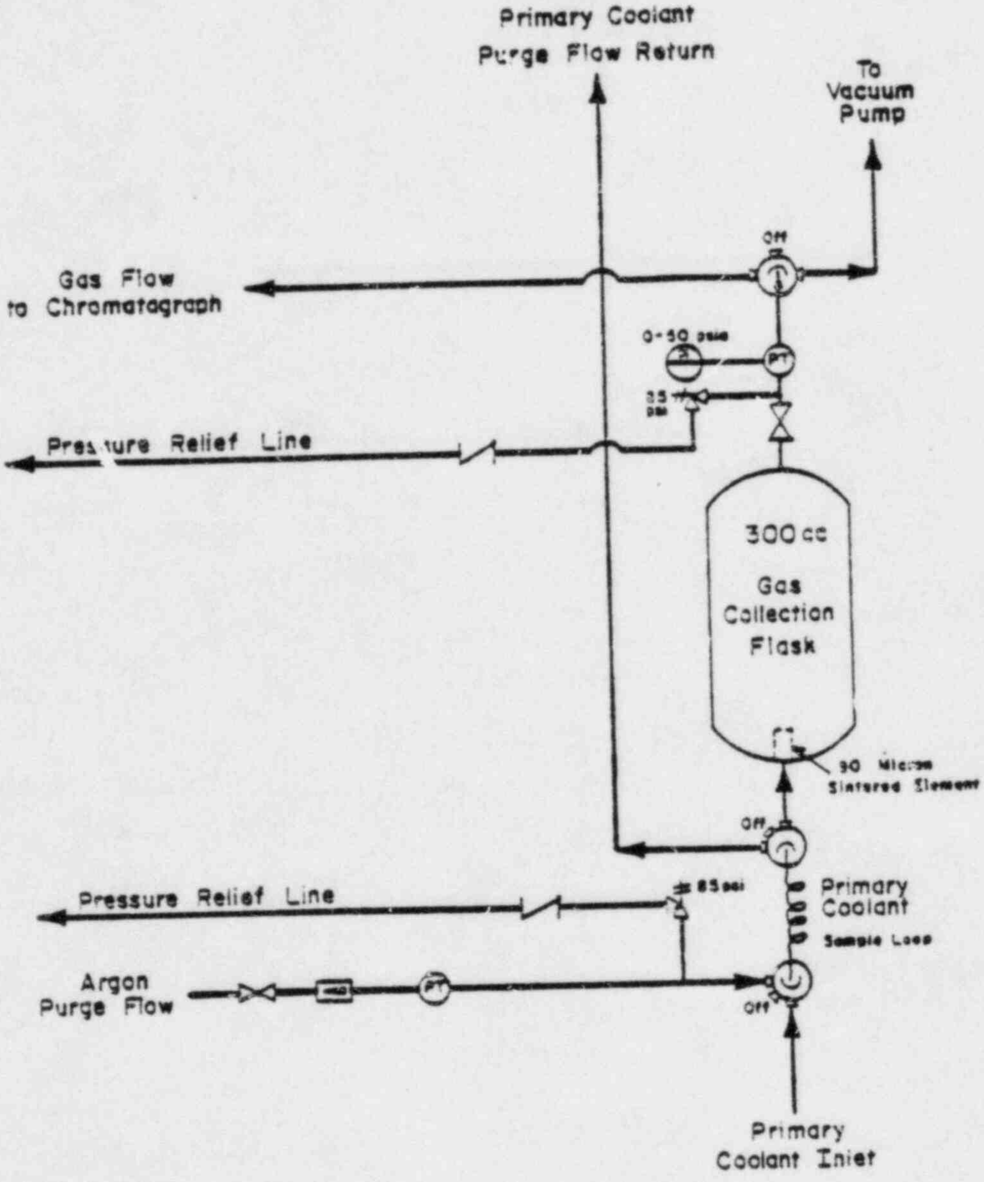
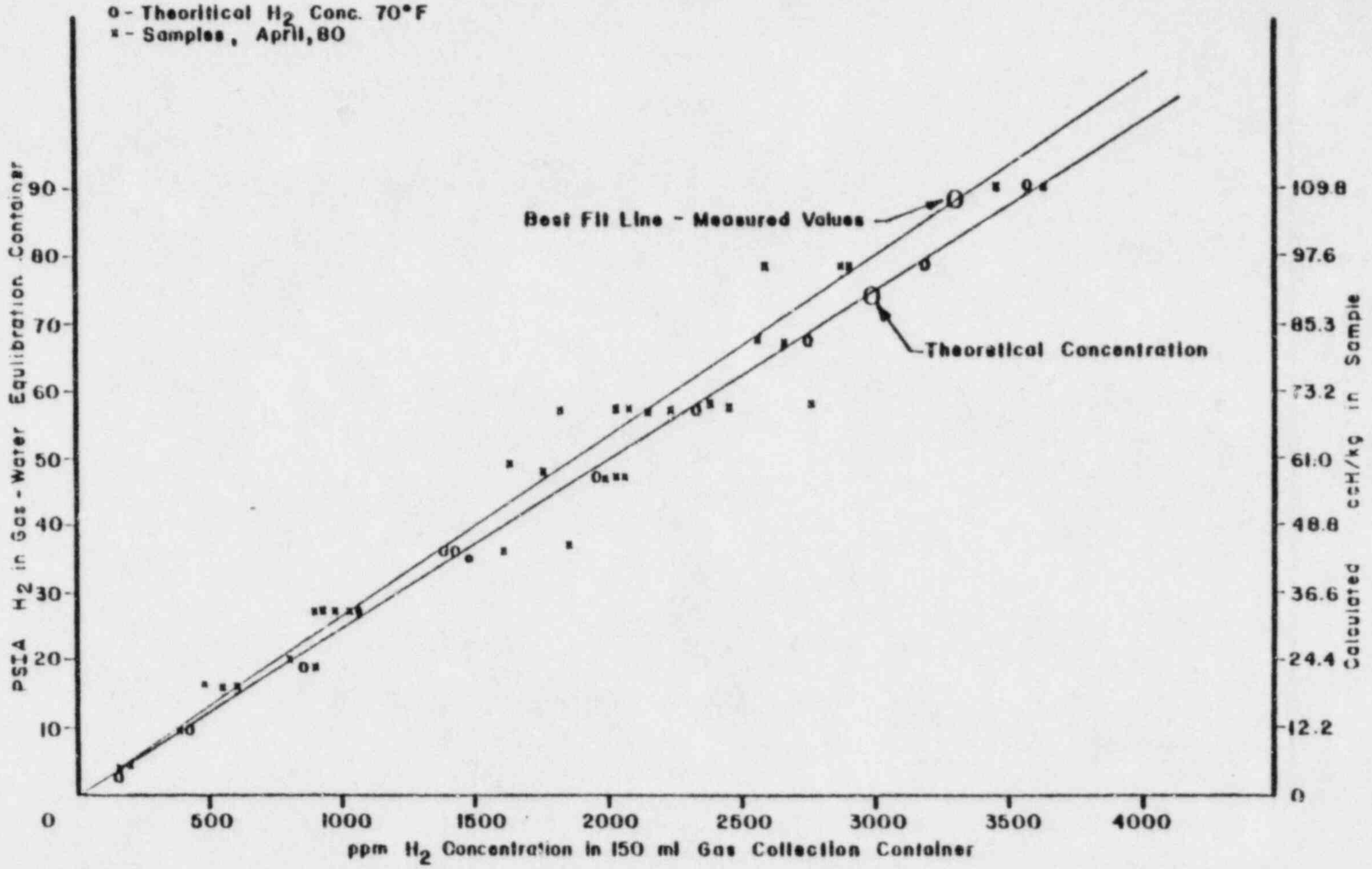


