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FINAL REPORT

AN EVALUATION OF THE BASELINE SYSTEM FOR DETERMINATION OF TOTAL GAS CONCENTRATION DURING NORMAL OR POST-ACCIDENT CONDITIONS

FOR

COMMONWEALTH EDISON COMPANY
CHICAGO, ILLINOIS

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1.0 INTRODUCTION

This report presents the results of a study performed to determine if the use of the Baseline gas chromatograph could be expanded to analyze a multicomponent gas mixture as might be expected under accident conditions. The study was commissioned by Commonwealth Edison (W. Nestel). The objective was to determine individual concentrations of gases in solution as well as determining the sum of the components to determine total gas concentration. Under accident conditions, the primary coolant of a PWR or BWR may contain appreciable concentrations of dissolved helium, krypton, and xenon released from damaged fuel rods. In addition, there could be some nitrogen in solution for a PWR. The end concentrations of these gases can exceed the hydrogen concentration; thus, a hydrogen determination is not necessarily a measure of total gas concentration under accident conditions. Total gas concentration should be known so that steps can be taken to protect against pump cavitation. The Baseline system as now designed provides only for hydrogen determination.

2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 TOTAL GAS CONCENTRATIONS

Calculations show that a total gas determination should be made under post-accident conditions, because the hydrogen concentration may be as little as 25 percent of the total gas concentration during post-accident conditions. This condition would occur if core damage was relatively minor but sufficient to release contained gas from a large number of rods. The potential dissolved gas concentrations during normal and accident conditions for a PWR and BWR are listed in Tables 2-1 and 2-2. Some of the accident conditions required to obtain the maximum gas concentrations listed in these tables are very unlikely, nevertheless, do exist. The potential sources of dissolved gases in the primary coolant of a BWR and PWR for both normal and accident conditions are listed in the section titled "Background Information."

Total gas concentration is essentially equal to hydrogen concentration during normal conditions for a PWR. A BWR will contain only trace concentrations of dissolved gas during normal conditions.

2.2 OPERATING TEMPERATURES

The system must be operated at a column temperature of 75°C to determine helium and hydrogen concentration during post-accident conditions. At lower temperatures, column poisoning from xenon gas will mask all peaks from other gases after a few gas determinations. Column temperature should be increased to 125°C for the oxygen, nitrogen, krypton, and xenon gas determinations. A column temperature of 125°C will also protect against residual poisoning from xenon gas.

2.3 KEYBOARD REPLACEMENT

In working with the Baseline gas chromatograph, problems were encountered with entering the computer code required to perform the gas analyses. This problem, if common to all instruments, could lead to serious delay in determining hydrogen concentration under accident conditions. In discussing this with Mr. Ken Forsburg, he indicated that Baseline was aware of the problem. He stated the problem would be corrected by replacing the keyboard.

Commonwealth Edison should take action to assure that the Bowmar keyboards on the Baseline system are replaced before they accept delivery of this system.

2.4 SEQUENCE OF GAS PEAK EVENTS

The gas peaks will pass through the columns in this sequence: helium, hydrogen, oxygen, nitrogen, krypton, and finally, xenon. Time sequence for these peaks is shown in Table 2-3. Resolution of the helium and hydrogen peak requires a column temperature of about 75°C, while the oxygen, nitrogen, krypton, and xenon peaks are best determined at a column temperature of 125°C. This involves a two-step analyses method. Helium and hydrogen concentrations will be determined at 75°C on a 0.25 cc sample in the first step, and concentrations of the remaining gases will be determined at 125°C on a 1 or 2 cc sample in the second step.

To obtain resolution of all potential gas peaks in the gas mixture, it will be necessary to install a switch or program the system to change temperature from 75°C to 125°C during the course of the analyses. This would be preferentially achieved by installation of a switch with a fixed resistor to increase the oven temperature by 50° after the helium and hydrogen determination. About ten minutes are required to heat the system from 75°C to 125°C. The fixed resistor to increase temperature from 75° to 125° could be manually operated, or the system could be backfitted to increase temperature programmatically. An indicator light would be required to show low or high range temperature.

An alternate approach to total gas determination would be to operate the system continually at 125°C. At this temperature, helium and hydrogen would emerge as a combined peak and the other gases in individual peaks. Depending on the ratio of gases present, the sum of the peak for helium and hydrogen could be less than would be obtained with individual peak determination at 75°C. A two-step analyses would still be required, for single temperature operation at 125°C, since the hydrogen-helium determination is best made with an 0.25 cc sample loop, while the other gases require a 1 or 2 cc sample loop.

2.5 DETECTOR ASSEMBLY POLARITY CHANGE

As shown in Table 2-4, xenon and krypton have negative thermal conductivities as compared to the argon carrier gas, or other potential gases in solution. With the system as is, these peaks would emerge on the negative side of the gas chromatograph recorder trace line. However, testing performed as is discussed later indicates that it is necessary to change polarity of the detector assembly to determine xenon and krypton concentrations in a gas mixture. Polarity reversal should be performed as a permanent change by switching the two end leads on the thermal conductivity detector. This change will give a negative peak indication for helium, hydrogen, oxygen and nitrogen. However, this will not affect gas analysis results as determined on the Speedomax recorder in the chemical analysis panel. The baseline of the Speedomax recorder pen will be set at the midpoint of the chart while the baseline of the Baseline recorder pen will remain unchanged at the left-hand edge of the chart. Peak height of helium, hydrogen, oxygen and nitrogen will be determined from the negative side of the baseline on the Speedomax recorder. Krypton and xenon peak height analyses will be determined from the positive side of the line.

2.6 LINEARITY

The system is fairly linear for helium and hydrogen from the range of 100 ppm to over 90,000 ppm when using a 0.25 cc sample loop. However, linearity falls off rather quickly when using the 1 cc loop. Hydrogen system linearity characteristics for the 0.25 and 1 cc sample loop size are shown in Figure 2-1 and 2-1A.

It is recommended that two 0.25 cc loops be installed in the system for hydrogen and helium determinations. The 0.25 cc loops will cover all conditions, with respect to the low range sensitivity requirements and the very high hydrogen concentrations that could occur under accident conditions. In addition, a 2 cc gas sample loop should be installed in another of the sample loops to obtain optimum sensitivity for all potential conditions of analyses. With these changes, the Baseline system will have two 0.25 cc sample loops, a 1 cc sample loop, and a 2 cc sample loop installed in that sequence. Changing sample loop size requires installation of a different length of tubing in the sample loop.

Good linearity was achieved with the 1 cc sample loop for oxygen, nitrogen, and krypton. Linearity characteristics for nitrogen, shown in Figure 2-2, are fairly typical of that observed for these gases. Sensitivity of detection was increased with use of a 2 cc sample loop at the expense of some deviation in linearity. There was more increase in peak area than there was in peak height. This deviation from linearity could be minimized by use of an integrator to determine the area under the curve.

For xenon, linearity characteristics are fair with the 1 cc loop and poor for the 2 cc loop. However, sensitivity of detection is increased with the 2 cc loop. It is anticipated that linearity characteristics can be improved with the use of an on-line integrator.

Sensitivity of detection via use of the Baseline gas chromatograph for the various gases discussed in this report are listed in Table 2-5. The sensitivities are listed for ppm in gas and for cc's of dissolved gas per kilogram of primary coolant. Sentry panel design parameters were used in developing this table. Based on thermal conductivities relative to argon, sensitivity of detection should be better for xenon than for krypton. Test results indicate that the reverse is true.

2.7 INTEGRATOR

Though not required for the hydrogen determination, the use of an integrator is recommended for total gas determination. The bases for this recommendation are indicated below.

Hydrogen gas concentration in the primary coolant as determined by the Baseline gas chromatograph in the Sentry system are based on the peak height of a strip chart recorder. This will give good results for all potential concentrations of hydrogen and helium when sampling with a 0.25 cc gas sample loop. Acceptable results are achieved for the other gases when using a 1 cc sample loop. However, linearity falls off rather badly at high gas concentrations when using a 1 cc sample loop for the hydrogen and helium determination, or a 2 cc sample loop for other gas analyses. This deviation from linearity can be reduced, but not eliminated, by integrating the area under the curve with an on-line integrator. An integrator can be selected that will give ppm readout of gas for each peak detected. It is, of course, necessary to compare these peaks with a standard solution to obtain this numerical printout of gas concentration. One integrator that lends itself very well to this application is the Hewlett-Packard Model No. 3390A unit. This system would provide for readout of dissolved gas concentration for each of the gas peaks detected. It will also indicate the date, year, time of day, and any other information that is programmed into this system. It would not serve as a substitute, but rather as an addition to the present strip chart recorder installed with the Sentry system.

2.8 GAS LEAKAGE

Initially, helium gas was used to actuate the air operated valves because it was convenient to use. Minor helium peaks were observed on a number of recorder tracings, indicating leakage of gas past the valve(s). This problem was corrected by using argon gas as the pressurization source. Even if argon leakage occurs, it will not contribute to extraneous peaks because it is used as the carrier gas.

2.9 TRAINING PROGRAM

One or two people from each plant should be given a basic course in gas chromatograph operation offered by the Baseline Corporation. This would acquaint these people with the subtleties of the system, and they could serve as service personnel as well as train other people.

2.10 BACKFLUSH SEQUENCE

In determining the individual gas concentrations in a mixture containing xenon, the precolumn backflush cannot be turned on until the xenon peak emerges. This requires about nine minutes at 75°C. No indication of a xenon peak will be observed with an early backflush.

3.0 BACKGROUND INFORMATION

Under accident conditions, the primary coolant of a PWR or a BWR may contain appreciable concentrations of dissolved helium, krypton, and xenon released from damaged fuel rods. High hydrogen concentrations may also be present from the reaction of Zircaloy with water at elevated temperatures. Calculated concentrations of these gases for a PWR and BWR system are indicated in Tables 2-1 and 2-2.

The various gases in the periodic table and their potential for introduction in the primary coolant of a PWR or a BWR for both accident or normal operating conditions are discussed below. Iodine is not included in this discussion because it would not normally behave as a true gas, even under accident conditions. It is expected that the iodine would be converted to the iodate by the basic solutions added during accident conditions.

3.1 HYDROGEN - PWR

The potential sources of dissolved hydrogen in the primary coolant of a PWR include the following:

(1) During normal power operations, hydrogen is added to the primary coolant by maintaining a hydrogen blanket in the letdown system. Typically, this results in a hydrogen concentration of about 25 to 30 cc hydrogen/kg of water.

(2) Tritium, the radioactive isotope of hydrogen, is produced from ternary fission of uranium and other nuclear reactions. Tritium concentration produced is too low to be measured with a gas chromatograph.

(3) Under accident conditions, hydrogen can be produced in rather large amounts by the reaction as follows:

$$Zr + 2\,H_2O + \text{heat} \rightarrow ZrO_2 + 2\,H_2$$

Assuming that 30 percent of the core cladding is converted to the oxide form and a 500 ft^3 gas-steam bubble in the reactor vessel, the hydrogen produced can result in a maximum end concentration of about 1300 cc hydrogen/kg of water. However, it is unlikely that the dissolved hydrogen concentration will ever exceed 100 cc/kg under accident conditions.

3.2 HYDROGEN - BWR

The only measurable source of hydrogen in the primary coolant of a BWR is that resulting from the reaction of Zircaloy with water under accident conditions to produce hydrogen. The maximum concentration that could result based on the volume of hydrogen that could be generated in an accident condition is on the order of 1500 cc hydrogen/kg of water. Again, this assumes a 500 ft^3 gas-steam bubble in the reactor vessel. It is unlikely that the dissolved hydrogen concentration will ever exceed 100 cc/kg under accident conditions.

3.3 HELIUM - PWR AND BWR

The potential sources of dissolved helium in the primary coolant of a PWR or BWR include the following:

(1) Helium gas pressurization of the fuel rods to provide for structural integrity of the fuel rods. The PWR rods are pressurized to a higher degree than are the BWR rods.

(2) Tritium decay to form the stable helium. The tritium is produced from ternary fission of enriched uranium, neutron reactions with boron, and naturally occurring deuterium.

(3) Helium formation from electron capture by an alpha decay particle.

Helium gas used for pressurization of fuel rods is contained, thus, would not contribute to helium concentrations in the primary coolant during normal operation. Under accident conditions, this gas could be released from a few or all of the rods to yield end gas concentration of up to 100 to 200 cc helium/kg of primary coolant for a PWR, or 10 to 20 cc/kg for a BWR. A range is specified for total helium concentration because of variations in manufacturing tolerances, and the degree of which helium penetrates the void volume in fuel pellets is unknown. Suffice to say that the end concentration of helium in solution for a PWR could exceed the dissolved hydrogen concentration. The helium concentration resulting from tritium decay or from electron capture of an alpha decay particle could not be detected with normal gas chromatograph analyses techniques under normal or accident conditions. End concentrations of helium resulting from this source would be well under 0.1 cc He/kg water.

3.4 NITROGEN - PWR

The potential sources of dissolved nitrogen in the primary coolant of a PWR include the following:

(1) During shutdown for refueling or other maintenance operations, there will be some buildup of dissolved nitrogen in the system when the hydrogen blanket in the letdown system is replaced with nitrogen. End concentration is not expected to exceed 10 cc nitrogen/kg of water.

(2) During normal power operations, there may be trace concentrations of nitrogen in the primary coolant if there is substandard operation of the deaerator to the primary storage tank.

(3) Under accident conditions, there can be dissolved N_2 in the primary coolant if the following scenario occurs:

  (a) Plant pressure is lost as a result of the pressurizer relief valve opening.

(b) The accumulators actuate to admit boric acid solution to the reactor vessel. Since the accumulators are pressurized with nitrogen, the boric acid solution will contain dissolved nitrogen. The overall system dissolved gas concentration will not necessarily be in equilibrium with the nitrogen overpressure, since a static column of water is involved. Migration rate of nitrogen gas through a static water column can be on the order of inches per month.

(c) The pressurizer relief valve closes before the nitrogen can be stripped from solution, and there is no further loss of pressure from the system.

The scenario postulated above is considered extremely unlikely. However, if it should occur, the primary coolant may contain an appreciable concentration of dissolved nitrogen. The estimated range is 10 to 100 cc nitrogen/kg.

Under accident conditions involving recirculation of water from the sump to the reactor, nitrogen in solution would ultimately attain equilibrium with the nitrogen in air. Assuming an equilibrium exists, the water would contain about 10 cc N_2/kg of water at 30°C decreasing to virtually zero at boiling temperature. Following cool down and assuming an open system, weeks would be required for water in the system to attain equilibrium with nitrogen in air.

3.5 NITROGEN - BWR

Under normal conditions, nitrogen would not be present in BWR coolant. Under accident conditions involving a break, there would be some pickup of nitrogen from the cover gas used in the contaminant.

3.6 OXYGEN - PWR

The potential sources of dissolved oxygen in the primary coolant of a PWR include the following:

(1) There can be low ppm or ppb concentrations existing when air saturated water or peroxide is added preparatory to refueling.

(2) Under shutdown or accident conditions, there can be low ppm or ppb concentrations of oxygen and peroxide existing from the radiolysis of water. Oxygen would only be found in the absence of hydrogen. There would always be hydrogen present in any accident condition involving damage to the core.

(3) Under accident conditions involving an open system with recirculation of water from the sump to the reactor, oxygen in the air would eventually attain equilibrium with dissolved oxygen in the water. It would probably take weeks for the coolant to achieve a saturation level of 5 to 6 cc oxygen/kg of water.

3.7 OXYGEN - BWR

The potential sources of dissolved oxygen in the primary coolant of a BWR include the following:

(1) Trace quantities of oxygen and peroxide will exist in an operating reactor from the radiolysis of water.

(2) Under shutdown or accident conditions, the combined concentration of oxygen and peroxide from radiolysis of water can increase to the low ppm level. No oxygen would be found if there was hydrogen present from an accident condition involving damage to the core.

(3) Under accident conditions involving a break and recirculation of the primary coolant, there may be some pickup of oxygen in the primary coolant from oxygen contamination in the nitrogen cover gas in the containment.

3.8 KRYPTON AND XENON - PWR AND BWR

The only source of dissolved krypton and xenon in the primary coolant of a PWR or BWR is from fission product gases. Since the gases formed are essentially all contained within the fuel rods, there will be no measurable concentration of krypton or xenon during normal operation. Under accident conditions involving damage to the rods with subsequent release of fission product gases to the coolant, there can be up to 15 cc krypton/kg and 200 cc xenon/kg of water for a PWR. Maximum BWR concentrations could range up to 20 and 200 cc/kg for krypton and xenon, respectively. About two percent of the total noble gas concentration is radioactive. It is possible that the krypton and xenon may be released rather slowly from the fuel pellets; if this is the case, it may take days or perhaps weeks to attain maximum concentration of these gases in solution.

3.9 ARGON AND NEON - PWR AND BWR

These gases would not be found in the primary coolant of a PWR or a BWR. Argon and neon are not formed in the fission process, nor are these gases used in any plant application for light water moderated reactors. Small, immeasurable amounts from air contamination may be present from recirculating primary coolant under accident conditions.

4.0 TESTING PERFORMED AND RESULTS ACHIEVED

4.1 TEST METHOD

Testing was performed with the Baseline gas chromatograph to determine if it was possible to analyze a multicomponent gas mixture as might be achieved by degassing primary coolant containing dissolved gases, as indicated in Tables 2-1 and 2-2. Total degasification was assumed in the calculations performed to determine gas concentrations in the gas mixture. Sentry system design parameters were assumed for the primary coolant degasification and gas collection system.

4.1.1 Test Equipment

The following components and gas samples were included in the test equipment.

(1) A Baseline gas chromotograph modified for use in the Sentry chemical analysis panel.

(2) A ten inch strip chart recorder external to the Baseline system. The data used in forming conclusions and making recommendations was taken from this recorder.

(3) Equipment to provide for various gas mixtures from individual tanks of pure gas. Included in the design of this system was a one liter mixing tank which was hard piped to the gas chromatograph. Gas mixtures were prepared by hypodermic injection of the gas of interest in the argon gas at 14.7 psia contained in the mixing tank. Uniform mixing of the gases was provided by a loose fitting plunger inside the tank. Inverting the tank would cause the plunger to fall from top to bottom, creating a mixing action inside the tank. Good mixing was achieved with one pass of the plunger through the tank. In the work performed, the tank was inverted three or four times each time a standard was prepared.

(4) A mercury vacuum gauge was attached to the sample tubing to establish that this line and associated lines were properly evacuated prior to introduction of the sample.

(5) Individual gas standards used included the following: helium, hydrogen, nitrogen, oxygen, krypton, and xenon. Argon gas was used as a base for the standards prepared, and as a carrier gas in the gas chromatograph.

(6) Two standards prepared by Matheson containing gas concentrations as follows were used in this work.

Gas	Mixture 1 - Low Concentration System	Mixture 2 - High Concentration System
Helium	95 ppm	910 ppm
Hydrogen	865 ppm	9.22%
Nitrogen	994 ppm	1.07%
Oxygen	582 ppm	2295 ppm
Krypton	493 ppm	1376 ppm
Xenon	955 ppm	1.98%
Argon	Balance	Balance

Testing was performed initially with single standards in an argon base to determine sensitivity of detection, linearity, and at what point in time after injection the peak for the subject gas could be seen on the strip chart recorder. Variables investigated in this testing included the following:

(1) Effect of temperature

(2) Reverse polarity operation

(3) Time the recorder was switched on after sample injection

(4) Time that the precolumn backflush flow was initiated after sample injection

(5) Operation with a 0.25 cc, 1 cc, and 2 cc sample loop

(6) Power interruption and voltage fluctuations.

After testing was performed with single gas standards, testing was performed with multicomponent systems. Results of all this work are described below.

4.2 THE EFFECT OF TEMPERATURE ON GAS ANALYSES RESULTS

Testing performed included an investigation on the effect of temperature on gas analyses results. Testing was performed for the range of 30 to 175°C. Results of this work are discussed below.

Analyses for hydrogen and helium must be performed at a relatively low temperature in order to obtain separation of the hydrogen and helium peaks. Acceptable operation is achieved in the range of 75°C with the helium peak emerging at about 34 seconds, and the hydrogen peak at 42 seconds. Separation of these peaks is decreased as temperature is increased until finally the two peaks are combined.

Hydrogen and helium analyses cannot be performed at temperatures below 75°C because of column poisoning caused by xenon. Good analysis results can be obtained initially at temperatures around 40°C, however, there is progressive deterioration of the peaks with continued operation at this temperature in the presence of xenon. Column poisoning can be eliminated by baking at a temperature of 125°C or above. There is no incentive to determine hydrogen and/or helium concentrations at a lower temperature and then bake the columns at a high temperature, since the system can be operated on a continuing basis at a temperature range of 75°C for helium-hydrogen determination followed by 125°C operation for determination of other gases.

In analyzing at temperatures below 75°C, a xenon peak may be observed for one or two analyses, then the peak progressively deteriorates until no indication of a peak occurs when xenon gas is present in the standard. The xenon gas is released from the columns over a long time period, contributing to unexceptable instrument noise and drift. The presence of this xenon apparently prevents the hydrogen from being released in a peak form when hydrogen is present in the standard.

The poisoning effect observed with xenon does not occur with oxygen or nitrogen. There may be a borderline effect with the krypton; therefore, it is assumed that krypton will contribute to the problem.

The optimum temperature range for operation is to perform the hydrogen and helium analyses at 75°C followed by an increase in column temperature to 125°C to determine the concentration of the other gases in solution. Better sensitivity of detection can be achieved for helium at 50°C; however, the xenon gas will remain in the columns to cause poisoning at this temperature. Xenon gas will pass through the columns at 75°C but not in a sharp peak form that can be used to determine gas concentration (Figure 4-1). Good separation of hydrogen and helium peaks cannot be obtained at temperatures above 75°C. A two-step analyses procedure is required with the hydrogen and helium determination made with a 0.25 cc sample loop and the remaining gas determinations performed with the 1 or 2 cc sample loop. Increasing the column temperature after the helium-hydrogen determination requires about five minutes. Ramp heat up rate is on the order of 15°C per minute. System heat up would be achieved by installation of a switch to put a fixed resistor in line. This fixed resistor would increase system temperature by 50°.

An alternate approach to total gas determination would be to operate the system continuously at 125°C. At this temperature, helium and hydrogen would emerge as a combined peak, and the other gases in individual peaks. Helium does cause a slight ramp in the initial slope of the hydrogen peak; however, this ramp is not readily discernible (Figure 4-2). Depending on the ratio of gases present, the sum of the peak for helium and hydrogen could be less than would be obtained with individual peak determination at 75°C. A two-step analyses would still be required since the hydrogen-helium determination is best made with a 0.25 cc sample loop, while the other gases require a 1 or 2 cc gas sample loop.

installation of the fixed resistor and switch requires an associated signal light installation to indicate high temperature or low temperature operation. It is possible to control temperature programmatically; however, the system as purchased does not include this design feature. Backfit installation to permit programming of temperature is not recommended. It is, of course, possible to increase temperature by manual adjustment of a resistor pot as indicated in the Baseline instruction manual. This is a time-consuming operation and it is not recommended for post-accident conditions.

When manually adjusting temperature, please note that is should only be performed when the attenuation switches are at the 250 position (25 x 10) as indicated in the Baseline manual. In theory, it is possible to make temperature adjustments at other ranges; however, problems resulted when this was attempted. Overheating occurred or the columns were below the required temperature. Column temperature control worked very well when adjusting at the 250 attenuation range.

In adjusting the system temperature manually, please note that zero temperature is the tracking point on the Baseline recorder scale. Prior to adjusting temperature, adjust the tracking pen to ride on the left-hand edge of the chart. Temperature adjustment is then made by switching in the appropriate command number (35) and turning the resistor pot until the tracking pen on the recorder moves to the required point on the Baseline recorder scale.

4.3 KEYBOARD CONTROL

Programming problems developed almost immediately with operation of the Baseline gas chromatograph. Initially, three of four attempts were required to enter a program into the computer. Apparently, the problem resulted from bad contacts on the keyboard, since the better results were achieved when firm contact was made as the key was depressed.

Keyboard operation continued to deteriorate as the system was operated. Initially, about five minutes was required to install a new program. After two weeks of testing, time requirements to install a new program were as long as two hours. The keyboard was subjected to more wear than would be the case in a utility plant, because a number of new programs were tried to find the best arrangement for determining total gas where a mixture containing xenon is present.

In conversations held with Mr. Ken Forsburg of Baseline, he indicated that they were aware of the problem with certain keyboards. It is Baseline's intent to replace defective keyboards with a model that has sealed contact points and push-button keys that offer tactile resistance when depressed. Commonwealth Edison should take action to assure that acceptable keyboards are provided.

4.4 REVERSE POLARITY OPERATION

Operation of the Baseline gas chromatograph to obtain the xenon and krypton peaks requires reverse polarity operation. A permanent change should be made by switching the two end leads on the thermal conductivity detector. When these leads are switched, the krypton and xenon will appear as a positive peak and the Baseline recorder will be off scale with negative peaks for helium, hydrogen, oxygen, or nitrogen. Since the oxygen, nitrogen, krypton, and xenon will be determined in one sequence, provision must be made to accommodate this reverse peaking effect. This is accomplished by adjusting the Speedomax recorder pen in Sentry equipment panel to the midpoint of the chart. Peak height for helium, hydrogen, nitrogen, and oxygen, will be measured from the negative side of the reference point or midpoint on this recorder chart. Krypton and xenon peak height will be measured from the positive side of the scale. The Baseline recorder chart will not be used to determine gas concentration, but its recorder pen should be adjusted to the left hand side of the chart.

Testing was performed to determine if good results could be obtained with respect to krypton and xenon determinations by using the system without switching polarity. Without switch polarity, it was necessary to adjust the Baseline recorder pin to track at the midpoint of the chart. Without this polarity change, the Speedomax strip chart recorder connected to the Baseline system would not track on both sides of the centerline to indicate positive and negative peaks. An internal bias was created in the Baseline system with the change, resulting in very poor resolution of the krypton and xenon peaks. The peaks were shallow and there was no change in peak height with increasing krypton or xenon concentration. No combination of adjustments could be found which would permit measurement of positive and negative peaks in a single gas determination using normal polarity.

4.5 LINEARITY CHARACTERISTICS AND THE NEED FOR INTEGRATION

Linearity characteristics for hydrogen concentration in argon gas for the Baseline system are shown in Figure 2-1 for a 0.25 cc and 1 cc sample loop. Raw data for hydrogen, helium, oxygen and nitrogen determinations are presented in Tables 4-1, 4-2, 4-3, and 4-4. Linearity characteristics are good for the 0.25 cc sample loop for the range from about 100 ppm to over 90,000 ppm. There is a slight bend to the line; results at the upper end of the range would be about five to ten percent low in assuming linearity over the entire range. There is considerable deviation from linearity with the 1 cc sample loop.

Based on visual observations, it is probable that better linearity could be achieved for hydrogen for the 1 cc loop with the use of an on-line integrator. However, it did not appear that true linearity could be achieved with this approach. The helium data show much the same results, as was observed with the hydrogen data. That is, peak height linearity was achieved with the 0.25 cc sample loop, but not with the 1 cc sample loop. The use of an integrator would have improved the quality of the 1 cc sample loop data, but would not have succeeded in achieving true linearity as based on visual observation.

Based on these data, it is recommended that helium and hydrogen gas determinations be made with a 0.25 cc sample loop. A typical example showing the helium and hydrogen peak is shown in Figure 4-4. Sensitivity of detection achieved with the 0.25 cc sample loop as shown in Table 2-5 will enable hydrogen determination to be made down to about 2 cc's of hydrogen/kg of water. This assumes complete stripping of gas from solution. Efficiency of the gas stripping operation is not known.

Linearity characteristics for nitrogen concentration in argon gas are shown in Figure 2-2 for a 1 cc sample loop. The data are linear over the measured range. Results from the 2 cc sample loop show considerable deviation from linearity. Use of an integrator would result in improvement in linearity characteristics for the 2 cc loop; however, it does not appear that true linearity would be achieved as based on visual observation.

The oxygen and krypton data do not differ significantly from the nitrogen data with respect to linearity characteristics for the 1 cc sample loop. Again, considerable deviation from linearity was observed with the 2 cc sample loop. Use of integration would improve the linearity characteristics of the system for the 2 cc sample loop.

The need for using a 0.25 cc and 1 cc sample loop is best demonstrated by the curves shown in Figures 4-4 and 4-5. Note that for the 0.25 cc loop (Figure 4-4) the hydrogen peak is on scale; however, the other peaks are barely visible. A gas determination can be made from the peak height shown for oxygen, nitrogen, krypton, and xenon on the 1 cc loop (Figure 4-5); however, the hydrogen peak is off scale. For high concentrations of gas, the shape of the peak for xenon changes with the 2 cc loop size. This indicates that a 1 cc sample represents the maximum size that can be used for xenon determination without integrating the area under the curve. The peaks shown in the figures referred to above are derived from the mixture 1 low concentration gas system described earlier in this report.

4.6 GAS LEAKAGE

A helium gas source was used initially to operate the gas-actuated valves. Some leakage past the valve(s) was noted based on indication of a small helium peak in the tracing when there was no helium in the standard. The helium peak was eliminated by using argon gas as a pressure source to actuate the gas valves. Argon gas should always be used to actuate the valves, since argon is used as a carrier gas and minor leakage will not contribute to extraneous peaks. Major leakage cannot be tolerated, since this would affect gas flows and thus create instrument noise.

4.7 POWER INTERRUPTION AND VOLTAGE FLUCTUATION

Power interruptions of a short-term nature will not affect the program stored in the memory of the Baseline system. If the power is off for perhaps an hour or longer, the program will generally be be wiped out and it will be necessary to reprogram to perform hydrogen or total gas determinations. The exact time that power interruption can be tolerated was not determined. It is expected that it will vary from system to system. If there has been a power interruption, the gas chromatograph should be checked prior to performing gas analyses to determine that a valid program exists in the system memory. A power interruption indication light should be installed in the system.

Line voltage fluctuations resulting from turning on a small motor on a common line created minor spikes in the recorder tracer. The spikes observed were of no consequence. The effect of major voltage fluctuations was not determined.

4.8 COLUMN DEGRADATION

The columns suffer two types of degradation from xenon or moisture poisoning. There is a low temperature affect (less than 75°C) in which xenon poisoning occurs rather quickly. The rate at which poisoning occurs increases with decreasing temperature. Symptoms of this poisoning include deterioration and then disappearance of the xenon peak. Soon thereafter, there will be no peaks evident from any gas. The low temperature poisoning effect is reversible by heating the column to 125°C or 150°C for an hour or more.

Degradation of the columns from moisture pickup will occur if the columns are operated continuously at 75°C or less using a backflush sequence starting at ten minutes. If the system is operated under these conditions the columns should be changed every three to six months. This degradation will not take place or will occur at a much lower rate if the columns are baked periodically at a temperatures of 125°C to 150°C.

5.0 OPERATING PROCEDURE

An operating procedure is provided in Appendix A of this report for single-step temperature operation at 125°C, and for a two-step temperature sequence at 75°C and 125°C. Operation with a two-step temperature sequence is recommended for determining total gas concentration under post-accident conditions. Single-step temperature operation at 125°C provides a single peak for helium and hydrogen, determined with a 0.25 cc sample loop. There is a ramp on the front part of the hydrogen peak which is indicative of helium gas. Height of the ramp from the baseline is proportional to helium concentration. However, this ramp is not readily discernible. The oxygen, nitrogen, krypton, and xenon determinations are made with a 1 or 2 cc sample loop to obtain the required degree of sensitivity. Thus, a two-step analysis process is involved. All four sample loops are charged with the unknown gas in the fill process, and then one, two, three, or four sample loops may be analyzed dependent on the gas concentrations present.

The two-step temperature sequence provides for helium and hydrogen determination on a 0.25 cc sample loop at 75°C. At this temperature, there will be separation of the two peaks; however, the intervening valley will be shallow. The oxygen, nitrogen, krypton, and xenon determinations are made on a 1 or 2 cc sample loop after the system is heated to 125°C. Both the 0.25 cc and the larger sample loop are charged with gas in the same fill process, and then one, two, three, or four sample loops may be analyzed dependent on the gas concentrations present. The oxygen and nitrogen analyses can be performed with the helium-hydrogen determination or the krypton-xenon determination, dependent on the gas concentrations present. Normally, the same size sample loop will be required for oxygen, nitrogen, krypton, and xenon determinations. About ten minutes are required for the helium-hydrogen analyses; five minutes to heat the system from 75°C to 125°C, and ten minutes for the oxygen, nitrogen, krypton, and xenon determination.

A starting point for gas loop sizes and attenuation factors required for determining various concentrations of dissolved gases in water is indicated in Table 5-1. Please note that the values indicated should only be regarded as a starting point. Each gas chromatograph may differ to some degree, and thus will require a slightly different attenuation factor.

APPENDIX A

TOTAL GAS DETERMINATION

TOTAL GAS DETERMINATION

(Two-Step Temperature)

1.0 Purpose

The purpose of this procedure is to detail the steps required to determine total gas concentration in the reactor coolant by gas chromatography (GC). This procedure describes GC operations to separate and identify the major gaseous components of the reaction coolant that can be expected under accident conditions. The procedure includes sections on GC standardization system calibration, and sample analysis. This procedure requires operator actions at the LSP and CAP/CMP.

2.0 Precautions

2.1 The GC calibration loop pressure must remain constant for correct gas analysis. Approval should be obtained from qualified technical management prior to adjusting the back pressure regulator or changing the calibration loop pressure in other ways.

2.2 Precautions shall be observed to prevent the release of radioactive gas or coolant to the LSP or CAP/CMP areas.

2.3 Radiological control monitoring and survey equipment shall be operational and available at the work site as required by local work rules.

2.4 Anti-contamination materials shall be available and installed at the work site as applicable.

2.5 Local work procedures shall be observed to prevent skin contact or ingestion of radioactive materials.

2.6 The gas chromatograph may be operated using only the following five (5) attenuation settings.

1 x 1
5 x 1
25 x 1
100 x 1
25 x 100

3.0 Prerequisites

The following prerequisites shall be met:

3.1 Services shall be available at the CAP/CMP as follows:

3.1.1 Electrical power, 110VAC 60Hz-10AMP
3.1.2 Argon for valve operations, approximately 100 psig.
3.1.3 Argon carrier gas, chromatography grade, flow to the GC.

3.2 The instrument shall be in the ON or STANDBY condition for a minimum of 30 minutes before sample analysis.

3.3 The temperature selector switch shall be in the low (75°) position.

3.4 The following or equivalent program shall be in the memory of the microprocessor and shall be functional: Verify the program as follows:

Release all buttons
Depress MANUAL then CLEAR
Release MANUAL
Enter "01", verify corresponding time and order on the digital readout.

Enter "02", "03", "04", etc., and verify each steps' time and code readout.

Step	Time		Code
01	00	01	03
02	00	25	25
03	00	30	01
04	09	00	04
05	12	00	00

3.5 The verification and calibration as specified in sections 5.2 and 5.4 shall be complete before analysis of gas from the LSP.

3.6 The instrument shall be recalibrated after any major maintenance/repair, detector change, component repair or replacement, or any other circumstances that could invalidate the calibration.

3.7 The gas sample for analysis must be available at the LSP for transfer to the GC.

3.8 Calibration and carrier gases shall be installed for use in the GC.

3.9 A set of calibration curves shall be available for conversion of peak height data to gas concentration (cc/kg). Helium, hydrogen, oxygen, nitrogen, krypton, and xenon calibration curves are required.

4.0 Equipment and Materials

4.1 Gas Chromatograph, Baseline, Model 1030A.

4.2 Recorder, Leeds and Northrup, Speedomax Mark III or equivalent.

4.3 Calibration and carrier gases:

Gas standards shall be mixed by use of strip heaters, mounted on one side of the tank, near the bottom of the tank. Prior to using the standards, the heaters shall be on (1000 or 2000 watt power) until the top side of the tank opposite to the heaters is slightly warm to the touch. Monitor the pressure gage during heating to protect against overpressurization of the tank.

4.3.1 Standard I - Low concentration gas mix (Cal. 1).

Helium	1000 ppm
Hydrogen	2000 ppm
Nitrogen	1000 ppm
Oxygen	500 ppm
Krypton	500 ppm
Xenon	1000 ppm
Argon	Balance

4.3.2 Standard II - High concentration for gas mix (Cal. 2)

Helium	10,000 ppm
Hydrogen	100,000 ppm
Nitrogen	2000 ppm
Oxygen	2000 ppm
Krypton	2000 ppm
Xenon	10,000 ppm

4.3.3 Argon, chromatography grade

4.4 Gas Syringes (2 each)

4.4 1	1.0cc
4.4.2	5.0cc
4.4.3	20.0cc

5.0 Procedure

5.1 Valve alignment and GC warm-up

5.1.1 Open or check open calibration gas valves V-31 and V-32.

Open or check open (V-1ater) and adjust argon valve operator supply pressure to 40± 2 psig.

Open or check open V-14 and adjust argon carrier gas pressure to 40±1 psig.

Open or check open V-1.

5.1.2 Select attenuation factor of 250 (25 x 10).

Place all function switches in the OFF (out) position.

5.1.3 Depress MAN and CLEAR switches.

5.1.4 Select Low (75°) position on temperature control switch.

5.1.5 Enter "00" and allow the GC to warm up and stabilize for a minimum of 30 minutes.

5.1.6 Enter 01 and set pen on the Speedomax recorder at the midpoint on the chart.

5.1.7 Enter then "35" to display set point of platen temperature and record for a minimum of 30 seconds.

5.1.8 Enter "45" to display actual platen temperature and record for a minimum of 30 seconds.

Note: Stabilization is complete when platen set-point and actual temperature are within 1/2 grid marking of each other. After stablization enter "00". Approximately five minutes will be required for temperature stabilization when resetting.

5.1.9 As necessary, repeat steps 5.1.7 and 5.1.8 at a minimum of 5 minute intervals until stablization in achieved.

5.2 Calibration Verification

5.2.1 Verify that the GC has stabilized as specified in Step 5.1.6.

5.2.2 Release or check released, AUTO, ENTER and SAMP switches to the OFF (out) position. Select Loop No. 1 (0.25 cc).

5.2.3 Depress or check depressed MAN and press CLEAR.

5.2.4 Enter "23" to evacuate the GC.
Continue evacuation until red HI VACUUM light is on.

Note: Follow steps 5.2.4a–5.2.8a for standard 1, the low concentration mix; and 5.2.4b–5.2.8b for Standard II, the high concentration mix.

5.2.4a Enter "24" to terminate evacuation of the GC. Select attenuation factor of 5 (5 x 1).

5.2.5a Depress CAL-1 switch and wait 10 seconds after amber LOW VACUUM light is on.

5.2.6a Release CAL-1 switch and wait 10 seconds. Start the L&N recorder, depress AUTO switch to ON position and press CLEAR. Wait until the GC display clock has timed to a minimum of 12 minutes.

5.2.7a Release AUTO switch to the OFF position.
Press MANUAL
Press CLEAR.
Enter "00".
Stop the recorder.

5.2.8a Identify the recorder trace with the date/time, [illegible] used, loop number, and attenuation factor. Only the helium and hydrogen concentration will be determined from this recorder tracing.

The peaks associated with the individual gases will appear in the following sequence:

	Approximate Time after Injection	
Gas	Min.	Sec.
Helium	-	34
Hydrogen	-	42
Oxygen	1	08
Nitrogen	1	33
Krypton	2	19
Xenon	8	50

5.2.4b Enter "24" to terminate evacuation of the GC. Select attenuation factor of 250 (25 x 10) for the Standard II mix.

5.2.5b Depress CAL-2 switch and wait 10 seconds after amber LOW VACUUM light is on.