Figure VI - 10

10 ML LIQUID SAMPLE
MODIFIED DESIGN GAS SCRUBBER
FIGURE VI - 11



VII. EVALUATION OF THE YSI OXYGEN ANALYZER

A. BACKGROUND

Under normal operating conditions, system parameters concerning flow rate and dissolved hydrogen concentration will remain relatively constant in the Sentry sampling and analysis panel. However, under accident conditions flow rate will be significantly lower if primary system pressure is lost or reduced to some low pressure. There was concern that this could affect accuracy of results with the YSI oxygen analyzer since circulation is required for system operation. Also, a reduction in plant pressure to 100 psig or less would reduce chemical analysis panel to some value below the 50 or 60 psig specified for normal operation. A reduction in pressure could result in the evolution of hydrogen from solution dependent on the concentration involved. The behavior of the YSI analyzer under conditions involving evolution of hydrogen from solution was not known. Accordingly, testing was performed to investigate the effect of these variables on performance of the YSI oxygen analyzer.

B. EQUIPMENT DESIGN

Design of the test loop used in the work performed is shown in Figure VII-1. The equipment included provided for the following:

1. A 50 gallon batch source of oxygen-saturated calibration water.

2. A 50 gallon batch source of controlled oxygen content test water. The oxygen content is controlled by sparging with nitrogen until the desired concentration is achieved as determined by Winkler test.

3. An isolatable recirculation loop to provide for continuous hydrogen saturation of test water.

4. A YSI oxygen probe and YSI Model readout instrumentation. Design of the probe holder assembly is shown in Figure VII-2.

5. Pumps, throttling valves, and flow meters to control and measure flow rate.

C. FLOW RATE LINEARITY TESTS

Linearity tests were performed over a flow range of 547 ml/min to 30 ml/min. Testing was performed with high level (7.85 ppm or 5.5 cc O_2/kg) and low level (0.7 ppm or 0.49 cc O_2/kg) oxygenated water. The system was initially calibrated to indicate the correct O_2 concentration at a flow rate of about 200 ml/min. This value was selected because it is anticipated that the system will be controlled at a flow rate of about 200 ml/min during normal operation. Flow rate through the probe was then increased to the maximum achievable level of 547 ml/min and progressively decreased to 30 ml/min. A readout of oxygen concentration was taken at each incremental change in flow rate. Winkler analyses were performed at periodic intervals to determine that there was no actual change in oxygen concentration during the course of the test.

Results of the testing performed indicate that the YSI oxygen analyzer is relatively insensitive to change in flow rate. The data are presented in Tables VII-1 and VII-2. For the high level oxygenated water (Table VII-1) indicated results were 102 percent of actual at a flow rate of 547 ml/min. The data obtained for the flow range of 547 ml/min (+2 percent error) to 58 ml/min (-5 percent error) is considered more than adequate to satisfy any plant needs.

For the low level oxygenated water (Table VII-2), no increase indicated oxygen concentration was noted with increasing flow. However, there was a decrease in an indicated value as flow rate was decreased below 228 ml/min. An indicated level of 75.7 percent of actual oxygen concentration was noted at the lowest flow rate tested which was 30 ml/min. Acceptable data was obtained for the flow range of 547 ml/min (no error) to 58 ml/min (-7 percent error).

The data developed in these tests is in marked contrast to data developed in previous flow linearity tests. Results of the initial work performed indicated that the YSI oxygen analyzer was highly sensitive to flow rate;

however, it was later determined that there was a pinhole in the membrane used in these tests. Replacement of this membrane with a new membrane resulted in the data shown in Tables VII-1 and VII-2.

D. THE EFFECT OF DISSOLVED HYDROGEN ON DISSOLVED OXYGEN INDICATION

Testing was performed to determine if the presence of dissolved hydrogen or pinpoint bubbles of hydrogen coming out of solution would affect accuracy of results for the YSI analyzer. This work was performed at three levels of oxygen concentration. One hydrogen concentration was used in all three tests. Conditions of test for this work were as follows.