5.2.6b Release CAL-2 switch and wait 10 seconds. Start the L&N recorder, depress AUTO switch to ON position and press CLEAR. Wait until the GC display clock has timed to a minimum of 12minutes.

5.2.7b Release AUTO switch to the OFF position.
Depress MANUAL
Press CLEAR.
Enter "00".
Stop the recorder.

5.2.8b Identify the recorder trace with the date/time, gas used, loop number, and attenuation factor.

5.2.9 Calculate the helium and hydrogen peak height as follows:

$$\text{Peak Height} = \frac{(\text{Trace peak height} - \text{baseline}) \times \text{attenuation}}{100}$$

Note: The peak height calculated above should agree within ±5 percent of the value shown on the concentration versus peak height curve for the same attenuation factor and calibration gas.

5.2.10 Increase the temperature by selecting the high (125°) position with the temperature control selector.

5.2.11 Depress MANUAL and CLEAR switches.

5.2.12 Enter "01" and then "45" codes to display actual platen temperature. Follow the temperature ramp to insure the 125° temperature is reached then enter "00".

Note: Stabilization at 125° is complete in approximately five minutes.

5.2.13 Release or check released, AUTO, ENTER, AND SAMP switches to the OFF (out) position. Select Loop No. 3 (1 cc).

5.2.14 Enter "23" to evacuate the GC. Continue evacuation until red HI VACUUM light is on.

Note: Follow steps 5.2.15a-5.2.18a for Standard I, the low concentration mix; and 5.2.15b-5.2.18b for Standard II, the high concentration mix.

5.2.15a Enter "24" to terminate evacuation of the GC. Select attenuation factor of 1(1x 1).

5.2.16a Depress CAL-1 switch and wait 10 seconds after amber LOW VACUUM light is on.

5.2.17a Release CAL-1 switch and wait 10 seconds. Start the L&N recorder, depress AUTO switch to ON position and press CLEAR. Wait until the GC display clock has timed to a minimum of 12 minutes.

5.2.18a Release AUTO switch to the OFF position.
Press MANUAL
Press CLEAR.
Enter "00".
Stop the recorder.

5.2.19a Identify the recorder trace with the date/time, gas used, loop number, and attenuation factor. The gas peaks will emerge in the following sequence on their recorder trace. Note that the helium and hydrogen peaks are combined.

Gas	Approximate Time after Injection Min.	Sec.
Helium-Hydrogen	-	41
Oxygen	1	02
Nitrogen	1	16
Krypton	1	51
Xenon	4	32

5.2.15b Enter "24" to terminate evacuation of the GC. Select attenuation factor of 5 (5 x 1).

5.2.16b Depress CAL-2 switch and wait 10 seconds after amber LOW VACUUM light is on.

5.2.17b Release CAL-2 switch and wait 10 seconds. Start the L&N recorder, depress AUTO switch to ON position and press CLEAR. Wait until the GC display clock has timed to a minimum of 12 minutes.

5.2.18b Release AUTO switch to the OFF position.
Depress MANUAL
Press CLEAR.
Enter "00".
Stop the recorder.

5.2.19b Identify the recorder trace with the date/time, gas used, loop number, and attenuation factor.

5.2.20 The high temperature analyses are performed only to determine oxygen, nitrogen, krypton and xenon concentrations. Calculate the height for each of the peaks as follows:

$$\text{Peak Height} = \frac{\text{(Trace peak height - baseline) x attenuation}}{100}$$

Note: The peak height calculated above should agree within ±5 percent of the value shown on the concentration versus peak height curve for the same attenuation factor and calibration gas for nitrogen, oxygen, and krypton. It should agree within ± 20 percent for xenon.

5.3 Sample Analysis

5.3.1 Complete calibration verification in Section 5.2. Open or verify open V-1.

5.3.2 Reset temperature control switch to the low (75°) position.

5.3.3 Depress MANUAL switch to the ON position and press CLEAR. Enter "00".

5.3.4 Enter "01" and then "45" to display set point of platen temperature and follow temperature range to 75°, then enter "00".

Note: Stabilization should occur within 10-12 minutes.

5.3.5 Depress SAMP switch. Verify red sample light is ON. Select loop No. 1 (0.25 cc).

5.3.6 Enter "23" to evacuate the GC until the HI VACUUM light is on. Cycle loop selector through loops 2, 3 and 4, pausing at each loop and evacuating until the HI VACUUM light is on. Cycle a minimum of three (3) times through loops 1, 2, 3 and 4, pausing at each loop for approximately 5 seconds.

Note: When cycling the sample loops depress the loop selector button for two seconds to insure the valve rotates to the next stop position.

5.3.7 Select loop number1.
Enter "24" to terminate evacuation.
For dissolved gas concentrations associated with normal reactor operations select an attenuation factor of 5. (5 x 1)
For accident conditions select attenuation factor of 250 (25 x 10) using the No. 1 or No. 2 (0.25 cc loop).

5.3.8 Notify the LSP operator that the G.C. is ready to receive a sample.

Note: Before performing step 5.3.6, verify with the LSP operator that the G.C. sample loops may be loaded.

5.3.9 Cycle loop selector through loops 1, 2, 3 and 4 pausing at each loop for approximately 5 seconds. Cycle 3 times. Select Loop No. 1.

5.3.10 After filling the sample loops, instruct the LSP operator to close valve RC-V-15.

5.3.11 Start the L&N recorder, release MANUAL, depress AUTO to the ON position and press CLEAR. Wait until the GC display clock has timed to a minimum of 12 minutes.

5.3.12 Release AUTO switch to the OFF position.
Depress MANUAL
Press CLEAR.
Enter "00".

5.3.13 Stop the recorder and identify the trace with sample, date/time, loop number and attenuation factor.

Note: If a repeat analysis is necessary, select the next loop, select an appropriate attenuation factor (5x1, 25x1, 100x1 or 5x100). Repeat steps 5.3.8 through 5.3.10 as necessary to obtain satisfactory data.

5.3.14 Reset the temperature control switch to the high (125°) position.

5.3.15 Enter "01" then "45" to display set point of platen temperature and follow temperature range to 125°, then enter "00".

Note: Stabilization should occur within 10 minutes.

5.3.16 Select loop No. 3 (1 cc).

5.3.17 Clear and release MAN switch to the OFF position. Start the L&N recorder, depress AUTO to the ON position and press CLEAR. Wait until the GC display clock has timed to a minimum of 12 minutes.

5.3.18 Release AUTO switch to the OFF position.
Depress MANUAL
Press CLEAR
Enter "00"

5.3.19 Stop the recorder and identify the trace with samples, date/time, loop numbers and attenuation factor.

Note: If a repeat analysis is necessary, select a 0.25 cc or 2 cc sample loop, select an appropriate attentuation factor (1 x 1)(5 x 1)(10 x 1)(25 x 1) (25 x 10). Repeat steps 5.3.16 through 5.3.18 as necessary to obtain satisfactory data.

5.3.20 Purge the GC of residual gas as follows:
Enter "23" and evacuate the GC until the red HI VACUUM light is on.

Cycle to each loop and evacuate until the HI VACUUM light is on.

5.3.21 Enter "13" to initiate argon purge.
Cycle loop selector through loops 1, 2, 3, and 4 pausing at each loop for approximately 5 seconds. Cycle 3 times.

5.3.22 Enter "14" to terminate the purge.
Enter "24" to terminate the evacuation.
Enter "00".
Release SAMP switch to OFF position.

5.3.23 If no additional analyses will be required within a day, close or check closed the following valves at the CAP.

V-1
V-14
V-10

5.3.24 Calculate the net peak height for each of the gases found on the sample tracer from step 5.3.18 and 5.3.12. Use the values obtained from the standards to determine the concentration of helium, hydrogen oxygen, nitrogen, krypton, and xenon in the unknowns.

5.3.25 The total gas concentration is the sum of the individual gas concentration determined in step 5.3.24.

TOTAL GAS DETERMINATION

(Single-Step Temperature)

The total gas determination at 125 °C is performed as follows:

1. Column temperature is set at 125°C as described in Sections 5.1.5 through 5.1.9. This adjustment can be performed manually rather than by using a switch.

2. The analyses is performed as indicated in the two-step temperature process using only that sequence described under the 75 °C temperature operation.

3. A 0.25 cc sample is required for the helium-hydrogen analyses and a 1 or 2 cc sample for the nitrogen, oxygen, krypton, and xenon analyses.

TABLE 2-1

PWR DISSOLVED GAS CONCENTRATIONS DURING NORMAL AND ACCIDENT* CONDITIONS (CC/KG)

	Normal Conditions			Accident Conditions	
Type Gas	Typical	Minimum	Maximum	Minimum	Maximum**
Helium	.0.1	.0.1	.0.1	.0.1	100-200
Hydrogen	25-35	5	50-75	15	1300
Krypton	.0.1	.0.1	.0.1	-	15
Nitrogen	.1	.1	5-10	.1	10-100
Oxygen	.0.1	.0.1	.0.1	.0.1	5
Xenon	0.1	.0.1	.0.1	-	200

---

* : 100 percent of gaseous fission products released from 3300 Mwt core to 2.74 x 10^5 kg of reactor water after approximately 650 days of irradiation.

**: The maximum values assume that all rods have been damaged to a degree which permits escape of gas from the rod. Concerning maximum hydrogen concentration, it is assumed that 30 percent of the core cladding is converted to the oxide form with its consequent release of hydrogen to the system. It is also assumed that a 500 ft^3 gas-steam bubble exists in the reactor vessel as a prerequisite to initiating core damage.

TABLE 2-2

BWR DISSOLVED GAS CONCENTRATIONS DURING NORMAL AND ACCIDENT CONDITIONS (CC/KG)

Type Gas	Normal Conditions			Accident Conditions	
	Typical	Minimum	Maximum	Minimum	Maximum**
Helium	0.1	0.1	0.1	0.1	20
Hydrogen	0.1	0.1	0.1	5-15	1500
Krypton	0.1	0.1	0.1	0.1	15-20
Nitrogen	0.1	0.1	0.1	0.1	.10
Oxygen	0.1	0.1	0.1	0.1	.1
Xenon	0.1	0.1	0.1	0.1	220

**: The maximum values assume that all rods have been damaged to a degree which permits escape of gas from the rod. Concerning maximum hydrogen concentration, it is assumed that 30 percent of the core cladding is converted to the oxide form with its consequent release of hydrogen to the system. It is also assumed that a 500 ft^3 gas-steam bubble exists in the reactor vessel as a prerequisite to initiating core damage.

TABLE 2-3

TIME SEQUENCE FOR GAS PEAK EMERGENCE FROM THE BASELINE GAS CHROMATOGRAPH

	Peak(1) Emergence in Seconds At	
Gas	75°C	125°C
Helium	34	(2)
Hydrogen	42	41
Oxygen	68	62
Nitrogen	93	76
Krypton	139	111
Xenon	530(3)	272

---

(1) Start of the peak.

(2) The helium peak can be combined with the hydrogen peak dependent on the concentration of gases present.

(3) The peak is very broad and shallow at this temperature.

These results were obtained with a 0.25 cc sample loop and at a 1X attenuation factor. Changing sample loop size and/or attenuation factor will change the time sequence slightly.

TABLE 2-4

GAS DATA

Element	Molecular or Atomic Weight	Thermal Cond. cal./(sec)(cm^2)(¼C/cm) x 10^{-6}; At 0¼C	Thermal Cond. Relative to */Ar	Solubility in Water** cc/kg
Argon	40	39.2	1	28.5 @ 30¼C
Helium	4	339	8.65	8.6 @ 20¼C
Hydrogen	2	400	10.2	18 @ 20¼C
Krypton	83.8	20.9	0.53	59.4 @ 20¼C
Nitrogen	28	58	1.48	16 @ 20¼C
Oxygen	32	58.5	1.49	6.35 @ 20¼C
Xenon	131	12.1	0.31	111 @ 20¼C

---

* : Gases other than argon
**: At 14.7 psia over pressure

Data taken from the following sources:

Matheson Gas Data Book, Fifth Edition, 1971
CRC Handbook of Chemistry and Physics, 51st Edition, 1970-71
Correlation of Solubility Data for Hydrogen and Nitrogen in Water, WAPD-TM-633, October 1976.

TABLE 2-5

SENSITIVITY OF DETECTION(1) FOR THE BASELINE GAS CHROMATOGRAPH

	ppm Gas Concentration			cc/kg Gas Primary Coolant(2)		
	0.25 cc Sample Loop	1 cc Sample Loop	2 cc Sample Loop	0.25 cc Sample Loop	1 cc Sample Loop	2cc Sample Loop
He	200	100	-	3.0	1.50	-
H_2	75	40	-	1.1	0.6	-
O_2	2000	600	350	30.2	9.1	5.3
N_2	700	200	125	10.6	3.0	1.9
Kr	-	380	200	-	4.6	3.0
Xe	-	500(3)	300(3)	-	7.6	4.5

---

(1) A peak indication can be seen at about half the concentrations indicated but cannot be accurately quantified. (2) Based on complete degassing of a 30 ml primary coolant sample into a 270 cc gas sample volume with an end pressure of 24.7 psia in the gas sample container. (3) Sensitivity of detection could be increased with the use of an integrator.

TABLE 4-1

HELIUM ANALYSES RESULTS WITH THE BASELINE GAS CHROMATOGRAPH

Test Number	Run Number	Percent Standard	Loop Size (cc)	Attenuation	Peak Height	Total Peak Height
1	1	0.00	0.25	5x	0	0
1	2	0.00	0.25	5x	0	0
1	3	0.00	0.25	5x	0	0
2	1	0.00	1	5x	0	0
2	2	0.00	1	5x	0	0
2	3	0.00	1	5x	0	0
3	1	0.05	0.25	5x	4	20
3	2	0.05	0.25	5x	4	20
3	3	0.05	0.25	5x	4	20
4	1	0.05	1	5x	12	60
4	2	0.05	1	5x	12	60
4	3	0.05	1	5x	12	60
5	1	0.15	0.25	5x	19	95
5	2	0.15	0.25	5x	19	95
5	3	0.15	0.25	5x	19	95
6	1	0.15	1	5x	26	130
6	2	0.15	1	5x	26	130
6	3	0.15	1	5x	26	130
7	1	0.30	0.25	5x	29	145
7	2	0.30	0.25	5x	29	145
7	3	0.30	0.25	5x	29	145
8	1	0.30	1	5x	45	225
8	2	0.30	1	5x	45	225
8	3	0.30	1	5x	45	225
9	1	0.5	0.25	5x	44	220
9	2	0.5	0.25	5x	44	220
9	3	0.5	0.25	5x	44	220
10	1	0.5	1	10x	34	340
10	2	0.5	1	10x	34	340
10	3	0.5	1	10x	34	340
11	1	1	0.25	10x	38	380
11	2	1	0.25	10x	38	380
11	3	1	0.25	10x	38	380
12	1	0.99	1	25x	26	650
12	2	0.99	1	25x	26	650

13	1	4.76	0.25	50x	27	1350
13	2	4.76	0.25	50x	27	1350
13	3	4.76	0.25	50x	27	1350

TABLE 4-1
HELIUM ANALYSES RESULTS WITH
THE BASELINE GAS CHROMATOGRAPH
PAGE 2

Test Number	Run Number	Percent Standard	Loop Size (cc)	Attenuation	Peak Height	Total Peak Height
14	1	4.76	1	100x	30	3000
14	2	4.76	1	100x	30	3000
14	3	4.76	1	100x	30	3000
15	1	9.09	0.25	100x	32	3200
15	2	9.09	0.25	100x	32	3200
15	3	9.09	0.25	100x	32	3200
16	1	9.09	1	100x	46	4600
16	2	9.09	1	100x	46	4600
16	3	9.09	1	100x	46	4600

TABLE 4-2

HYDROGEN ANALYSES RESULTS WITH THE BASELINE GAS CHROMATOGRAPH

Test Number	Run Number	Percent Standard	Loop Size (cc)	Attenuation	Peak Height	Total Peak Height
1	1	0.05	0.25	5x	5	30
1	2	0.05	0.25	5x	5	30
1	3	0.05	0.25	5x	5	30
2	1	0.05	1	5x	8	40
2	2	0.05	1	5x	8	40
2	3	0.05	1	5x	8	40
3	1	0.15	0.25	5x	19	95
3	2	0.15	0.25	5x	19	95
3	3	0.15	0.25	5x	19	95
4	1	0.15	1	5x	28	140
4	2	0.15	1	5x	28	140
4	3	0.15	1	5x	28	140
5	1	0.30	0.25	5x	36	180
5	2	0.30	0.25	5x	36	180
5	3	0.30	0.25	5x	36	180
6	1	0.30	1	10x	28	280
6	2	0.30	1	10x	28	280
6	3	0.30	1	10x	28	280
7	1	0.50	0.25	10x	31	310
7	2	0.50	0.25	10x	31	310
7	3	0.50	0.25	10x	31	310
9	1	0.99	0.25	25	24	600
9	2	0.99	0.25	25	24	600
9	3	0.99	0.25	25	24	600
10	1	0.99	1	25	41	1025
10	2	0.99	1	25	41	1025
10	3	0.99	1	25	41	1025
11	1	4.76	0.25	100	25	2500
11	2	4.76	0.25	100	25	2500
11	3	4.76	0.25	100	25	2500
12	1	4.76	1	100	43	4300
12	2	4.76	1	100	43	4300
12	3	4.76	1	100	43	4300
13	1	9.09	0.25	250	16	4000
13	2	9.09	0.25	250	16	4000
13	3	9.09	0.25	250	16	4000
14	1	9.09	1	250	25	6250
14	2	9.09	1	250	25	6250
14	3	9.09	1	250	25	6250

TABLE 4-3

OXYGEN ANALYSES RESULTS WITH THE BASELINE GAS CHROMATOGRAPH

Test Number	Run Number	Percent Standard	Loop Size (cc)	Attenuation	Peak Height	Total Peak Height
1	1	0.05	0.25	1	–	–
1	2	0.05	0.25	1	–	–
1	3	0.05	0.25	1	–	–
2	1	0.05	1	1	2	2
2	2	0.05	1	1	2	2
2	3	0.05	1	1	2	2
3	1	0.15	0.25	1	–	–
3	2	0.15	0.25	1	–	–
3	3	0.15	0.25	1	–	–
4	1	0.15	1	1	7	7
4	2	0.15	1	1	7	7
4	3	0.15	1	1	7	7
5	1	0.3	0.25	1	6	6
5	2	0.3	0.25	1	6	6
5	3	0.3	0.25	1	6	6
6	1	0.3	1	1	15	15
6	2	0.3	1	1	15	15
6	3	0.3	1	1	15	15
7	1	0.5	0.25	1	11	11
7	2	0.5	0.25	1	11	11
7	3	0.5	0.25	1	11	11
8	1	0.5	1	1	23	23
8	2	0.5	1	1	23	23
8	3	0.5	1	1	23	23
9	1	1	0.25	1	22	22
9	2	1	0.25	1	22	22
9	2	1	0.25	1	22	22
10	1	1	1	5	10	50
10	2	1	1	5	10	50
10	3	1	1	5	10	50
11	1	5	0.25	5	23	115
11	2	5	0.25	5	23	115
11	3	5	0.25	5	23	115
12	1	5	1	10	22	220

12	3	5	1	10	22	220
13	1	10	0.25	10	22	220
13	2	10	0.25	10	22	220
13	3	10	0.25	10	22	220

TABLE 4-4

NITROGEN ANALYSES RESULTS WITH THE BASELINE GAS CHROMATOGRAPH

Test Number	Run Number	Percent Standard	Loop Size (cc)	Attenuation	Peak Height	Total Peak Height
1	1	0.05	0.25	1	–	–
1	2	0.05	0.25	1	–	–
1	3	0.05	0.25	1	–	–
2	1	0.05	1	1	3.5	3.5
2	2	0.05	1	1	3.5	3.5
2	3	0.05	1	1	3.5	3.5
4	1	0.15	1	1	12	12
4	2	0.15	1	1	12	12
4	3	0.15	1	1	12	12
5	1	0.3	0.25	1	11	11
5	2	0.3	0.25	1	11	11
5	3	0.3	0.25	1	11	11
6	1	0.3	1	1	24	24
6	2	0.3	1	1	24	24
6	3	0.3	1	1	24	24
7	1	0.5	0.25	1	19	19
7	2	0.5	0.25	1	19	19
7	3	0.5	0.25	1	19	19
8	1	0.5	1	1	37	37
8	2	0.5	1	1	37	37
8	3	0.5	1	1	37	37

TABLE 5-1

RECOMMENDED* GAS SAMPLE LOOP SIZE AND ATTENUATION FACTORS FOR GAS ANALYSES WITH THE BASELINE GAS CHROMATOGRAPH

Gas	Dissolved Gas Conc.	Gas Sample Loop Size (cc)	Attenuation Factor	Dissolved Gas Conc.	Gas Sample Loop Size (cc)	Attenuation Factor
He	1-5 cc/kg	1	1	5-50 cc/kg	0.25	5
H_2	1-5 cc/kg	1	1	5-50 cc/kg	0.25	5
O_2	5-20 cc/kg	2	1	20-50 cc/kg	1	1
N_2	5-10 cc/kg	2	1	10-50 cc/kg	1	1
Kr	5-20 cc/kg	2	1	20-50 cc/kg	1	1
Xe	5-20 cc/kg	2	1	20-50 cc/kg	1	1

---

*: The parameters indicated are recommended as a starting point. Actual plant experience may dictate other values.

LINEARITY CHARACTERISTICS FOR HYDROGEN FOR 0.25 AND 1 CC SAMPLE

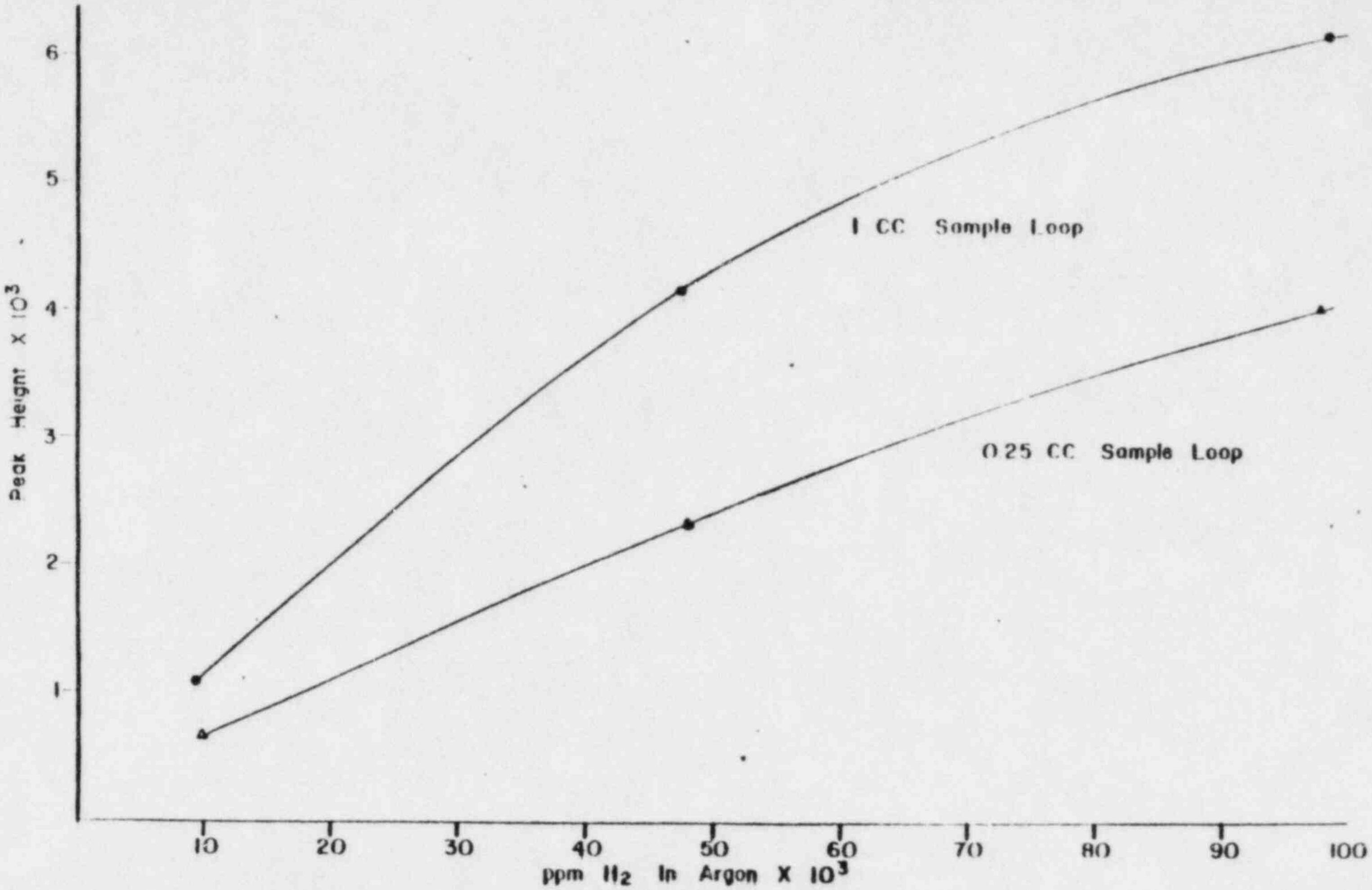


FIGURE 2-1

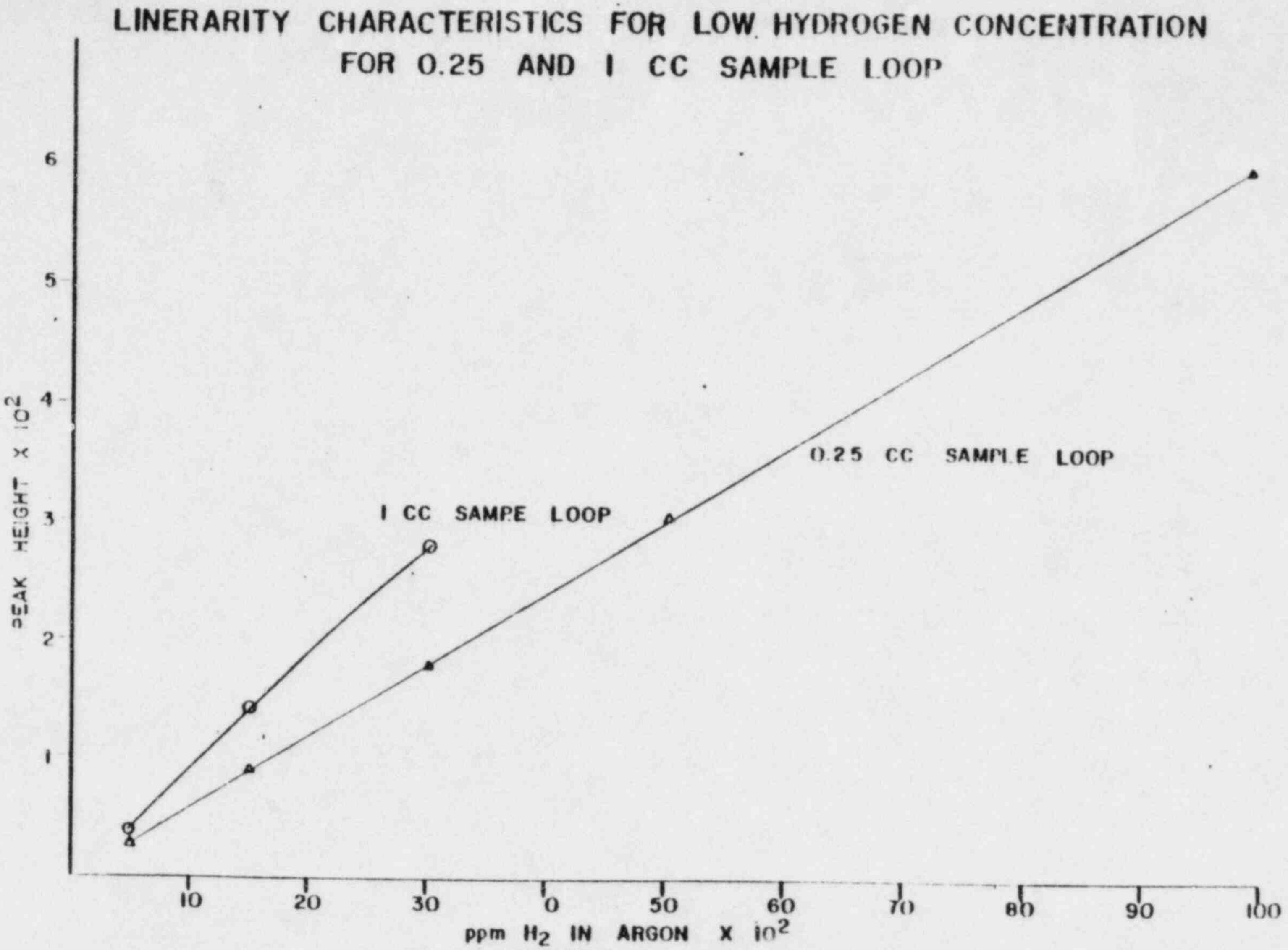
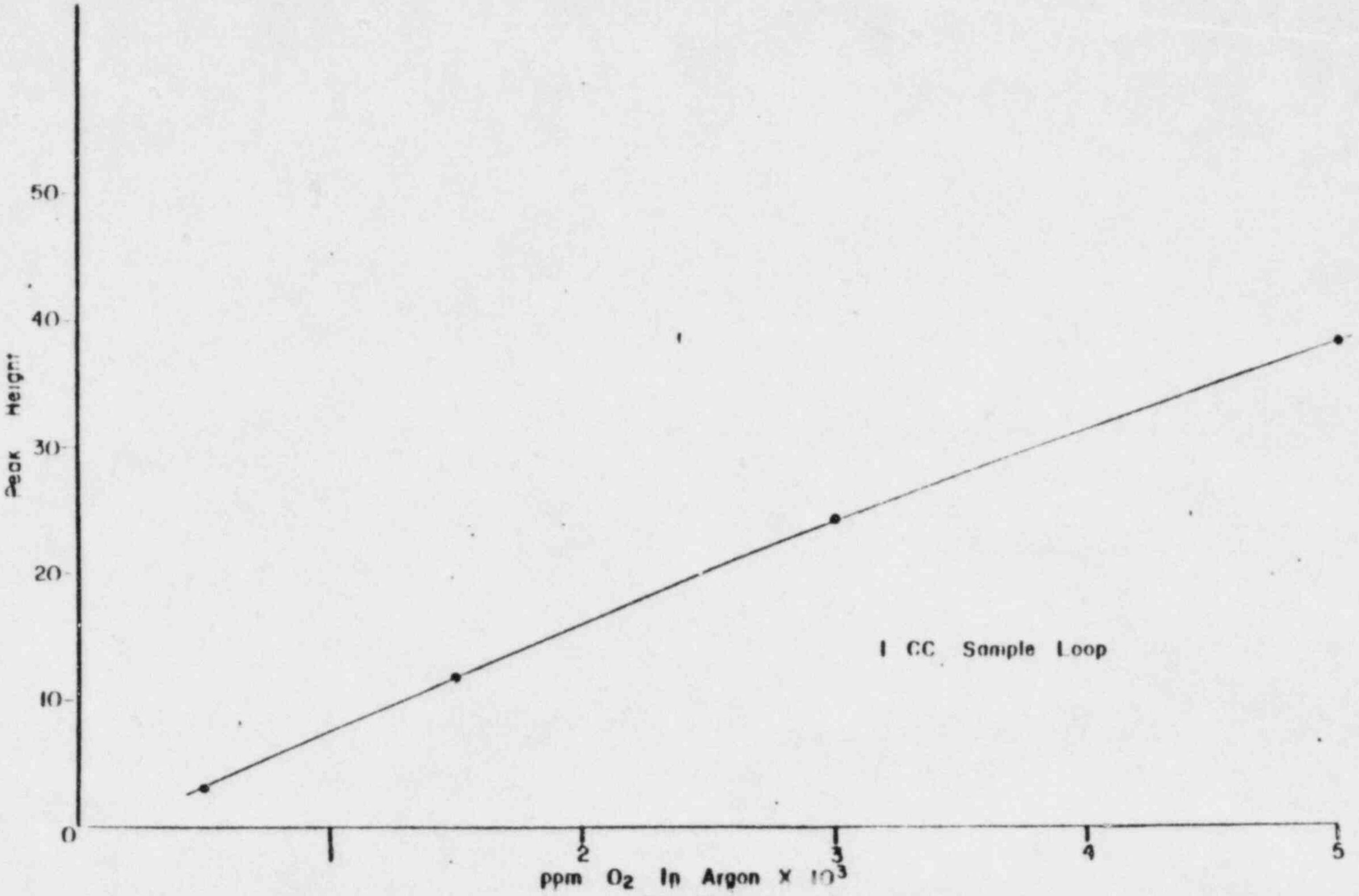

LINERARITY CHARACTERISTICS FOR LOW HYDROGEN CONCENTRATION FOR 0.25 AND I CC SAMPLE LOOP

FIGURE 2-1A

LINEARITY CHARACTERISTICS FOR OXYGEN FOR I CC SAMPLE



FIGURE

FIGURE 4-1

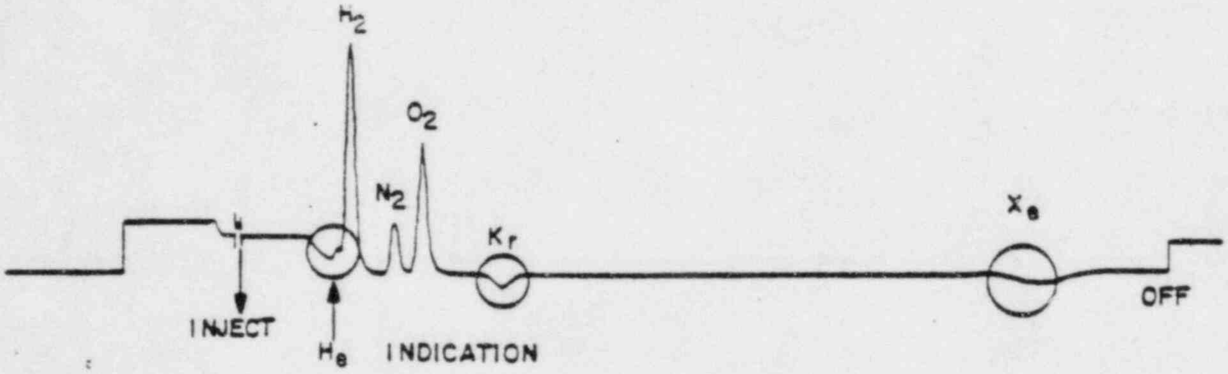
1 X ATTENUATION
0.25 CC SAMPLE LOOP
1000 ppm X_e

XENON PEAK OCURRING AT 530 SECONDS
AFTER INJECTION.