System flow rate	200 ml/min
Water temperature	75°F
Hydrogen concentration*	78 cc/kg or 6.96 ppm
Oxygen concentrations as determined by Winkler analyses	0.102, 0.68 and 0.93 ppm

*Some appreciable portion of the total was present as pinpoint bubbles in the water.

The influence of dissolved and pinpoint bubbles of hydrogen on dissolved oxygen results are as follows.

Dissolved O_2 Concentration*		O_2 Indication with 78 cc H_2/kg**		Error
ppm	cc/kg	ppm	cc/kg	
0.102	0.071	0.102	0.071	0%
0.68	0.476	0.70	0.49	3%
0.93	0.651	0.90	0.63	-3%

* No hydrogen present.

**Dissolved and pinpoint bubbles of hydrogen.

The conclusion drawn from this work is the presence of hydrogen in solution with pinpoint bubbles will not affect accuracy of the YSI oxygen analyzer. Some earlier work performed indicated that large amounts of hydrogen bubbles will affect performance of this YSI probe; however, the membrane used in the earlier testing is now suspect because of a pinhole in the membrane.

In connection with the above investigation, work was also to determine accuracy of the YSI oxygen analyzer at low level oxygen concentration as compared to the Winkler analysis. Results of these tests are as follows.

O_2 Concentration Winkler Results		YSI Results		Error
ppm O_2	cc O_2/kg	ppm O_2	cc O_2/kg	
0.32	0.224	0.35	0.245	9.4%
0.20	0.14	0.22	0.154	10.0%
0.10	0.07	0.102	0.071	2.0%

The data indicate that the Model 54 YSI oxygen analyzer has acceptable accuracy at low oxygen levels. Lower limits of detection for the instrument used are about 0.1 ppm oxygen. However, the Model 56 YSI oxygen analyzer that Sentry is installing in the CAP is a later model and has better sensitivity than is the model used in the NUS work. The Model 54 analyzer was used because it was immediately available.

E. CONCLUSIONS ON YSI ANALYSIS CAPABILITIES

1. The YSI oxygen analyzer is relatively insensitive to flow for the range of 58 ml/min (-5 percent error) to 547 ml/min (+2 percent error). This assumes the use of the probe holder shown in Figure VII-2. A change in probe holder design can affect flow velocity in the membrane area and thus affect results.

2. Hydrogen in solution or pinpoint bubbles of hydrogen in the water have no effect on oxygen readout.

3. Lower limit of detection for the YSI analyzer is 0.1 ppm or better.

TABLE VII-1

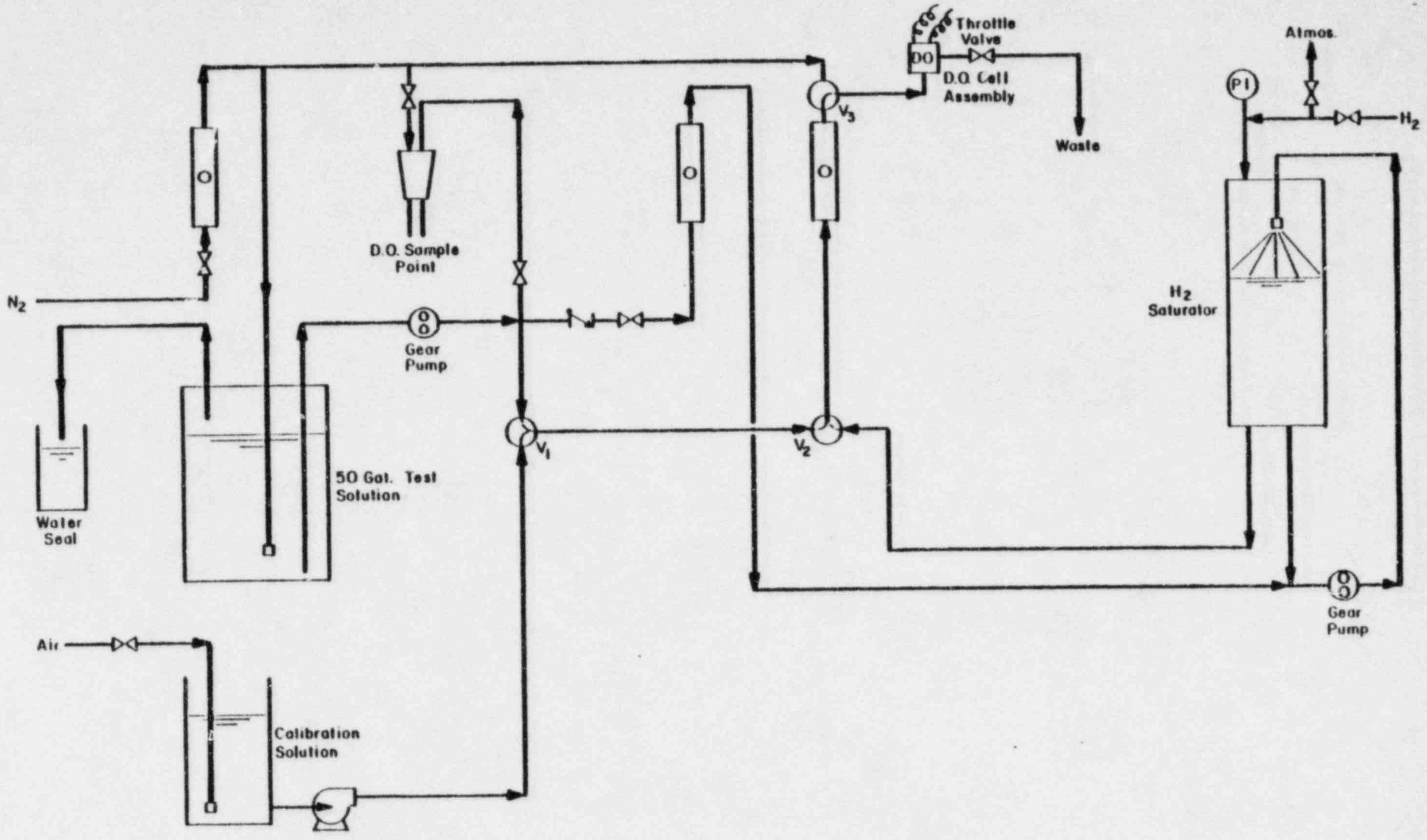
YSI FLOW LINEARITY TEST

Flow Rate ml/min	Actual O_2 Concentration ppm	YSI Indicated Level ppm	Error
547	7.85	8	2%
480	7.85	8	2%
415	7.85	8	2%
350	7.85	8	2%
287	7.85	7.9	1%
228	7.85	7.85	0
168	7.85	7.8	-1%
112	7.85	7.7	-2%
58	7.85	7.45	-5%
30	7.85	6.4	-18.5%

TABLE VII-2

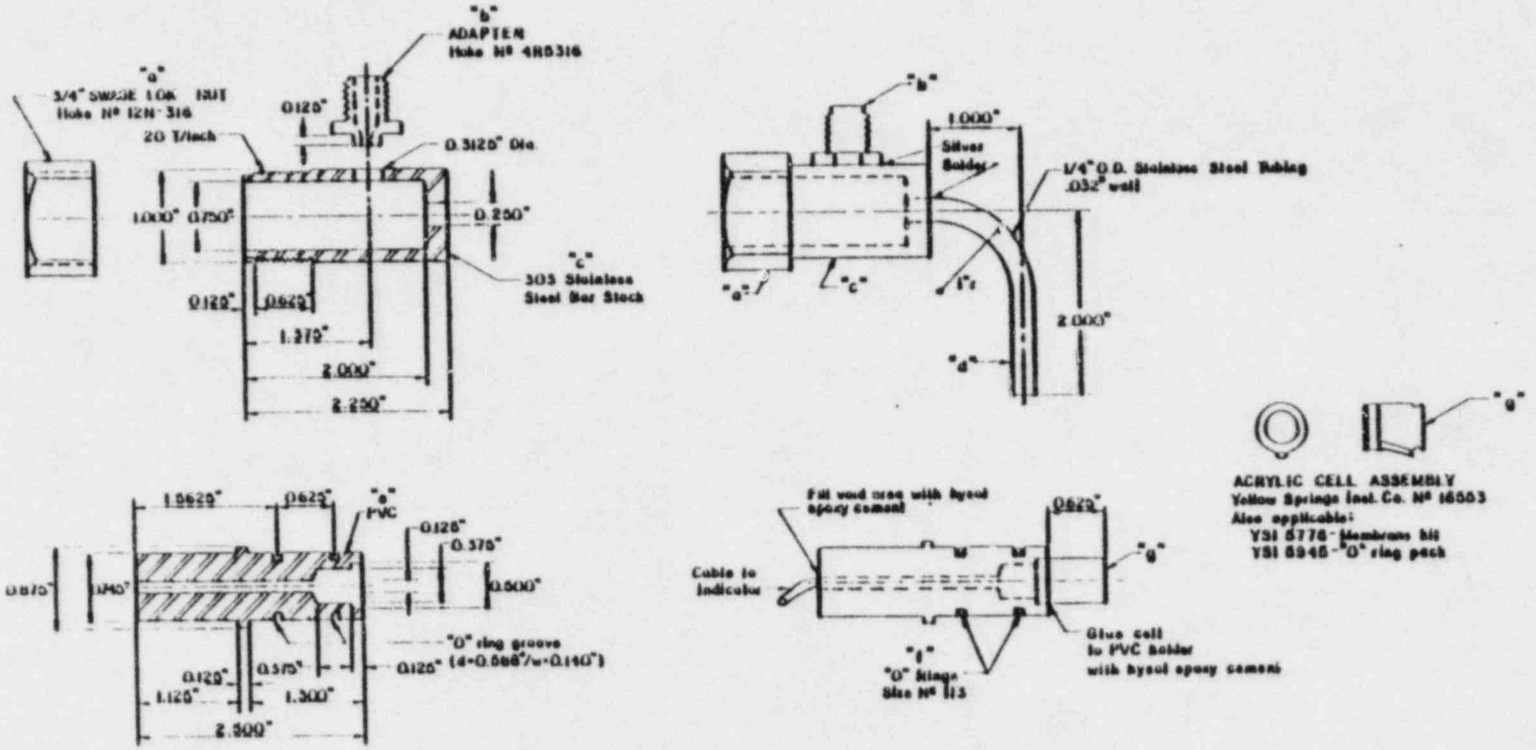
YSI FLOW LINEARITY TEST

Flow Rate ml/min	Actual O_2 Concentration ppm	YSI Indicated Level ppm	Error
547	0.7	0.7	0
480	0.7	0.7	0
415	0.7	0.7	0
350	0.7	0.7	0
287	0.7	0.7	0
228	0.7	0.7	0
168	0.7	0.68	-3%
112	0.7	0.68	-3%
58	0.7	0.65	-7%
30	0.7	0.53	-24%



EQUIPMENT FOR DETERMINING THE EFFECT OF DISSOLVED HYDROGEN ON THE YSI DISSOLVED OXYGEN ANALYZER

FIGURE VII - I



DISSOLVED OXYGEN PROBE HOLDER ASSEMBLY
FIGURE VII-2

VIII. REFERENCES

(a) Doman, D. R., "Gamma Irradiation Effects on Candidate Electronic, Lighting, Optical, Instrument, and Structural Components For In-Reactor Monitoring Equipment," HW-76263, Hanford Atomic Products Operation, January 23, 1963.

(b) Broadway, et al, "The Effect of Nuclear Radiation on Elastomeric and Plastic Materials (Second Addendum)," REIC-3, Addition 2, BMI, April 30, 1960.

(c) Kubota, H., "In-Field Behavior of and Cumulative Effects on Certain Electrodes in a Gamma Field," Analytical Chemistry, Volume 42, No. 13, November 1970 (1593).