75° C COLUMN TEMPERATURE

FIGURE 4-2

0.25 CC SAMPLE LOOP
5 X ATTENUATION

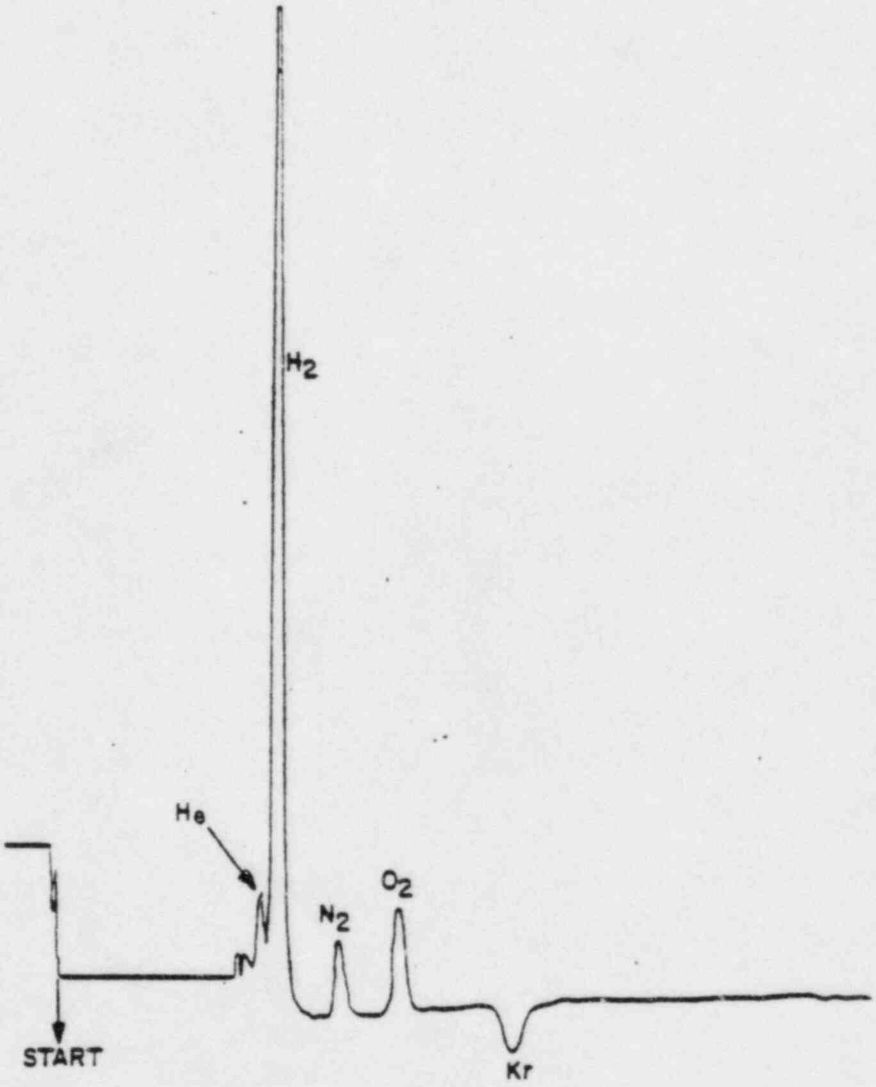


NOTE HOW HELIUM PEAK COMBINES WITH HYDROGEN WHEN OPERATING WITH A COLUMN TEMPERATURE OF 125° C

FIGURE 4-3

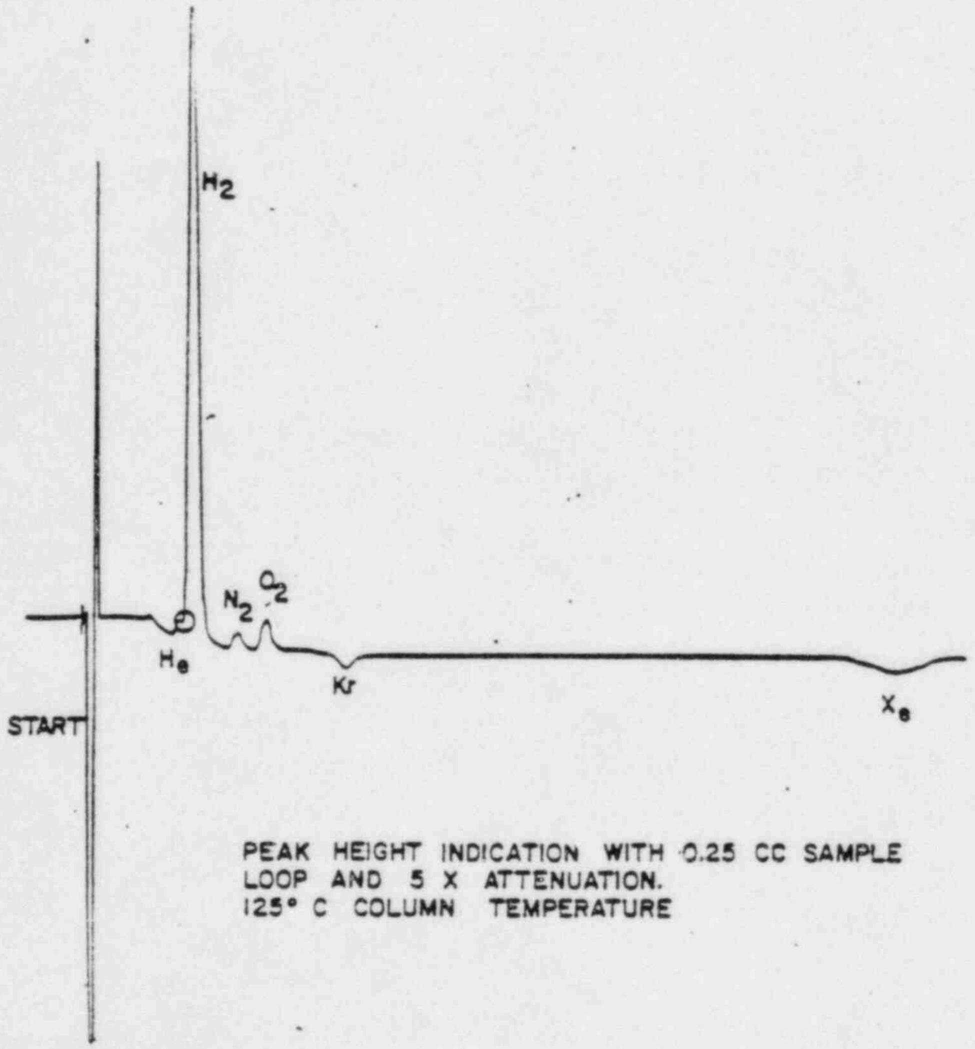
0.25 CC SAMPLE LOOP

I X ATTENUATION



NOTE SEPERATION OF He AND H_2
PEAK AT 75° C COLUMN TEMPERATURE

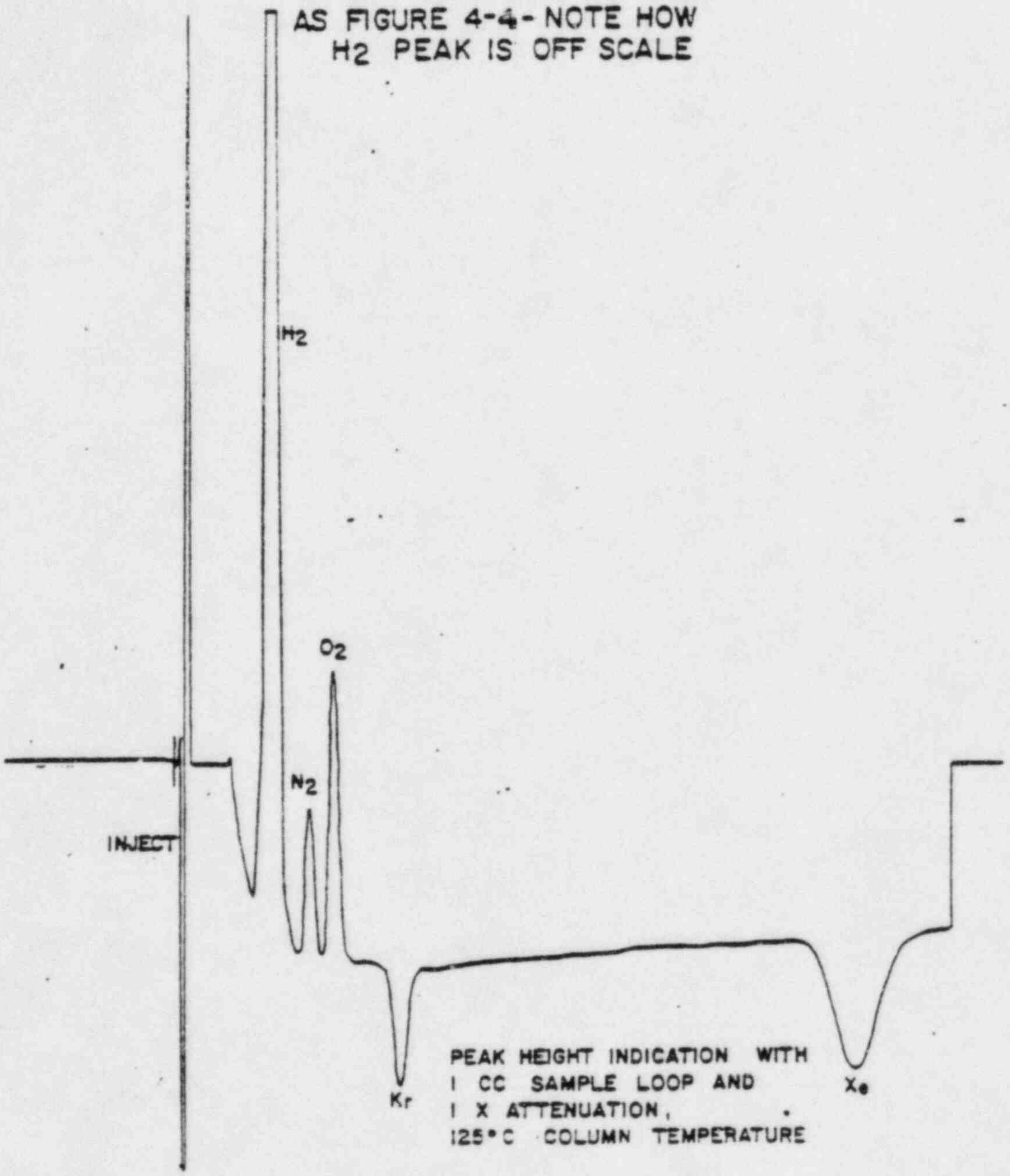
FIGURE 4-4



PEAK HEIGHT INDICATION WITH 0.25 CC SAMPLE LOOP AND 5 X ATTENUATION.
125° C COLUMN TEMPERATURE

FIGURE 4-5

SAME GAS CONCENTRATION AS FIGURE 4-4- NOTE HOW H_2 PEAK IS OFF SCALE



PEAK HEIGHT INDICATION WITH 1 CC SAMPLE LOOP AND 1 X ATTENUATION, 125°C COLUMN TEMPERATURE

NSAC/46

April 1982

An Evaluation of On-Line Boron Analyzers

Prepared by
NUS CORPORATION

STONE & WEBSTER
ENGINEERING CORPORATION

☒ APPROVED AS DEFINED IN THE SPECIFICATION

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BY RJ Kiernan

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The Nuclear Safety Analysis Center is operated for
the electric utility industry by the Electric Power Research Institute

An Evaluation of On-Line Boron Analyzers

NSAC-46

Final Report, April 1982

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Prepared by
NUS Corporation
Pittsburgh, Pennsylvania

NSAC PERSPECTIVE

PROJECT DESCRIPTION

Boron dissolved in the reactor coolant is a primary means of reactivity control in pressurized water reactors and a backup means of reactivity control in boiling water reactors. Thus, boron concentration is a fundamental safety parameter and must be measured.

Under normal conditions the boron concentration is determined by analyzing a grab sample and in some cases by an on-line boron analyzer. However, under postaccident conditions grab samples may involve unwarranted personnel exposure and not all of the new postaccident sample systems provide rapid measurements. Conventional on-line boron analyzers are overwhelmed by the radiation expected during an accident. To overcome these shortcomings, several new on-line boron analyzers are on the market. These have been especially designed to function during an accident.

In this service, high radioactive fluids will expose components of on-line analyzers to radiation levels which can be as high as 10^6 R/hr. Radiation of this magnitude can damage some types of electronic components and elastomers that are present in the instruments. Photoelectric devices and small solid state components are particularly sensitive to radiation damage. It is also possible that high radiation levels may temporarily affect sensing elements.

The market for on-line analyzers is limited. Because of this, NSAC was concerned that this equipment might not be thoroughly and independently tested. This test program was sponsored as a result of that concern. Three commercially available postaccident boron analyzers were tested in radiation fields up to and exceeding those that would be encountered in an accident.

PROJECT OBJECTIVE

The three boron analyzers were tested under normal conditions and at radiation levels as high as 10^5 to 10^6 R/hr. The tests sought to determine the accuracy of the analyzers, their reliability under normal conditions, their susceptibility to radiation damage, and their accuracy when exposed to high radiation levels.

PROJECT RESULTS

The Ionics Digichem analyzer as modified by Sentry, the Westinghouse Mark V boron analyzer, and the Combustion Engineering Boronmeter are all suitable for postaccident service if properly installed and maintained. The testing did indicate improvements that could be made to some of this equipment. These suggestions were accepted by the manufacturers and are being incorporated into the product line.

Robert N. Kubik
NSAC Project Manager

ABSTRACT

Testing has been performed to evaluate the performance of three on-line boron analyzers and determine the effect of a high intensity gamma field (10^3 to 10^6 R/hr) on this instrumentation. The main objective of this work was to verify the applicability of the analyzers for boron analyses under post-accident conditions. The on-line analyzers tested included an Ionics model (DigiChem Analyzer) as modified by Sentry, the Westinghouse Mark V Analyzer, and the Combustion Engineering High Radiation Borononeter System. Irradiation testing was also performed on elastomers, solid-state electronics, and pH probes. Results of this work indicate that the three on-line analyzers tested are suitable for boron determinations during accident conditions. Radiation exposure levels involved in determining boron concentration with these systems would be essentially zero.

Results from gamma irradiation tests indicate that teflon will remain serviceable at 10^6 rads exposure. Other elastomers tested were more radiation resistant than is teflon. Solid-state components tested showed radiation damage at between 10^4 and 10^5 rads exposure. A slight but constant bias in readout was noted when pH probes were exposed to high radiation levels. This bias has no significant effect on boron analyses results obtained from titrating the boron-mannitol acid complex.

ACKNOWLEDGMENTS

We wish to note the cooperation of the Sentry Corporation, Ionics Corporation, Westinghouse Electric, and Combustion Engineering. These companies furnished the equipment used in this test program and provided the manpower required for initial startup of the equipment. In particular, we wish to thank Joe Leon of the Sentry Corporation, Dale Lueck of the Ionics Corporation, Rick Pod of Westinghouse Electric, and Joe Kowles of Combustion Engineering.

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Section 1

INTRODUCTION AND SUMMARY

Four vendors of in-line boron analyzers were invited to participate in a program to test the ability of their equipment to withstand postaccident environmental conditions. Three vendors responded to this invitation as follows:

- Sentry and Ionics with the DigiChem Analyzer. This boron analyzer is manufactured by the Ionics Corporation and is modified by Sentry to withstand the high gamma radiation levels encountered in post-accident application. The modified instrument is sold only through Sentry.
- Westinghouse with their Boron Concentration Monitoring System (BCMS) Mark V Analyzer.
- Combustion Engineering with their High Radiation Boronometer System.

The Sentry Modified Digichem Analyzer provides for boron determination by remote titration of the boron-mannitol acid complex. It is assumed that the boron solution contains the normal isotopic concentration of ${}^{10}B$ to provide for reactivity control of the system. The procedure followed is identical to the referee method used for normal laboratory determination of boron concentration. The Westinghouse and Combustion Engineering analyzers provide for boron determination by measuring the ${}^{10}B$ concentration or the neutron absorption characteristics of the system. Since neutron absorption is determined directly, it provides for an absolute measurement of reactivity control.

Equipment provided by these vendors was tested under normal operating conditions and in the presence of high-level radiation. The high-level radiation testing was performed in a hot cell using ${}^{60}Co$ as the radiation source. Energy level of the ${}^{60}Co$ gammas are normalized so that the energy absorbed by the materials in test will be comparable to the accident case. Maximum radiation levels were on the order of 10^5 - 10^6 R/hr. Test description and results for each analyzer are described separately in the main body of the report.
For those who are interested in results on irradiation testing of elastomers, solid-state electronics and pH probes, your attention is called to the Sentry-Ionics report.

The general conclusions derived from this overall study and the advantages of using these on-line analyzers are summarized below:

- Sentry Modified DigiChem Analyzer

  --The Sentry modified DigiChem analyzer is acceptable for use to determine boron concentration under post-accident conditions. Concerning its use for normal power operations, the accuracy is probably acceptable.

  --All boron analyses operations can be performed remotely. The exposure involved in determining boron concentration would approach zero.

  --Sample volume requirements are on the order of 1-2 ml per analysis, thus shielding requirements would be minimal.

  --Analyses results can be achieved within 10 minutes after the sample line is purged to obtain a representative sample.

  --Though not sealed gas tight, there would be little tendency for release of gaseous activity to the atmosphere. This would be particularly true if the sample addition sequence is changed to add water prior to addition of the sample.

- Westinghouse BCMS Mark V Analyzer

  --The Westinghouse Mark V boron analyzer is acceptable for use under post-accident conditions. It should be possible to obtain an analysis within 5 or 10 minutes with this system. Concerning its use for normal power operations, the accuracy is probably acceptable.

  --Count rate increases, and thus the ppm boron readout decreases with increasing radiation levels, however, the effect is a predictable one and accuracy is still quite acceptable.

  --For maximum anticipated exposure levels of 5×10^5 R/hr (10 Ci/cc activity level), the fissioning count rate will increase by about

5 percent. This 5 percent increase in count rate will result in a small error relative to the accuracy required for post-accident conditions.

--The increase in count rate from irradiation is essentially a constant (as percent of count rate) for the three conditions tested (pure water, 2570 and 5140 ppm boron). The increased count rate does not linger when the radiation field is removed.

- Combustion Engineering High Radiation Boronometer System

--The CE Boronmeter is acceptable for use under post-accident conditions.

--Reproducibility of results is excellent as based on fission count rate, however, conversion of count rate to ppm is somewhat below the accuracy desired for daily operations. CE indicates, however, thst the proper curve fit routine in the microcomputer will provide proper ppm indication.

--A 500 second count rate is recommended for determining boron concentrations below 1,000 ppm.

--The use of a strip chart recorder is recommended for use with the boronometer. This will improve statistics and show trending.

--There is some increase in the standard deviation from radiation levels in the range of 10^6 R/Hr at the planned discriminator setting of 50 millivolts. The increase is not significant with respect to post-accident analyses requirements.

Section 2

SUMMARY OF RESULTS - SENTRY DIGICHEM ANALYZER

The Ionics DigiChem Analyzer, as modified by Sentry, performed properly at radiation levels of 8.64×10^4 R/hr. Maximum radiation levels anticipated under credible accident conditions are on the order of 10^4 R/hr.

The analyzer operated at an integrated dose of 2.7×10^7 rads. This corresponds to about three months of operation at maximum dose rates anticipated under accident conditions.

If this system is used, NUS recommends that the analyses to determine boron concentration be performed titrating the boron-mannitol acid complex from a pH of about 5.5 to pH 8.5. Actual pH used for the low and high pH end points should be determined by titrating known boron standards after addition of mannitol to the boron solution. Titrating from a low pH inflection point (pH 4-6) to a high pH inflection point (pH 8-8.5) can also be used, however, results of previous testing performed by NUS indicates better precision can be achieved by titrating to specific pH end points. Either method of titration (pH end point or inflection point) is acceptable for post-accident use.

If the production model DigiChem analyzer is modified as indicated below it should perform properly at radiation levels of 10^4 - 10^5 R/hr and continue to operate at an integrated dose of 10^7 rads.

- Separate the rotary spin assembly and sample addition module so that only these components are exposed to high radiation fields.
- Replace the photon coupled modules H21AY3 and MCA8 with mechanical switches. Alternately. it would be possible to provide localized shielding for these modules to limit exposure level to about 10^5 rads.
- Move the solid state relay for the solenoid actuated valve on the rotary reaction cell to a location outside the high radiation zone.
- Replace the two nylon pulleys used to drive the rotary reaction cell with metal pulleys.

- Replace the teflon with elastomers that are more resistant to radiation. The teflon does not have to be replaced if the integrated exposure is limited to 10^5 rads.

BACKGROUND INFORMATION

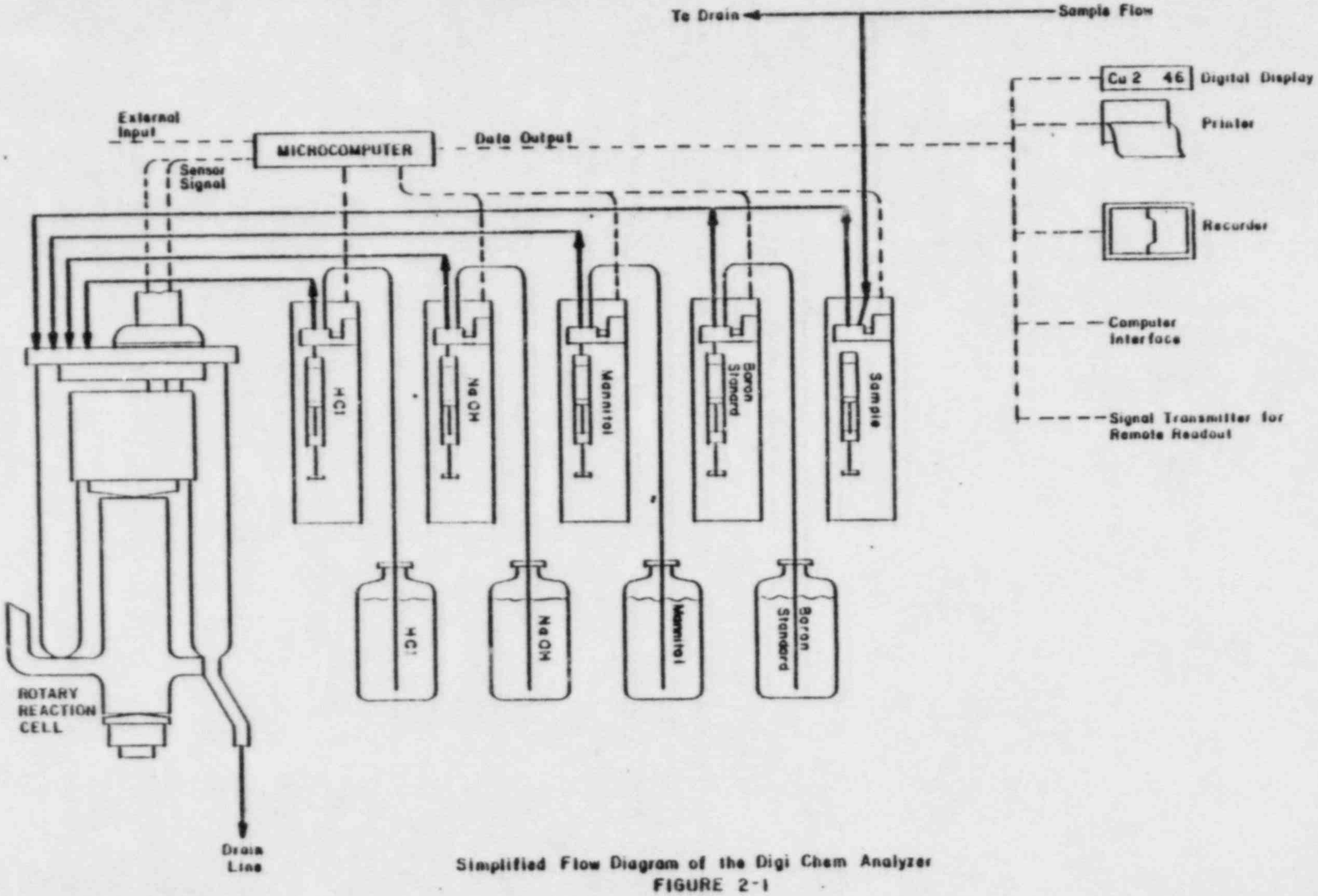
TEST PURPOSE

Testing was performed to determine if the Sentry modified DigiChem analyzer and selected components from an unmodified DigiChem analyzer would suffer radiation damage in analyzing for boron at radiation exposure levels anticipated under post-accident conditions. In addition. testing was performed to determine the accuracy that could be achieved with the DigiChem analyzer for boron determinations during normal operating conditions. Modifications made by Sentry to the DigiChem analyzer include replacement of selected components that would be in a high radiation field with components made of more radiation resistant material. The selected components tested from the unmodified system include all solid state components and elastomers that would be exposed to high radiation fields, the rotary spin assembly, and sample burette assembly. Both the rotary spin and sample burette assemblies would be exposed to relatively high radiation levels if the system is used in post-accident testing.