(d) Kinderman, E. M. and Carson, W. M., U.S. Atomic Energy Comm. Rep., TID 280 (1949).

(e) Kass, S. "The Corrosion and Hydrogen Absorption Characteristics of Zirconium Alloys Containing Iron and Chromium in High Temperature Water and Steam," WAPD-TM-517, February 1968.

(f) Anderson, T. S. "Correlation of Solubility Data For Hydrogen and Nitrogen in Water," WAPD-TM-633, October 1967.

(g) Sedriks, J. A. "Corrosion of Stainless Steels," John Wiley and Sons, New York, 1979.

APPENDIX A

DISSOLVED HYDROGEN CONCENTRATION IN THE PRIMARY COOLANT OF A PRESSURIZED WATER REACTOR DURING ACCIDENT CONDITIONS

The dissolved hydrogen concentration in the primary coolant of a pressurized water reactor during normal operations is on the order of 25 cc/kg. Some deviation from this level would not be unusual; however, it is unlikely that the dissolved hydrogen concentration will ever exceed 50 cc/kg provided that hydrogen pressure on the volume control tank is maintained within or near specified limits.

During accident conditions the dissolved hydrogen concentration in the primary coolant can increase from the reaction of steam with Zircaloy to form hydrogen:

vis, $Zr + 2H_2O = ZrO_2 + 2H_2$

Based on this reaction, one gram molecular weight of Zr (91 grams) will react with 2 gram molecular weights of steam (36 grams) to form one gram molecular weight of ZrO_2 (123 grams) and 2 gram molecular weights of hydrogen (4 grams). Two gram molecular weights of hydrogen are equal to 44.8 liters of hydrogen gas. However, only a very limited quantity of this hydrogen gas is released to the coolant as discussed below.

When steam reacts with Zircaloy to form hydrogen, the hydrogen released reacts in large part with zirconium to form the hydride. Data presented in reference (e) indicate that the weight of the hydrogen reacting with the zirconium will be at least 10 percent of the weight gain attributed to the formation of ZrO_2. As indicated above, the 32 grams of oxygen reacting with one gram molecular weight (91 grams) of zirconium will release 4 grams of hydrogen. Since at least 3.2 grams of this hydrogen will react with zirconium, about 0.8 grams of hydrogen will be released to the coolant. Thus, one gram molecular weight (91 grams) of zirconium will, on conversion to ZrO_2, release 0.8 grams or 8.9 liters of gas at STP to the primary coolant.

The release of 8.9 liters of H_2 gas per 91 grams of zirconium converted to ZrO_2 is based on a core cladding temperature of 950°F. Actual cladding temperature during an accident would be substantially above 950°F. This higher temperature may result in a higher percentage of the hydrogen converting to the hydride as indicated by the data presented in Figures A-1, A-2 and A-3. Note that the weight percentage of hydrogen to oxygen is 3 percent at 750°F, 5 percent at 850°F and 10 percent at 950°F. Extrapolation of this data to higher temperatures indicates that a higher percentage of hydrogen would be converted to the hydride at a higher temperature. However, in the absence of data at a higher temperature the hydride formation rate at 950°F is assumed.

The core of a typical large pressurized water reactor contains about 21.2 tons of Zircaloy in the core cladding material. Consideration of core damage is limited to the cladding since only this area will attain the temperature required to achieve rapid degradation of the Zircaloy. In calculating the hydrogen released, it is assumed that about 40-50 percent of the core cladding suffers major damage and 30 percent of the core (6.63 tons) is converted to the oxide form. This is probably a pessimistic assumption.

Conversion of 6.63 tons of zirconium to the oxide is equivalent to 63,460 gram molecular weights of zirconium.

$$\frac{(6.63 \text{ tons} \times 2000 \text{ lbs/ton} \times 454 \text{ grams/lb})}{91 \text{ grams}} = 63{,}460 \text{ GMW}$$

It was indicated earlier that one gram molecular weight of Zirconium will, on conversion to the oxide form, release 8.9 liters of gas to add to the inventory in the coolant. Thus the conversion of 6.63 tons of zirconium to the oxide form will release about 564,800 liters of hydrogen at STP to the coolant.

A substantial volume of the core will be in the steam phase under an accident condition. This must be assumed since only very limited damage can occur to the core in the absence of a steam bubble. The volume that will be in the steam bubble is subject to conjecture, however would probably be in excess of 500 ft^3. This volume must be taken into consideration in calculating the end concentration of gas in the primary coolant since a large percentage of the hydrogen released remains in the steam phase. There is substantially more hydrogen per unit volume in the steam phase than in the water phase, consequently the calculated concentration of dissolved hydrogen in the coolant is very sensitive to size of the steam bubble. That is, the dissolved hydrogen concentration is inversely proportional to the size of the steam bubble. A steam volume of 500 ft^3 is assumed in this calculation.

The solubility of hydrogen in water at a given temperature is very nearly proportional to the partial pressure of the hydrogen in the steam phase (Henry's Law). This law is used here to determine the ratio of gas in the liquid vs. vapor phase for a given temperature. The Henry's Law coefficient for the temperature of interest is taken from reference (f). A primary coolant temperature of 600°F is assumed in this calculation; however, the temperature during post-accident conditions could vary substantially in either direction from this reference point. The percentage of hydrogen in the coolant increases with increasing temperature.

Volume external to the reactor vessel in a large pressurized water reactor system is on the order of 5,500 ft^3 excluding the pressurizer. The pressurizer is not included because there will be little or no flow to the pressurizer. Volume of the reactor vessel is about 5000 ft^3. A volume of 500 ft^3 should be subtracted from the reactor system and reactor vessel volume because of the steam bubble that will be present during an accident condition. Thus, total system volume excluding the pressurizer is on the order of 10,000 ft^3. These volumes are used in calculating dissolved hydrogen concentrations listed below.

Assuming a reactor coolant temperature of 600°F and the release of 564,800 liters of hydrogen to the coolant as discussed earlier will result in a partial pressure for hydrogen of 200 psia in the steam bubble. With equilibrium conditions as would exist at that time and with some circulation to distribute the hydrogen, there would be about 1320 cc of H_2/liter of coolant in the reactor system. The vapor phase would contain about 190,000 liters of hydrogen at STP conditions. If there was no circulation in the system and all hydrogen released was confined to the reactor system there would be about 2940 cc of H_2/liter of coolant in the reactor vessel.

With an initial concentration of 1320 cc of H_2/liter of coolant there would be no degassing as the water is cooled to room temperature preparatory to obtaining a pressurized sample. With an initial concentration of 2940 cc of H_2/liter of coolant it would probably not be possible to obtain a completely representative sample with respect to determining gas concentration. However, the sample obtained would indicate that there were very high gas concentrations present.

The gas concentrations indicated above should be considered as estimates which are listed here to provide a general indication of the concentrations that can occur under accident conditions. Actual concentrations observed could be significantly lower or perhaps higher than the values indicated here. Perhaps the greatest uncertainty involved concerns the amount of hydride formed during accident conditions. Extrapolation of available data would indicate that more hydride will be formed than is indicated here. This would result in lower dissolved hydrogen concentrations than the 1320 cc of H_2/liter calculated above.

The conclusions formed from this study and the effect of these conclusions on plant operations are listed below:

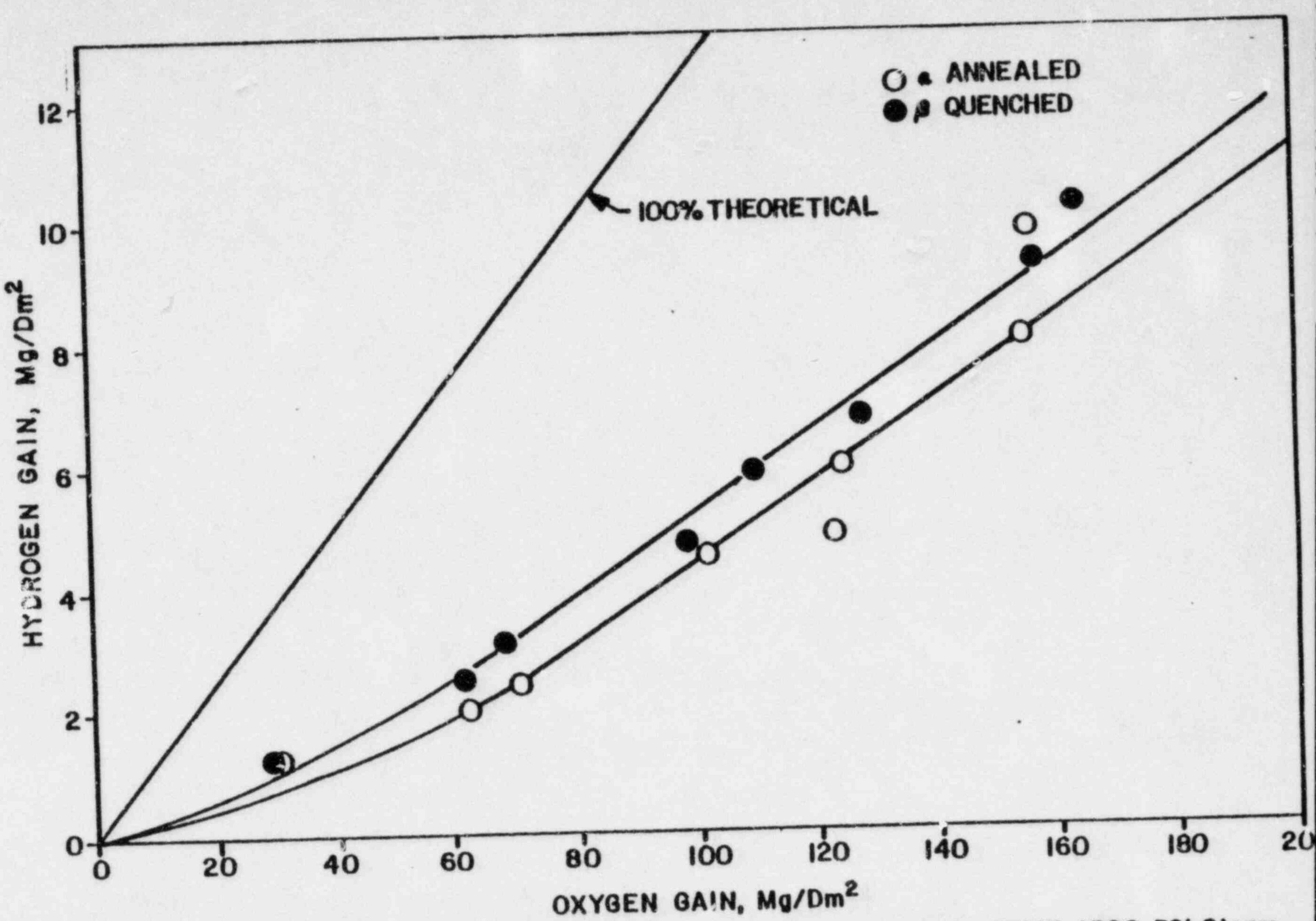
1. The concentration of dissolved hydrogen in the reactor coolant system under accident conditions can be on the order of 1320 cc of H_2/liter of coolant.

2. It will be possible to obtain a representative sample of pressurized coolant with this gas concentration provided system pressure remains at 2000 psi.

3. If all the hydrogen gas released is confined to the reactor vessel, the resulting dissolved hydrogen concentration could be on the order of 2940 cc/liter. The degassing occurring during cool down in the sample cooler may make it impossible to obtain a truly representative sample with respect to gas concentration. The sample obtained would indicate that there are very high gas concentrations present.