The system provides for boron determination by remote titration of the boron-mannitol acid complex. It is assumed that the boron solution contains the normal isotopic concentration of ^{10}B to provide for reactivity control of the system. The procedure followed is identical to the standard method used for normal laboratory determination of boron concentration.

SYSTEM DESCRIPTION

The DigiChem analyzer 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. A simplified flow diagram of the system is shown in Figure 2-1. The microcomputer consists of a series of plug-in circuit boards and the keyboard control panel devices. A motherboard of bus lines and connectors is spread along the inside rear for plugging in the circuit boards as needed. All boards are easily replaced.



Simplified Flow Diagram of the Digi Chem Analyzer
FIGURE 2-1

The rotary spin assembly is of modular construction, located at the lower left side of the DigiChem analyzer enclosure. The reaction cell inside the spin assembly is fabricated from teflon. It forms the heart of the assembly. As programmed, the microcomputer controls a variable speed motor which spins the reaction cell to provide for mixing of the solution as reagents are added. A cover to the spin assembly provides entrances for the sample and reagent addition lines and the pH probe. Reagent addition and sensing occurs below the surface of the sample.

The sample and reagent dispensing 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 provide a dispensing capability for up to five fluids. such as samples, reagents, and buffers. Three reagent (acid, base, and mannitol) addition modules, one boron standard addition module, and one sample addition module are used in this application. The digital controlled module has a stepper-motor which pushes a plunger through a burette to dispense fluids in precise microliter increments.

The DigiChem analyzer was designed for process control applications, providing on-line analyses and control for continuous, semicontinuous, and batch processes. It automatically performs titrimetric, colorimetric or selective-ion analyses. The microcomputer controls the automatic functions of sample and reagent dispensing, solution mixing, and concentration sensing through a programmed sequence of analyses. The instrument as it is normally used takes and measures a sample from an on-line stream and performs the following programmed operations automatically:

- A fixed but programmable volume of sample is forced into the reaction vessel. Sample volume required for boron analyses 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.

- Next the instrument adds dilution water to flush the sample line and provide sufficient volume to cover the tip of the pH probe. If it is planned to use the instrument for post-accident analyses, the programming sequence should be changed to add water first. This will dilute the sample and thus reduce the potential for release of iodine gas which may be present. After the sample is added, a little more water (2-5 ml) is required to flush the sample addition tip.

- If the solution is basic, as could be the case during an accident. the system can be programmed to add acid to neutralize the base. The manufacturer should be consulted concerning programming requirements.

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

- The solution is titrated with NaOH to an end point pH of 8.5 Alternately, the volume of titrant used can be determined by automatic derivation of the change in slope of the pH line (inflection point), which occurs when the caustic titration of the boron-mannitol complex is complete.

- 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.

- 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 are gravity drained to a collection tank.

SYSTEM MODIFICATION FOR OPERATION IN A RADIATION ENVIRONMENT

For operation in a radiation environment, it is necessary to separate the rotary spin assembly and the sample addition module from the microcomputer section to provide for localized shielding of components containing primary coolant. The microcomputer section and other components which are not exposed to the primary coolant probably cannot withstand high radiation exposure levels. Separation poses no serious technical problem since the units are of modular construction. However, this task should not be undertaken lightly since there are many electrical lines which must be lengthened, three solid state components which must be changed or shielded and longer length tubing must be provided for sample and reagent feed. Preamplification of the pH signal is also required.

SENTRY MODIFICATIONS TO THE DIGICHEM ANALYZER

The Sentry approach in providing a system that is suitable for on-line boron analyses under post-accident conditions was to replace all elastomers with more radiation resistant materials where necessary. Specific changes made to the DigiChem analyzer by Sentry prior to this test work are indicated below. Other changes have since been made to correct problems identified in the high level irradiation experiments.

- All teflon and Kel-F parts in the system were replaced with more radiation resistant elastomers.

- O-rings in the radiation zone were replaced with O-rings made of materials known to be more resistant to radiation.

- Solid state controls that will be in the high radiation zone were replaced with mechanical switches.

- The rotary spin assembly, sample addition module and reagent addition modules were separated 25 feet from the control module. Only the rotary spin assembly and sample addition module will be in the high radiation area. Shielding is provided for these components.
- A separate pH preamplifier was added.

TEST DESCRIPTION

DIGICHEM COMPONENTS PROVIDED BY IONICS

The irradiation testing was performed at the hot cell test facilities at Georgia Tech. Components tested were those from the DigiChem Analyzer which would be subjected to moderately high radiation levels during boron analyses under post-accident conditions. In selecting the components that will be exposed to high radiation levels, it was assumed that the rotary spin assembly and sample addition module would be located behind a lead shield to separate other components from the high radiation area. The components tested were in the form provided by the manufacturer in their standard version of the DigiChem Analyzer. These components are as follows:

- Rotary Spin Assembly - This was exposed to 10^7 rads.
- Sample Addition Module - This was exposed to 10^7 rads.
- Separate photo-interrupter cells for the rotary spin assembly and sample addition module were tested at 10^4, 10^5 and 10^6 rads. This additional testing was performed to determine the failure point since the photo-interrupter cells included as part of the rotary spin assembly and sample addition module failed totally after exposure to 10^7 rads.
- O-Rings (Buna, Kalrez and Viton) - These were tested to 10^6 and 10^7 rads exposure.
- Delivery Tips (Kel-F) - These were tested at 10^6 and 10^7 rads exposure.
- Teflon Tubing - Two separate lots of teflon tubing were tested at 10^5, 10^6 and 10^7 rads exposure.
- pH and Reference Electrodes - Testing was performed with two sets of pH probes with external reference cells of the type used by Ionics in their DigiChem analyzer. In addition, testing was performed on a pH probe with an internal reference cell. Four series of tests were performed at maximum radiation levels of 10^6 R/hr, as follows:

  --Testing was performed using the buffer solutions indicated below. Buffer solutions were used to minimize the effect of CO_2 pickup from air on pH of the solutions. It was necessary to leave the solutions exposed to air during the course of this testing.

Organic buffers were not used because these buffers will degrade under irradiation, resulting in a change in pH. This change in pH could be wrongfully attributed to radiation induced degradation of the pH probes.

pH	Compound	Concentration	Comments
4.5	Potassium dihydrogen phosphate	0.2 Molar	Laboratory preparation
7.0	Monobasic potassium phosphate and sodium hydroxide	—	Commercial preparation
10.0	Potassium carbonate, potassium borate and potassium hydroxide	—	Commercial preparation

--One set of buffer solutions was exposed to the radiation field in the hot cell, checking the pH of each solution periodically during the course of the working day. The pH probes and reference cell were exposed to the same radiation field as were the buffer solutions. The pH meter was installed outside the hot cell. A 10 foot lead was required for connection of the probe to the pH meter.

--The temperature of the solution in the hot cell was monitored so that correction could be made for the temperature effect on pH. The hot cell lights were turned off when not in use so that temperature inside the hot cell would remain relatively constant.

--The control buffer solutions were stored outside the hot cell. checking the pH at the same frequency as were the solutions inside the hot cell.

MODIFIED DIGICHEM ANALYZER

The Sentry modified DigiChem analyzer is programmed to determine boron concentration by automatic derivation of the change (inflection point) in slope of the pH line which occurs when the caustic titration of the boron-mannitol complex is complete. After the sample is added to the rotary reaction cell, deionized water and mannitol are added to the sample. A pH determination is made at this point and if the solution is basic, acid is added automatically to reduce the pH to the range of 2 to 2.5. Then a back titration is performed to neutralize the excess acid, indicated by an inflection point at around pH 5-6 in the slope of the pH line. Titration of the boron-mannitol complex begins at this time and is complete at the high pH inflection point.

Analyses performed with the production model DigiChem analyzer followed the pattern indicated above except that a pH of 5.5 was used as a start point for titration of the boron-mannitol complex and a pH of 8.5 was used as the end point.

Initially the equipment was operated outside the hot cell using four standard solutions containing 60, 600, 1200 and 3000 ppm boron to verify operation of the system. The equipment was operated with a 25-foot separation between the control unit and other components as it would be in post-accident conditions. Following the initial testing the rotary spin assembly, with its pH probe, the sample addition module, and the 3000 ppm boron standard were installed inside the hot cell. The other components, the preamplifier for the pH probe, and the 1200 ppm standard remained outside the hot cell.

Testing was performed at radiation levels of 1.75×10^4 R/hr, 8.64×10^4 R/hr and 1.57×10^5 R/hr. The central point for determining the radiation level was adjacent to, and just above the top of the rotary spin assembly. Other areas may have been slightly higher or lower than the reported radiation level. Total radiation exposure for the Sentry modified equipment was approximately 2.7×10^7 rads.

PRODUCTION MODEL DIGICHEM ANALYZER

A series of boron standards and post-accident matrix solutions prepared by NUS were analyzed with the DigiChem analyzer at the Ionics, Inc., plant in Watertown, Massachusetts. The analyses were performed by a NUS representative using a production model analyzer. Titration of the samples were performed with 0.5N and 0.1N NaOH to determine if there is an advantage to using a more dilute titre. No radiation exposure was involved in this testing.

The solutions analyzed are listed below. Concentration of the additives used to make up these solutions are shown on Table 2-1.

- Boron standards based on the weight of boric acid used to prepare the solutions.
- Boron standards containing low concentrations of lithium hydroxide. This was to simulate the buildup of lithium in the primary coolant during normal power operations.
- Post-accident fission product matrices containing known concentrations of boron.
- Simulated solutions that might be expected to develop in the reactor containment sump after a loss-of-coolant-accident and activation of caustic containment spray.
- Solutions containing calcium, this testing was performed to determine if calcium that is leached from the concrete during a loss-of-coolant-accident would affect the boron analysis results.

TABLE 2-1

COMPOSITION* OF MATRIX SOLUTIONS USED IN TESTING THE DIGICHEM ANALYZER

Sample	mg/l B	mg/l Li OH	mg/l La Cl_3	mg/l Ba NO_3	mg/l KI	mg/l Cs Cl_3	mg/l Ce $(NO_3)_6$ $(NH_4)_2$	mg/l $CaCl_2$
Matrix 1	60	6.9	4.0	15.4	51.0	312.9	20.7	0
Matrix 2	2000	6.9	4.0	15.4	51.0	312.9	20.7	0
Matrix 3	6000	6.9	4.0	15.4	51.0	312.9	20.7	0
Matrix 4	6004	0.7	0.4	1.5	5.1	31.3	2.1	0
Matrix 5	0	0.7	0.4	1.5	5.1	31.3	2.1	0
Matrix 6	0	6.9	4.0	15.4	51.0	312.9	20.7	0
Matrix 7	600	1.4	0	0	0	0	0	2018
Matrix 8	60	6.9	0	0	0	0	0	0

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* The ppm concentrations indicated are based on weighed amounts of salts dissolved in one liter of water. The boron is indicatd as mg/l of boron. The other salts are indicated as mg/l of Li OH, La Cl_3 and so forth.

TEST RESULTS

IRRADIATION TESTING OF SELECTED COMPONENTS FROM THE DIGICHEM ANALYZER

Prior to reporting results it should be noted that the maximum radiation level expected in the DigiChem analyzer would be 10^6 R/hr to the teflon plunger of the sample addition module. This considers both gamma and beta radiation levels. Radiation levels in the other areas of the analyzer would be in the range of 10^4 - 10^5 R/hr. Radiation exposure for other components would be less than 10^5 rads. Estimated radiation exposures are based on the following assumptions:

- The first boron analysis will be performed in triplicate at one hour after the accident occurs. Approximately 25 minutes will be required to perform the triplicate analyses.
- The primary coolant will contain a maximum activity concentration of 4 curies per ml during the first boron analysis performed.
- Total volume of primary coolant contained within the tubing. The one ml sample addition module and rotary reaction cell will be on the order of 3 ml. This volume is assumed to exist as a point source within an imaginary sphere of one foot diameter.
- The radioactive coolant will be flushed from the system with water when the triplicate analysis is complete. Flushing will require the use of manual commands to the DigiChem analyzer.
- There will be two additional triplicate analyses performed within the next 24 hours. Boron analyses performed on a once per day basis after this time will not add significantly to total radiation exposure.

Limited radiation damage was observed in the testing performed; however, this was to components which have been replaced with radiation resistant components in the Sentry modified system. Solid state components which were damaged were subsequently tested at irradiation levels of 10^4, 10^5, and 10^6 rads to establish the threshold level at which damage occurs.

ROTARY SPIN ASSEMBLY

After irradiation to 10^7 rads, the rotary spin cell assembly was installed in an operational DigiChem analyzer and the system was activated. The teflon reaction

TABLE 2-2

RADIATION TESTING OF VARIOUS ELASTOMERS

Item	Exposure in Rads	Material	Results
O-Ring	10^6	Buna	Control, 75 Durometer$^{(1)}$; Irradiated, 70-75 Durometer
O-Ring	10^7	Buna	Irradiated, 75-80 Durometer
O-Ring	10^6	Kalrez	Control, 84-85 Durometer$^{(1)}$; Irradiated, 80-85 Durometer
O-Ring	10^7	Kalrez	Irradiated, 83-89 Durometer
O-Ring	10^6	Viton	Control, 78-80 Durometer$^{(1)}$; Irradiated, 75-80 Durometer
O-Ring	10^7	Viton	Irradiated, 75-80 Durometer
Delivery Tips	10^6	Kel-F	No visible effect; material would still serve its intended purpose
Delivery Tips	10^7	Kel-F	Slight darkening noted; material would still serve its intended purpose
Tubing (Lot 1)$^{(3)}$	10^5	Teflon	No irradiation effect
Tubing (Lot 1)	10^6	Teflon	Rupture pressure - 1600 psi$^{(2)}$ for three specimens
Tubing (Lot 1)	10^7	Teflon	Severly embrittled; tubing would break when bent
Tubing (Lot 2)$^{(3)}$	10^5	Teflon	No irradiation effect
Tubing (Lot 2)	10^6	Teflon	Rupture pressure - 1600 psi$^{(2)}$
Tubing (Lot 2)	10^7	Teflon	Longitudinal cracking occurred when the tubing was bent
Tubing	10^7	Tygon	Rupture pressure - 300 psi$^{(4)}$ for three irradiated specimens

---

(1) Evaluation of results was based on change in hardness. There was no visual indication of damage.

(2) Control samples from both lots ruptured at 1600 psi. The failure mode differed in that a bubble developed on the control sample prior to rupture. Pressure failure of the irradiated samples resulted from development of pin-hole cracks.

(3) Two lots of tubing from separate sources were tested.

(4) One control specimen ruptured at 270 psi and the other at 290 psi.

TABLE 2-3

IRRADIATION TESTING OF PHOTO-INTERRUPTER CELL MCA8

Irradiation Level	Milliamp Output	*Comments
0 rads (Control Sample)	30	1 cell tested
10^4 rads	24	1 cell tested
10^5 rads	0.1	2 cells tested
10^6 rads	0	2 cells tested

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*20 ma source, 5V detector excitation

TABLE 2-4

IRRADIATION TESTING OF PHOTO-INTERRUPTER CELL H21A3

Irradiation Level	Milliamps Output*
0 rads (control Sample)	17.5
0 rads (Control Sample)	14.3
10^4 rads	14.0
10^5 rads	9.8
10^5 rads	10.4
10^6 rads	0.5
10^6 rads	0.9

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*60 ma source, 10V detector excitation

cell within the rotary spin cell assembly spun momentarily and stopped. Testing performed indicated that the photon coupled interrupter module had failed. Sentry has replaced this module with a mechanical system which is not sensitive to radiation. The photo interrupter module was replaced and the teflon reaction cell was operational. Also, a solenoid valve would not operate because the solid state relay which activates this valve had failed. Replacement of this relay was required to activate the valve. This relay can be located outside the radiation zone in the computer control system, without making any change other than installing longer connection wires. Output from this relay is 120 VAC.

A visual inspection was then made of the rotary spin assembly with the following results:

- All glass and clear plastics had darkened. This darkening does not detract from the physical properties of the material.
- The two nylon pulleys which provide the driving force to spin the teflon cell had a myriad of cracks, however the pulleys held together when operated. It would be pointless to do any further test work with these nylon pulleys since they are easily replaced with metal pulleys which are not affected by radiation.
- No visual indication of degradation (cracks, loss of elasticity) could be found in the elastomer belt which connects the nylon pulleys.
- The teflon tubing which feeds reagents and sample to the assembly had become very brittle. Other testing performed with teflon tubing indicates the threshold damage indication for teflon tubing is between 10^6 and 10^7 rads. Considering radiation damage alone. the safety factor involved with the use of teflon tubing in this application is several orders of magnitude.
- The teflon reaction cell suffered no apparent visual damage. No cracking occurred when the cup-shaped cell was spread apart and squeezed together with maximum hand pressure.

SAMPLE ADDITION MODULE

The teflon plunger of the sample addition module may see total radiation exposures in the range of 10^6 rads. This component is discussed separately because it is the high exposure item in the overall assembly. Testing performed, as discussed below, indicates that this plunger will be functionally adequate at 10^7 rads exposure. However, the system failed at this exposure level for another reason as identified below.

After irradiation to 10^7 rads exposure, the system was installed in an operational DigiChem analyzer and the system was activated. The module did not operate.

Testing performed indicated that the photon coupled solid state limit switch had failed. (Sentry has replaced this solid state switch with a mechanical limit switch which is not sensitive to radiation.) After the solid state limit switch was replaced, the sample addition module was operated continuously for about 1.5 hours without problem. Around 100 samples could have been processed during this period. The operational test was terminated at this time.

A visual inspection was made of this module with the following results:

- The glass and clear plastics had darkened.
- There was no visual indication of degradation of the teflon plunger or leakage past this plunger as it was operated.
- The teflon tubing was severely embrittled. However, actual irradiation level that will occur under post-accident conditions is on the order of 10^5 rads or less. The tubing is still serviceable at 10^6 rads exposure.

O-RINGS AND OTHER ELASTOMERS

The elastomers were tested at several different radiation levels with results as indicated in Table 2-2.

The result of the testing clearly indicates that all elastomers in the DigiChem analyzer will withstand 10^7 rads exposure except for the teflon tubing. Exposure level for the teflon tubing should be limited to 10^6 rads. This is beyond the exposure levels anticipated under accident conditions. Heavier components, such as the teflon reaction cell and the teflon plunger in the reagent addition module, remained operational at 10^7 rads exposure. However, it would be desirable to limit all teflon components in the system to 10^6 rads of cumulative exposure.

Data from the pressure tests performed on the irradiated and control samples of teflon tubing are somewhat unusual in that all specimens failed at exactly 1600 psi. All specimens were pressure tested with compressed nitrogen in the same manner, slowly increasing the pressure while monitoring a pressure gauge till failure occurred. About one minute was required to increase pressure to the 1600 psi failure level.

Tygon tubing was tested even though none is used in the DigiChem analyzer to develop alternate materials in the event that the teflon tubing failed at some low irradiated exposure level. This material is very resistant to irradiation based on no indication of change or darkening of this material even at 10^7 rads exposure.

Results of the test work with teflon tubing reported here are consistent with results of testing performed by General Electric on their nuclear plane project. In the General Electric work, teflon hose that was maintained under static pressure with a liquid at 1200 psig while under gamma irradiation, started to leak at slightly above 10^6 rads exposure. Five irradiation tests were performed in the temperature range of 100 to 350°F. Temperature had no effect on test results. The hose was pressurized with a liquid identified as MIL-L-7808C.

Observations made indicate that failure of the elastomers tested ultimately occurs because of embrittlement. This failure mode does not present a problem with the DigiChem analyzer since there are no components in the system that are flexed on a constant basis. There may be some very minor flexing of the teflon tubing but this would occur very infrequently.