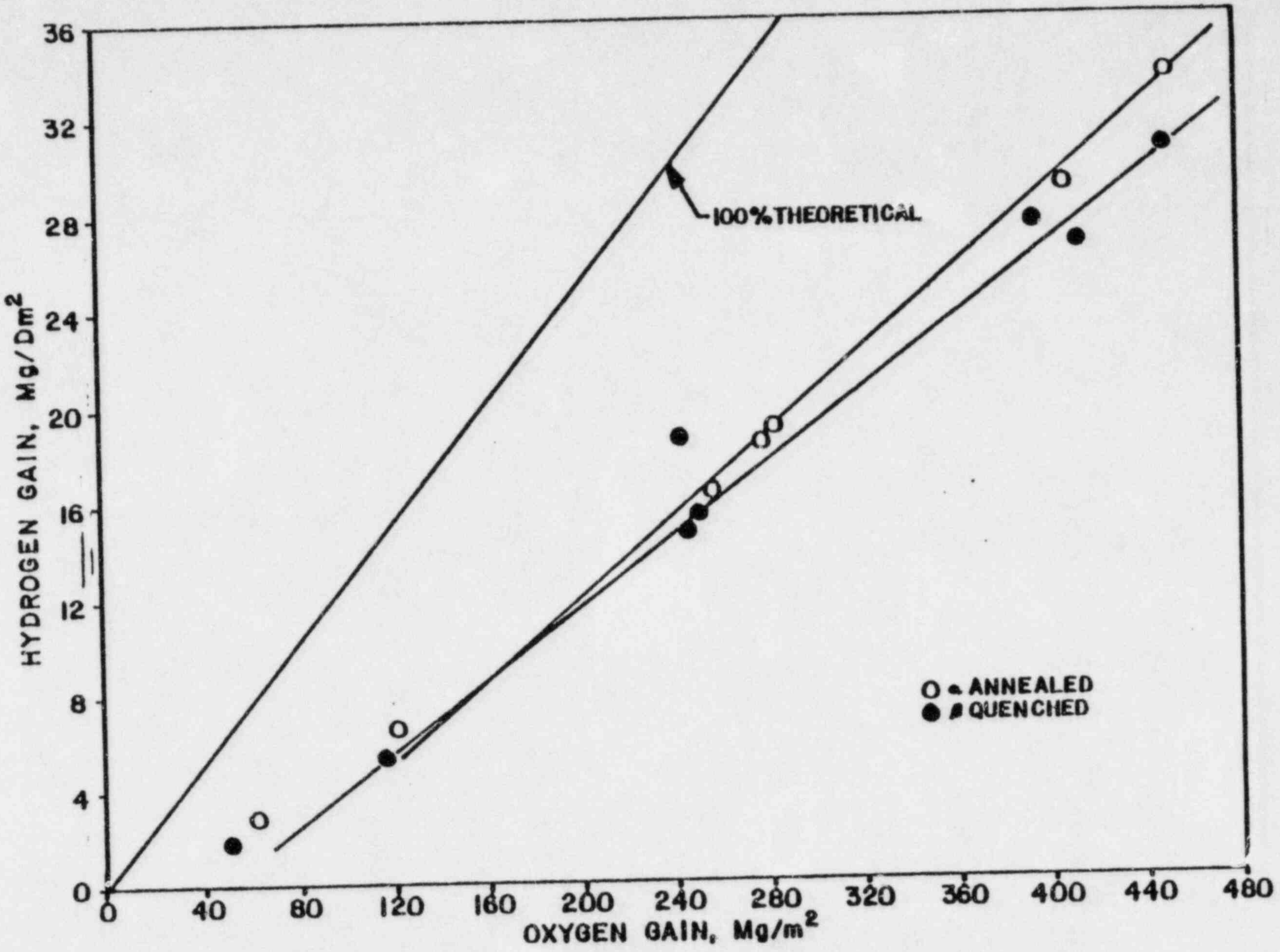
4. A cavitation problem can result if pumps are operated with these high gas concentrations in solution. Venting would be required before the pumps can be operated.

5. Precautions should be taken to protect against formation of an explosive mixture if the primary coolant is released to a depressurized system. There can be no formation of an explosive mixture within the pressurized reactor system itself since there is no formation of free oxygen in the system. The reaction of zirconium with water results only in the production of hydrogen. Oxygen from the water is combined with the zirconium in a form that is not available for reaction with hydrogen.