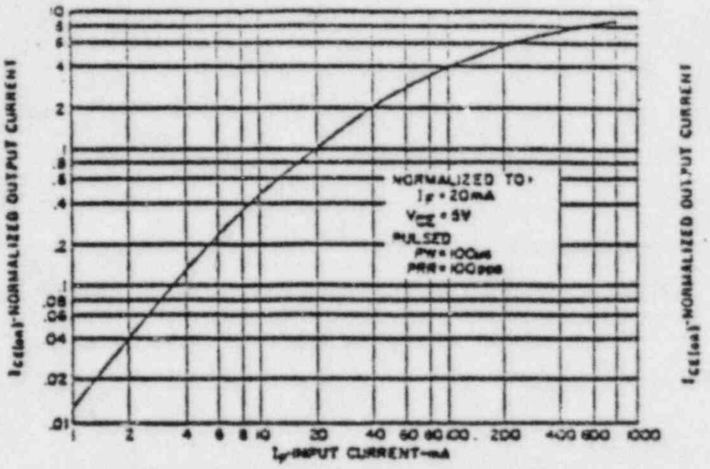
PHOTO-INTERRUPTER CELLS

Evaluation of results for these solid state components is based on typical characteristic curves developed by the manufacturers. Typical curves for the unirradiated cells are shown in Figures 2-2 and 2-3. A comparison was made of output current verses input current for the control samples and for separate samples tested after irradiation. As indicated in Tables 2-3 and 2-4, testing was performed at 10^4, 10^5 and 10^6 rads. Data reported in these tables indicate that threshold damage occurs between 10^4 and 10^5 rads for module H21A3 and about 10^4 rads for module MCA8. It cannot be concluded that the MCA8 module will withstand 10^4 rads on a consistent basis since only one module was tested at this exposure level. Slight damage resulted from the irradiation, however, the module was still operational.

IRRADIATION TESTING OF THE pH PROBES

A separate test was performed to determine the effect of irradiation on pH probes because satisfactory performance on their part while under irradiation is an absolute must to operation of the DigiChem analyzer. This topic is of additional interest because of NRC regulations concerning pH determination requirements for all nuclear systems under post-accident conditions. There is limited data available indicating that pH probes should perform satisfactorily under high level irradiation. However, additional testing was considered necessary to provide direct experience.

TYPICAL CHARACTERISTICS OF MODULE H21A3



OUTPUT CURRENT VS. INPUT CURRENT

FIGURE 2-2

TYPICAL CHARACTERISTICS OF MODULE MCA8

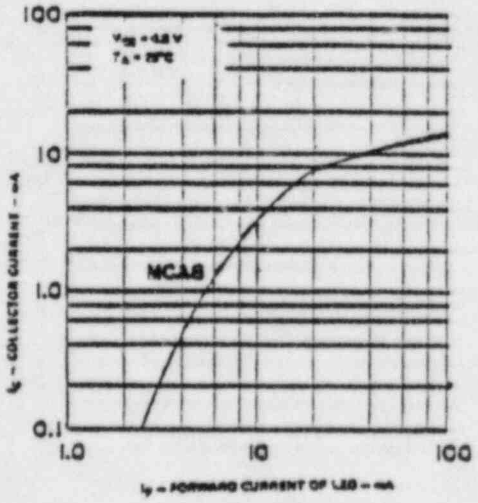


FIGURE 2-3

The results of irradiation testing performed on an internal reference pH probe are presented in Table 2-5. There is no effect on pH indication at a exposure level of 3×10^5 R/hr, however the pH showed a decrease of around 0.1 pH units for the pH 4 and 7 range at a radiation level of 9.77×10^5 R/hr. This differs from external reference probes response which showed a slight increase during irradiation as is later discussed. The high level radiation had no significant effect on the internal reference probes for the pH 10 buffer solution.

Total exposure on the internal reference probe was about 2×10^6 rads at the time it was broken while being moved with the hot cell manipulators. There was no observed change with time in the behavior of the pH electrodes during the two hour period the probe was under test.

The results of irradiation testing performed on an external reference pH probe are presented in Table 2-6. An increase in pH of 0.14 units was observed for the pH range of 4 through 10 at a radiation level of 3×10^5 R/hrs. A further increase of 0.21 pH units was observed when the radiation level was increased to 9.77×10^5 R/hr. The radiation effect is reversible based on data taken when the radiation level was reduced and later eliminated. Note in the subject table that the pH of the neutral buffer increased from 7.06 to 7.20 at a radiation level of 3×10^5 R/hr. This pH increased to 7.28 at a radiation level of 9.77×10^5 R/hr and then dropped to 7.19 when the radiation level was reduced to 3×10^5 R/hr. The final pH reading at the end of the test was 7.10 for both the control and the irradiated sample. The pH of the control sample was taken with the irradiated probe and with a probe that had not been irradiated.

Some radiation degradation of the pH 10 solution was observed after exposure to an integrated dose of 5×10^6 rads. Note that the measured pH of this solution dropped from 10.06 to 9.60, however, the control sample outside the hot cell showed no change in pH level when measured with the irradiated probe. If the reduction in pH of the basic solution had resulted from radiation damage to the probe, the pH of the control sample should also have indicated a lower pH.

The results of irradiation testing performed on an external reference probe with a previous history of 5×10^6 rads exposure are presented in Table 2-7. Note that the effect of irradiation on pH is slightly enhanced over that previously experienced. The increase for exposure at a radiation level of 3×10^5 R/hr and 9.77×10^5 R/hr is 0.15 and 0.3 pH units respectively versus an increase of 0.14 and 0.21 pH units during the initial testing reported in Table 2-6.

TABLE 2-5

EFFECT OF RADIATION(3) ON AN INTERNAL REFERENCE pH PROBE (L & N CAT #117495)

Type Buffer Solution	Initial pH No Radiation	pH at 3×10^5 R/Hr	pH at 9.77×10^5 R/hr
KH_2PO_4	4.60	4.60(1)	4.50(2)
KH_2PO_4 + NaOH	7.05	7.06(91)	6.93
K_2CO_3, K_3BO_3 + KOH	10.10	10.13(1)	10.12

---

(1) No change in pH from the instantaneous reading was noted over a 5-10 minute exposure period.

(2) After taking the initial readings, the probe was left immersed in this solution. Readout of the pH meter varied between 4.48 and 4.51 during a 90 minute exposure period. The probe was broken at this time when it was moved.

(3) Total exposure = 2×10^6 rads.

TABLE 2-6

EFFECT OF RADIATION ON EXTERNAL REFERENCE PROBES
(FISHER CAT # 13-639-8 and 13-639-63)

Types Buffer Solution	Initial pH No Radiation	pH At 3×10^5 R/Hr	Rads Cum. Ex	pH At 9.77×10^5 R/Hr	Rads Cum. Ex	pH At 3×10^5 R/Hr	Rads Cum. Ex	pH At 3×10^5 R/Hr	Rads Cum. Ex.	Final pH(1) No Radiation
KH_2PO_4	4.39 -	4.53	1.5×10^5	Spilled buffer solution	-	-	-	-	-	buffer
KH_2PO_4 + NaOH	7.06	7.20	1.5×10^5	7.28	5×10^5	7.19	10^6	7.19	5×10^6	7.10
K_2CO_3, K_3BO_3 & KOH	10.06	10.19	1.5×10^5	10.27	5×10^5	Not(3) determined	10^6	Not(3) determined	5×10^6	9.60(2)

---

(1) A pH determination was made after all sources were removed from the hot cell.

(2) A control sample that was exposed to the same environmental conditions without radiation exposure had a pH of 10.05.

(3) Readings were not taken because of the extreme difficulty in moving the pH probe with the manipulators.

TABLE 2-7

EFFECT OF RADIATION ON EXTERNAL REFERENCE pH PROBES WITH 5×10^6 RADS PREVIOUS EXPOSURE (FISHER CAT #13-639-8 and 13-639-63)

Type Buffer Solution	Initial pH(1) No Radiation	pH at 3×10^5 R/Hr	pH at 9.77×10^5 R/Hr
$KH_2 PO_4$	4.45	4.60	4.75
$KH_2 PO_4$ + NaOH	7.08	7.26	7.37
K_2CO_3, K_3BO_3 + KOH	10.08	10.24	10.37

---

(1) The pH measurements were taken on probes that were previously irradiated as indicated in Table 2-6. No change was noted after about 2 hours exposure in the test indicated above.

The results of long term irradiation testing performed on external reference probes are presented in Table 2-8. Note that there is an increase of 0.1 and 0.15 pH units at a radiation level of 10^3R/hr. Overall results differ somewhat from previous experiments in that there is little effect at the high radiation level exposure (9.1 x 10^5 R/hr). This may be because the high radiation exposure was preceded by 60 hours exposure at 10^3 R/hr. Other experiments did not have this low level exposure preceding the high level test.

IRRADIATION TESTING OF THE SENTRY MODIFIED DIGICHEM ANALYZER

Checkout of the modified equipment was performed outside the hot cell for nominal boron concentrations of 60, 600, 1200 and 3000 mg/l. The boron solutions used were obtained by known dilution of a 6000 mg/l stock solution. The system was set up as it would be under accident conditions with 25 feet of separation between the control module and the components that will be exposed to irradiation. Multiple analyses were were performed at each boron concentration. The end point of the titation was determined by automatic derivation of the change in slope of the pH line which occurs when titration of the boron-mannitol titration is complete. Maximum deviation noted from actual boron concentration was 1.1 percent with an average deviation on the order of 1 percent. Accuracy requirements for boron determination during normal power operation, as specified by many utilities, are on the order of plus or minus 0.5 percent.

When checkout of the equipment was completed, the rotary reaction cell assembly, the 3000 ppm boron standard, and the sample addition module were installed in the hot cell. The 1200 ppm boron standard remained outside the hot cell. The eight ^{60}Co frames (53,000 curies, total) were arranged around the rotary reaction cell assembly and the sample addition module to achieve a radiation level of 1.75 x 10^4 R/hr, as measured near the top center of the rotary reaction cell assembly. This value is comparable to the general radiation level that may be present during a post-accident condition, assuming a 4 Ci/cc activity in the coolant. Boron analyses results with the Sentry modified DigiChem analyzer in a 1.75 x 10^4 R/hr radiation field are presented in Table 2-9. This testing was performed in the hot cell where temperature was on the order of 95°F. Testing performed outside the hot cell to checkout the equipment was performed at a temperature of 72°F. This change in temperature could have had some effect on results because of

TABLE 2-8

EFFECT OF LONG TERM RADIATION EXPOSURE ON pH PROBES

Two Fisher external reference pH probes were irradiated for 60 hours at 10^3 R/Hr while one probe was in a pH 3.98 and the other probe in a pH 7.00 buffer solution. One probe was new and the other probe had 5×10^6 rads previous exposure. The probe with the previous exposure was not identified in the data that was taken. Results from this test are as follows:

pH With No Radiation	pH at 10^3 R/Hr	pH After 60 Hours Exposure at 10^3 R/hrs
3.98	4.09	4.09
7.00	7.15	7.15

The probes were then restandarized with new buffer solutions and the radiation level was increased to 9.1×10^5 R/Hr. One probe was left in a pH 3.98 and the other probe in a pH 7.00 solution. Results from this test are as follows:

Radiation Level = 9.1×10^5 R/Hr

pH With No Radiation	pH At 5 Min	pH At 1 Hr	pH At 2.33 Hrs	pH At 17.33 Hrs	pH At 20 Hrs	Total Exposures*
3.98	4.01	3.98	3.99	4.00	3.98	1.8×10^7 rads
7.00	7.06	7.04	7.05	7.05	7.06	1.8×10^7 rads

---

* One probe which was not identified prior to performing the test had a previous exposure history of 5×10^6 rads.

evolution of gas bubbles from degasification occurring as the liquids were heated. The boron analyses results had a higher error band and more scatter than was observed in testing performed outside the hot cell or in testing performed at Ionics with a production in model analyzer. However, the results observed were totally acceptable for post-accident use.

Testing was then performed at a radiation level of 8.64×10^4 R/hr (factor of five higher). The higher radiation level was achieved by moving the ^{60}Co frames closer to the test equipment. Results of this test work are presented in Table 2-10. Note that there is little or no change in variability from results shown in the last part of Table 2-9.

The final test phase was performed at a radiation level of 1.75×10^5 R/hr. This was the maximum radiation level achievable at the top center of the rotary reaction cell assembly with the 53,000 curie source. This work was performed over the a weekend. The test was started late Friday afternoon. Reasonable results were achieved for the first few analyses, at which time, the test personnel departed for the weekend. The equipment started behaving erratically soon after the personnel departed and continued this behavior for most of the weekend. Results achieved at the beginning of this weekend run are presented in Table 2-11. Note that the results of the 1200 ppm and 3000 ppm boron standards are unacceptable for post-accident use. However, equipment problems were identified that are responsible for this condition and changes have been made to the equipment design to prevent repeat of this occurrence. This is discussed later in more detail. In any event, it should be noted that the radiation levels anticipated under post-accident conditions will not approach the radiation level used in the final testing of the equipment.

As shown in Table 2-12, results improved near the end of the weekend run. Note, in particular, that all values in the 3000 ppm column, except two, are within plus or minus 5 percent of actual. The two exceptions both indicate a boron concentration of 953 ppm (68.2 percent low). Improving results with increased time under exposure is not consistent with the behavior pattern expected from radiation damage. In particular, radiation damage would not be expected to result in a pattern where both exceptions to general results indicate a boron concentration of 953 ppm.

The test was terminated when a nylon pulley broke on the rotary reaction cell assembly. This nylon pulley is internally stressed with a press fit brass bushing.

TABLE 2-9

BORON ANALYSIS RESULTS WITH THE SENTRY MODIFIED DIGICHEM ANALYZER IN A 1.75 x 10^4 R/HR RADIATION FIELD

Nominal 1200 ppm Boron Solution(1)			Nominal 3000 ppm Boron Solution(1)		
Steps(2) of 0.1105 N NaOH	Indicated ppm Boron	Percent Deviation From Nominal	Steps(2) of 0.1105 N NaOH	Indicated ppm Boron	Percent Deviation From Nominal
524	1258	4.8	1243	2983	-0.57
537	1291	7.6	1263	3031	1.0
546	1310	9.2	1233	2959	-1.4
535	1284	7.0	1198	2875	-4.2
506	1214	1.2	1201	2882	-0.39
503	1207	0.6	1272	3053	1.8
498	1195	-0.4	1250	3000	0
505	1212	1.0	1276	3062	2.1
528	1267	5.6	1236	2966	-1.1
529	1270	5.8	1254	3009	0.3
536	1286	7.2	1187	2849	-5.0
539	1294	7.8	1199	2878	-4.1
538	1291	7.6	1187	2849	-5.0
529	1294	7.8	1199	2878	-4.1
538	1291	7.6	1246	2990	-0.3
529	1270	5.8	1234	2962	-1.3
531	1274	6.2	1271	3050	1.7
529	1270	5.8	-	-	-
538	1291	7.6	-	-	-
$\bar{x}$ 527	1267	5.6	1232	2957	±2.1
σ ±13.9	±34.2	±2.8	±31.1	±74.6	±1.7
2σ ±27.8	±68.4	±5.6	±62.2	±149.2	±3.4

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(1) The historical samples could not be found at the Georgia Tech. test facility, so boron concentration cannot be verified. The indicated concentrations were obtained by known dilution of a 6000 mg/l boron stock solution.

(2) One step = 2.17 x 10^{-6} liters.
The analyzer was programmed to alternately analyze the 1200 ppm and 3000 ppm boron standards.

TABLE 2-10

BORON ANALYSIS RESULTS WITH SENTRY MODIFIED DIGICHEM ANALYZER IN A 8.64 x 10^4 R/HR RADIATION FIELD

Nominal 1200 ppm Boron Solution			Nominal 3000 ppm Boron Solution		
Steps(1) of 0.1105 N NaOH	Indicated ppm Boron	Percent Deviation From Nominal	Steps(1) of 0.1105 N NaOH	Indicated ppm Boron	Percent Deviation From Nominal
538	1291	7.6	1250	3000	0
540	1296	8.0	1257	3017	0.6
536	1286	7.2	1256	3014	0.5
544	1306	8.8	1288	3091	3.0
544	1306	8.8	1260	3024	0.8
545	1308	9.0	1258	3019	0.6
-	-	-	1166	2798	-6.7
$\bar{X}$541	1299	8.2	1248	2995	1.7
σ±3.7	±9.2	±0.7	±38.1	±91.6	±2.4
2σ±7.4	±18.4	±1.4	±76.2	±183.1	±4.8

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(1) One step = 2.17 x 10^{-6} liters
The analyzer was programmed to alternately analyze the 1200 ppm and 3000 ppm boron standards.

TABLE 2-11

BORON ANALYSIS RESULTS WITH THE SENTRY MODIFIED DIGICHEM ANALYZER IN A 1.75 x 10^5 R/HR RADIATION FIELD BEGINNING OF A WEEK END RUN

Nominal 1200 ppm Boron Solution			Nominal 3000 ppm Boron Solution		
Steps (1) of 0.1105 N NaOH	Indicated ppm Boron	Percent Deviation From Nominal	Steps (1) of 0.1105 N NaOH	Indicated ppm Boron	Percent Deviation From Nominal
538	1291	7.6	1265	3036	1.2
538	1291	7.6	1260	3024	0.8
364	874	-27.2	633	1519	-49.4
490	1176	-2.0	747	1793	-40.2
457	1097	-8.6	838	2011	-33.0
458	1099	-8.4	1000	2400	-20.0
392	941	-21.6	1213	2911	-3.0
367	881	-26.6	824	1978	-34.1
404	970	-19.2	1452	3485	16.2
440	1056	-12.0	1265	3036	1.2
468	1123	-6.4	1257	3017	0.6
538	1291	7.6	783	1879	-37.4
540	1296	8.0	1257	3017	0.6
528	1267	5.6	902	2165	-27.8
538	1291	7.6	1268	3043	1.4
528	1267	5.6	1246	2990	0.3
482	1157	-3.6	383	919	-69.4
521	1250	4.2	622	1493	-50.2
574	1378	14.8	619	1486	-50.5
561	1346	12.2	331	794	-73.5
542	1301	8.4	759	1822	-39.3
537	1289	7.4	684	1642	-45.3
541	1298	8.2	1209	2902	-3.3
527	1265	5.4	922	2213	-26.2
608	1459	21.6	937	2249	-25.0
481	1154	-3.8	1274	3058	1.9
$\bar{X}$498	1196	10.4	960	2303	25.1
σ±63.8	±153.0	±7.1	±309	±743	±22.8
2σ±127.6	±306.0	±14.2	±619	±1486	±45.6

---

(1) One step = 2.17 x 10^{-6} liters
The analyzer was programmed to alternately analyze the 1200 ppm and 3000 ppm boron standards.

TABLE 2-12

BORON ANALYSIS RESULTS WITH THE SENTRY MODIFIED DIGICHEM ANALYZER IN A 1.75 x 10^5 R/HR RADIATION FIELD NEAR END OF A WEEK END RUN

Nominal 1200 ppm Boron Solution			Nominal 3000 ppm Boron Solution		
Steps(1) of 0.1105 N NaOH	Indicated ppm Boron	Percent Deviation From Actual	Steps(1) of 0.1105 N NaOH	Indicated ppm Boron	Percent Deviation From Actual
531	1274	6.2	1289	3094	3.1
488	1171	-2.4	1292	3101	3.4
534	1287	7.2	1283	3079	2.6
564	1354	12.8	397	953(2)	-68.2
530	1272	6.0	1269	3046	1.5
471	1130	-5.8	1287	3089	3.0
542	1301	8.4	1277	3065	2.2
473	1135	-5.4	1291	3098	3.3
570	1368	14.0	1269	3046	1.5
534	1282	6.8	1295	3108	3.6
482	1157	-3.6	1284	3082	2.7
537	1289	7.4	1287	3089	3.0
531	1274	6.2	1298	3115	3.8
480	1152	-4.0	1292	3101	3.4
534	1282	6.8	1283	3079	2.0
564	1354	12.8	397	953(2)	-68.2
530	1272	14.3	1269	3046	1.5
471	1130	-5.8	1287	3089	3.0
542	1301	8.4	1277	3065	2.2
473	1135	-5.4	1291	3098	3.3
570	1368	14.0	1269	3046	1.5
534	1282	6.8	1295	3108	3.6
482	1157	-3.6	1284	3082	2.7
537	1289	7.4	1287	3089	3.0
			1293	3103	3.4
$\bar{X}$ 521	1251	7.6	1285	3083	2.8
$\sigma \pm 34$	± 82	± 3.5	± 9.0	± 21.5	± 0.75
$2\sigma \pm 68$	± 163	± 7.0	± 18.0	± 43	± 1.5

---

(1) One step = 2.17 x 10^{-6} liters
The analyzer was programmed to alternately analyze the 1200 ppm and 3000 ppm boron standards.