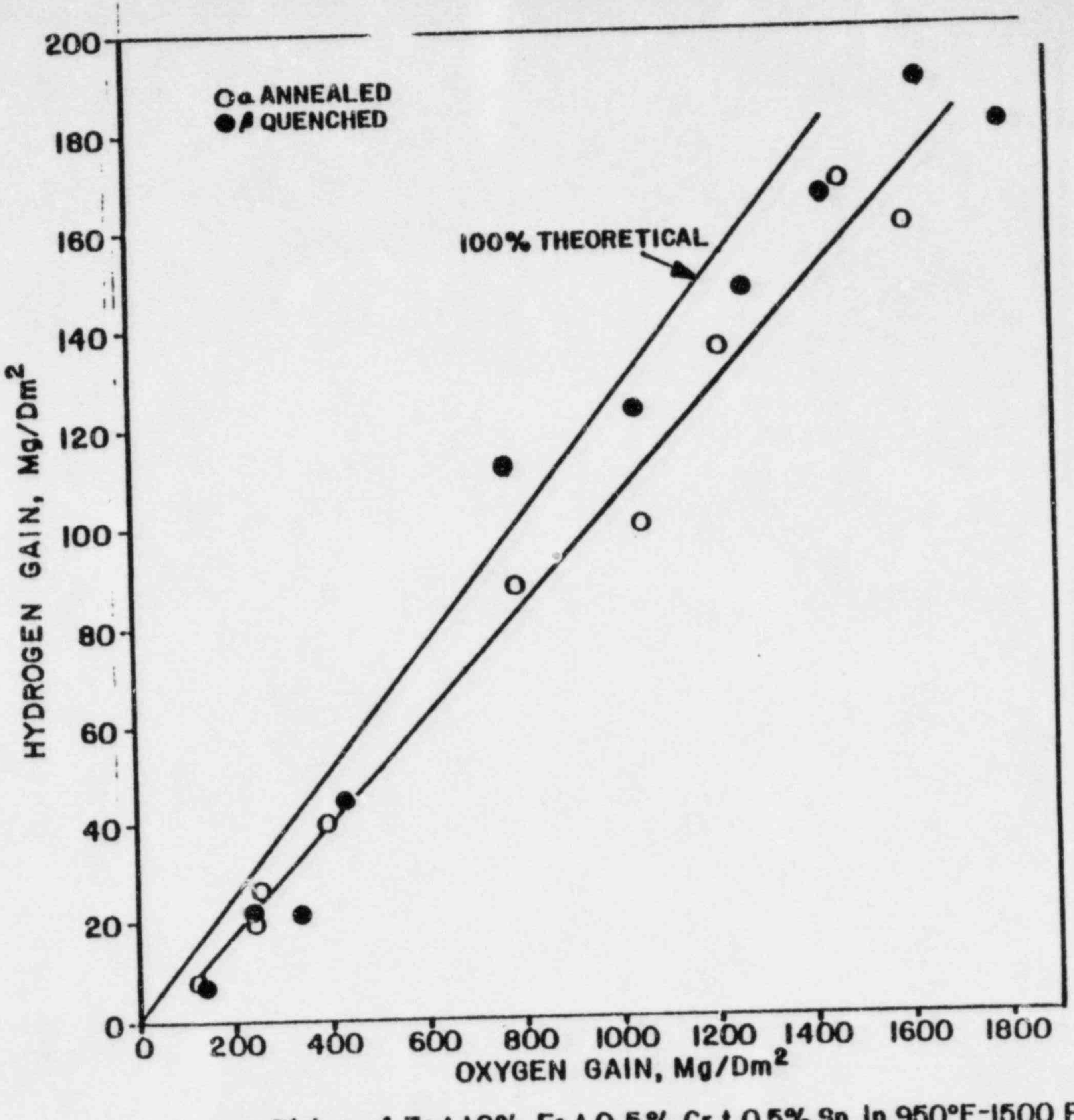
Hydrogen Pickup of Zr + 1.0% Fe + 0.5% Cr + 0.5% Sn in 750°F-1500 PSI Steam

FIGURE A-1



Hydrogen Pickup of Zr + 1.0% Fe + 0.5% Cr + 0.5% Sn in 850°F-1500 PSI Steam

FIGURE A-2



Hydrogen Pickup of Zr + 1.0% Fe + 0.5% Cr + 0.5% Sn in 950°F-1500 PSI Steam

FIGURE A-3

APPENDIX B

DILUTION FACTORS REQUIRED FOR ISOTOPIC ANALYSES OF GASEOUS SAMPLES DURING POST-ACCIDENT CONDITIONS

Calculations have been made concerning the degree of dilution required for reactor coolant gaseous and containment air samples to reduce activity levels to the degree necessary to provide for isotopic analyses of the samples. The calculations are based on the assumption that a 1 cc sample of the final dilution used for isotopic analyses will be added to a 10 cc vial for counting with a Ge(Li) detector. Dilution factors indicated are based on achieving an end objective of a 10 mr/hr gamma level at the 10 cc vial.

Design of the Sentry system provides for obtianing a 30 ml sample of primary coolant during post-accident conditions for hydrogen and gaseous activity determinations. The primary coolant will be purged with argon gas to yield an end volume of 600 cc of gas at STP conditions in a previously evacuated 300 cc gas collection container. This end volume is required to achieve a dilution for hydrogen analyses that will better cover the range of dissolved hydrogen concentrations that may result from an accident condition.

Further dilution of the 600 cc argon-hydrogen gas mixture is required for isotopic analyses of gas since the gas is too radioactive to handle or count directly. The dilution factors required are listed in Table 1. Note that a substantially lower dilution factor is required at 24 hours after an accident condition than at one hour. System design, therefore, should include a two step dilution capability.

The source term used in determining dilution factors required for isotopic analyses are listed in Table 2. These source terms are based on NRC definitions concerning fuel damage occuring.

TABLE B-1

DILUTION FACTORS REQUIRED FOR ISOTOPIC ANALYSIS OF GASEOUS SAMPLES

Dilution to achieve 10 mR/hr; 1 cc of final dilution placed in 10 cc vial.

	1 cc from Detector		10 cm from Detector	
Source	1 Hour	24 Hours	1 Hour	24 Hours
30 ml RCS purged with 600 cc Ar; 0.75 percent halogen partition into gas.	1:2000	1:200	1:100	1:10
Containment Air: 50 percent halogens initially present, zero percent halogens at 24 hours.	1:2000	1:50	1:100	1:2

TABLE B-2

ESTIMATED CONTRIBUTORS TO REACTOR COOLANT GAMMA DOSE RATES AFTER A POSTULATED REACTOR ACCIDENT (GAMMA RADIATION DOSE RATE IN mR/hr @ 1 METER PER ml)

		Time After Accident							
Source	**Release from Fuel**	**1 Hr.**	**2 Hr.**	**4 Hr.**	**8 Hr.**	**24 Hr.**	**48 Hr.**	**168 Hr.**	**236 Hr.**
Noble Gases	100%	230.1	145.3	94.3	48.5	11.7	5.95	2.73	1.08
Iodines	50%	621.0	514.6	419.4	342.9	220.1	159.8	59.3	18.6
Cesiums	1%	1.70	0.73	0.40	0.37	0.37	0.37	0.35	0.33
	35%	59.5	25.6	14.0	13.0	12.9	12.8	12.1	11.4
Solids	1%	17.3	17.0	16.4	15.5	13.3	11.6	8.97	7.21
TOTAL: Cesiums	1%	870.1	677.6	530.5	407.3	245.5	177.7	71.4	27.2
Cesiums	35%	927.9	792.5	544.1	419.9	258.0	190.2	83.1	38.3