(2) Not within 3 STD Deviations of the mean, thus are not included in the calculations.

There was 2.7 x 10^7 rads exposure on the test equipment at this time. Testing subsequently performed with the Ionics equipment indicates that extensive cracking will develop on this nylon pulley with 10^7 rads exposure. While the pulley on the Ionics supplied equipment did not fail after operation at the 10^7 rads exposure level, its appearence was such that it could have easily failed.

Subsequent examination of the equipment performed by Sentry indicated that the nylon and Kel-F parts that were not replaced had become severely embrittled. This was expected, based on the total exposure levels involved. All metal and electronic components were fully operational.

TEST RESULTS FROM THE PRODUCTION MODEL DIGICHEM ANALYZER

The DigiChem analyses results and laboratory analyses results for standard boron solutions are presented in Table 2-13. There is reasonable agreement between these results, however, there is more variation than was seen in previous testing performed with the DigiChem analyzer (Table 2-15). Results of this other work indicate that it should be possible to obtain a precision of ± one percent with the DigiChem analyzer. Note in Table 2-13 that part of the titrations were perfomed with 0.5 N NaOH and part with 0.1 N NaOH solutions. A comparison of the data indicate that essentially equivalent results were achieved with either normality.

The analyses results for matrix solutions containing simulated fission product species and caustic solutions are presented in Table 2-14. These data indicate that the concentrations of fission product species expected following an accident will not interfere with boron analyses results. The data also indicate that boron analyses results will not be affected by the caustic added to the primary coolant when the containment sprays are activated during a LOCA event. The limited testing performed concerning the effect of lithium alone on boron analyses results indicates this addition had no apparent effect on accuracy or precision.

TABLE 2-13

STANDARD BORON AND BLANK ANALYSES RESULT WITH THE PRODUCTION MODEL DIGICHEM ANALYZER

Sample	Nominal Boron mg/1	Number of Analyses	Titrant Normality	Mean Boron(2) mg/1	Laboratory Analyses Results(3)	% Error $\frac{\text{Mean-Lab}}{\text{Lab}}$
Standard	6000	4	0.5	6124	6108	1.90
Standard	6000	6	0.5	5962	6108	-2.39
Standard	6000	5	0.1	5914	6108	-3.18
Standard	2000	6	0.5	2082	2017	3.22
Standard	2000	4	0.1	2102	2017	4.21
Standard	1000	6	0.5	1002	1025	2.24
Standard	1000	3	0.5	1048	1025	2.24
Standard	1000	1	0.1	1065	1025	3.90
Standard	60	6	0.5	57.25	61	6.15
Standard	60	6	0.1	59.05	-1.58	
Blank (1)	0	3	0.5	0.40	-	-
Blank (1)	0	5	0.5	-1.12	-	-
Blank (1)	0	7	0.1	-3.57	-	-

---

(1) Deionized water
(2) Analyses results with the Digichem Analyzer
(3) As determined by caustic titration of the boron-mannitol complex

TABLE 2-14

MATRIX SOLUTION ANALYSES RESULTS WITH THE PRODUCTION MODEL DIGICHEM ANALYZER

Sample	Nominal Boron mg/l	Number of Analyses	Titrant Normality	Mean Boron[1] mg/l	Laboratory Analyses Results[2]	% Error Mean-Lab / Lab
Matrix-1	60	3	0.5	59.92	65	-7.82
Matrix-1	60	3	0.1	58.79	65	-9.55
Matrix-2	2000	3	0.5	2082	2022	2.97
Matrix-2	2000	3	0.1	2079	2022	2.82
Matrix-3	6000	3	0.5	5897	6101	-3.34
Matrix-3	6000	3	0.1	5840	6101	-4.28
Matrix-4	6000	3	0.5	5995	6136	-2.30
Matrix-4	6000	3	0.1	5927	6136	-3.41
Matrix-8	600	3	0.5	608.4	624	-
Matrix-7	60	3	0.5	56.73	66	-14.0
Matrix-7	60	3	0.1	59.76	66	-9.59
Matrix-5	0	3	0.5	-3.61	-	-
Matrix-5	0	5	0.1	-0.61	-	-
Matrix-6	0	7	0.5	-2.92	-	-
Matrix-6	0	3	0.1	-0.46	-	-
Boron + 0.4N NaoH	600	3	0.5	663.8	666	-0.33
Boron + 0.4N NaoH	600	3	0.1	653.8	666	-1.83
Boron + 0.4N NaoH	6000	3	0.5	5916	6056	-2.31
Boron + 0.4N NaoH	600	3	0.5	626.8	666	-5.88
Boron + 0.4N	600	3	0.1	624.4	666	-6.25

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(1) Analyses results with the Digichem Analyzer

(2) As determined by caustic titration of the boron-mannitol complex

DISCUSSION OF RESULTS AND CONCLUSIONS

DISCUSSION OF RESULTS

Test results from the irradiation experiments clearly indicate that the critical components in the production model the DigiChem analyzer with respect to radiation damage are as follows:

- Photon coupled interrupter module (H21A3). This is a light activated speed control system for the rotary reaction cell.
- Solid state relay for a solenoid actuated valve on the rotary reaction cell.
- Photon coupled solid state limit switch (MCA8) in the sample addition module.
- Two nylon pulleys used to drive the rotary reaction cell.

Threshold damage level for photon coupled interrupter module H21A3 is between 10^4 and 10^5 rads. For module MCA8 it is about 10^4 rads. Total radiation exposure for H21A3 and MCA8 could be at the 10^4 rad level in a accident condition, dependant on the overall design and operating philosophy of the sampling system. No conclusions can be drawn that MCA8 will withstand 10^4 rads exposure since only one module was tested at this level. The module suffered minor damage with 10^4 rads exposure, however, it remained operational. Threshold level for the solid relay (total failure at 10^7 rads) was not determined since it is easier to locate this relay outside the radiation zone than it would be to determine the threshold damage level. The nylon pulleys would almost certainly remain operational at 10^6 rads exposure, however, should be replaced with metal pulleys since this change can be accomplished with little difficulty.

The solid-state components listed above that can be damaged by radiation have been replaced with mechanical switches in the modifications made to the DigiChem analyzer by Sentry. The nylon pulleys were replaced by Sentry with stainless steel pulleys as a consequence of the irradiation experiments performed at Georgia Tech.

Teflon tubing can withstand 10^6 rads exposure while the heavier teflon components remained operational at 10^7 rads exposure. It is not expected that radiation damage would preclude the use of teflon components in a DigiChem analyzer during a post-accident condition. However, the change made by Sentry to eliminate teflon in favor of more radiation resistant materials will add a higher degree of conservatism to the system, For example, the need for flushing the sample lines of highly radioactive coolant within a specified time period becomes less critical with the Sentry system since the teflon has been replaced with more radiation resistant material.

Concerning pH probes the data indicate that high radiation levels (10^6 R/hr) will decrease the indicated pH by about 0.1 pH units for an internal reference probe. Indicated pH will increase by about 0.1 or 0.2 pH units for external reference probes in a high radiation field. An initial effect is noted at 10^3 R/hr. The increase in pH is immediate. The effect is fully reversible when the radiation source is removed. The DigiChem system has an external reference pH probe.

The shift in pH resulting from radiation should have a slight effect on accuracy of analyses with the DigiChem analyzer, however, the effect will not be significant as concerns post-accident requirements. During normal operating conditions, the system will be titrating from pH 5.5 to 8.5 to determine boron concentration. Under high radiation conditions the system will still titrate from an indicated pH 5.5 to pH 8.5. However, in reality it may be titrating from say a pH of 5.3 to 8.3 because of the radiation induced shift in pH.

The erratic results noted in the high radiation level testing (Table 2-11) occurred because of an electronic "loophole" created by the high radiation field. This resulted in the leakage of current, causing erratic pH electrode behavior. A design change has been made which includes a driven shield concept that will prevent radiation induced leakage in the cable shield to the pH electrode. This driven shield will be a standard feature in all DigiChem analyzers. It should be emphasized, however, that the system tested without the driven shield operated satisfactorily at radiation levels anticipated under post-accident conditions. Increased reliability can be anticipated with the addition of the driven shield.

Results of testing performed with the production model DigiChem analyzer are not equivalent to results previously achieved with this instrument. Compare for example, the data in Table 2-13 with the data from previous testing presented in Table 2-15. The difference between these results is not understood. One possibility is that there may have been some degassing of the titrant solutions or of the sample itself as system pressure is reduced when the plungers of the sample or titrant burettes are withdrawn to replenish system volumes. Introduction of bubbles adds to the error because these bubbles are measured and computed as liquid volume.

It is apparent from the data presented in Table 2-15 that there is very little scatter to the results. Virtually all the results are low by about the same percentage value. This pattern has appeared again and again, with some results consistently low and others consistently high by some small percentage value. Generally, the analyses results have been computed based on normality of the caustic solution used for titration. From examination of the data, it would appear that some improvment in accuracy can be achieved if results were compared directly to results achieved with a known boron standard. The computer can be programmed to provide for such a comparision.

If the DigiChem analyzer is used for normal operation or post-accident analyses, it should be noted that the primary coolant must be degassed to a low level prior to introduction of the sample to the sample burette. With high concentrations of gas present, as can occur in an accident involving core damage, bubbles will be produced in the sample stream when system pressure is reduced as the plunger in the sample burette is withdrawn. This would result in values which are lower than actual. The error would be proportional to the ratio of gas volume to liquid volume in the sample stream.

Another feature that would be desirable though not mandatory for this system, would be to inject a small volume of water to the rotary reaction assembly prior to injecting the sample itself. The reason for this is to dilute the sample immediately so that there is less tendancy for radioactive iodine to escape from solution during post-accident conditions. It would also be necessary to inject a small volume of water after the sample addition to properly flush the sample tip. The system can be programmed to provide this sample addition sequence.

The overall advantages of using the DigiChem analyzer for the boron determinations during accident conditions are as follows:

- All operations can be performed remotely. The exposure involved in determining boron concentration would approach zero.
- Sample volume requirements are on the order of 1-2 ml per analysis, thus shielding requirements would be minimal.

TABLE 2-15

BORON REPRODUCIBILITY RESULTS
2000 ppm 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
1074	-26	-1.3	1974	-26	-1.3
1977	-23	-1.15	1975	-25	-1.25
1977	-23	-0.15	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	-24	-0.2	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
$\bar{X}$1975	21.9	1.1	1979	21.2	0.6
σ±5.8	±8.9	±0.4	±6.5	±6.5	±0.3
2σ±11.6	±17.8	±0.8	±13.0	±13.0	±0.6

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

- Analyses results can be achieved within 10 minutes after the sample line is purged to obtain a representative sample.

- Though not sealed gas tight, there would be little tendency for release of gaseous activity to the atomsphere. This would be particularly true if the sample addition sequence is changed to add water prior to addition of the sample.

The disadvantages of using the DigiChem analyzers under post-accident conditions are as follows:

- Waste solutions cannot be pumped back to the primary system since chemicals are added to the system in the analysis procedure.

- A small pumping system must be provided to pump the gravity drain waste solutions from the analyzer to a waste disposal facility if the waste disposal system is above the level of the analyzer. Most plants using this equipment have gravity drain collection tanks.

CONCLUSIONS AND RECOMMENDATIONS

- The Sentry modified DigiChem analyzer is acceptable for use to determine boron concentration under post-accident conditions. Concerning its use for normal operations, the accuracy is probably acceptable.

- If the DigiChem analyzer or Sentry modified system is used for boron determination during normal operations, results should be compared to known boron standards rather than computed solely on normality of the titrant solution. The system can be programmed to provide for such comparison.

- The primary coolant must be degassed to a low lever prior to introduction of the sample to the sample burette. This is to prevent introduction of gas bubbles in the sample stream.

- It would be desirable (but not necessary) to program the system to add a small volume of water to the rotary reaction assembly prior to addition of the sample. This will further reduce an existing low potential for release of radioactive gas to the environment.

Section 3

SUMMARY OF RESULTS - WESTINGHOUSE ANALYZER

The Westinghouse Mark V boron analyzer performed well, both at high radiation levels (3.45×10^5 R/hr) and under steady state conditions in the absence of radiation. There was an increase in fissioning count rate resulting from high level irradiation, however, the effect of this increase on accuracy of the boron analyses is not significant. With operation at radiation levels anticipated under NRC post-accident reference conditions, the accuracy achievable is equal to, or better than other methods of boron analyses available for use during post-accident conditions.

The system can be used to monitor boron concentration during normal power operations. Accuracy expected at intermediate or high level boron concentrations should be suitable for normal requirements. Determination of low-level boron concentrations would probably require a 500 or 1000 second count rate period.

No problems of any kind were experienced in operation during a test period of about 15 days total. This is a relatively short period compared with duty in a power plant, however, we believe the analyzer will work for a long time in a power plant.

BACKGROUND INFORMATION

TEST PURPOSE

Testing was performed to determine if the prototype unit of the Westinghouse Mark V boron analyzer would suffer radiation damage or reduction in accuracy when operated at radiation levels anticipated under post-accident conditions. Testing was also performed to establish reliability of the equipment when operated under normal conditions.

SYSTEM DESCRIPTION

General

The Boron Concentration Monitoring System (BCMS) Mark V is an electronuclear system that continuously measures the boron content in the primary coolant of a pressurized water reactor (PWR) power plant and digitally displays the results in parts total boron per million parts of water (ppm). In a shielded tank, a sample of the primary coolant is positioned between a neutron source and a fission chamber. Neutrons originating at the source are thermalized, then pass through the boron solution (where some are absorbed) and impinge upon the enriched uranium in the fission chamber. Fissioning occurs with the release of charged particles, resulting in voltage spikes in the fission detector that are translated into ppm boron. The charged particle population is directly proportional to the fissioning process, and therefore proportional to the neutron population. This provides a measure of the boron concentration in the water since the fissioning rate and resulting charged particle population varies inversely as does the neutron absorption characteristics of the primary coolant. The charged particle count rate is translated into ppm boron by an algorithm programmed into the system's microcomputer which accounts for non-linear response and for temperature correction. Calibration is performed by determining the count rate for three known concentrations of boron solutions and entering this information into the computer unit. The system is self-calibrating at this point. The microcomputer transmits this boron concentration data to local or remote displays.

The BCMS Mark V is comprised of three major assemblies: the sampler tank, which detects the charged particle count rate and coolant temperature; the electronic processor enclosure, which contains the processing control and monitoring electronics for most of the system; and the remote display, which enables a remote indication of boron concentration. The sampler tank is shown in Figure 3-1, and the overall system is shown in Figure 3-2. Test equipment evaluated in this work did not include the use of a remote display unit. This equipment is not required for system operation. Also provided are an interrupt line output and serial data output which permit the processor enclosure to transmit data to the plant computer. General descriptions of the three main BCMS Mark V assemblies are given below.

Sampler Tank Assembly

The sampler tank assembly is a stainless steel cyinder, approximately 15.12 inches (38.4 cm) in diameter, 19 inches (48.3 cm) high, and weighing 100 pounds (45.3 kg), which is secured to the mounting platform by four hold-down clips. The cylinder contains polyethylene which functions as a neutron shield and moderator. The unit has two cavities, one neutron source well and one annulus assembly containing the fission detector. The neutron well is 1 inch in diameter by 7 inches deep in a high density polyethylene epoxy resin. The neutron source is provided by one curie of americium/beryllium (Am-Be). The fission detector has 2 grams of enriched uranium. The Am-Be source is in the center of the tank in a vertical cavity which is inserted on the end of a polyethylene rod. Surrounding the fission detector is a one liter stainless steel annulus assembly. Coolant flow to and from this tank is provided by 0.5 inch tubes with Swagelok fittings for connection to the plant piping.

The sampler tank assembly receives reactor coolant solutions from a sampling location such as the letdown heat exchanger or Boron Thermal Regeneration System (BTRS). Reactor coolant samples are routed to the input port of the sampler tank. A thermocouple inserted through the cover plate extends 8 inches into the polyethylene material. Sample flow through the unit is determined by the pressure drop between the inlet and outlet tube connections.

Two electrical signals are derived from the sampler tank assembly: (1) fission count rate from the fissioning detector and (2) thermocouple potential (in millivolts). Detector pulses are applied to the preamplifier in the processor enclosure via a coaxial cable attached to the detector. The thermocouple signal is applied to a digital thermometer in the processor enclosure via thermocouple wire.

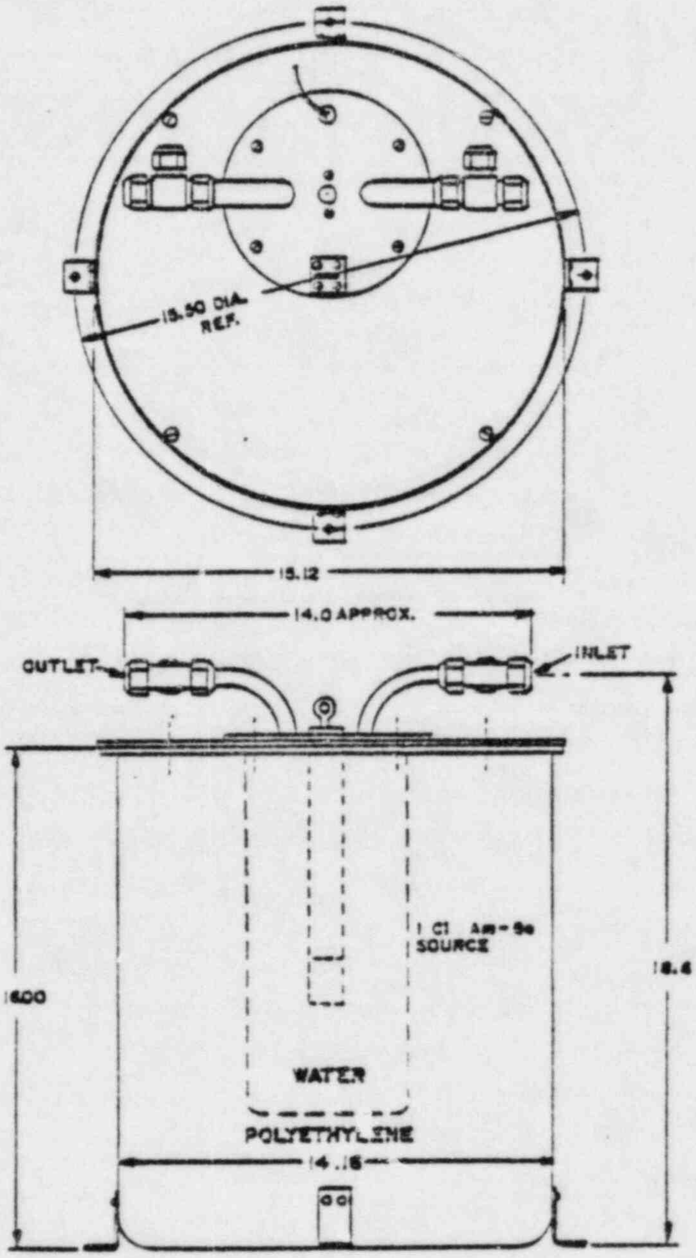


FIGURE 3-1
Ⓦ SAMPLER TANK ASSEMBLY

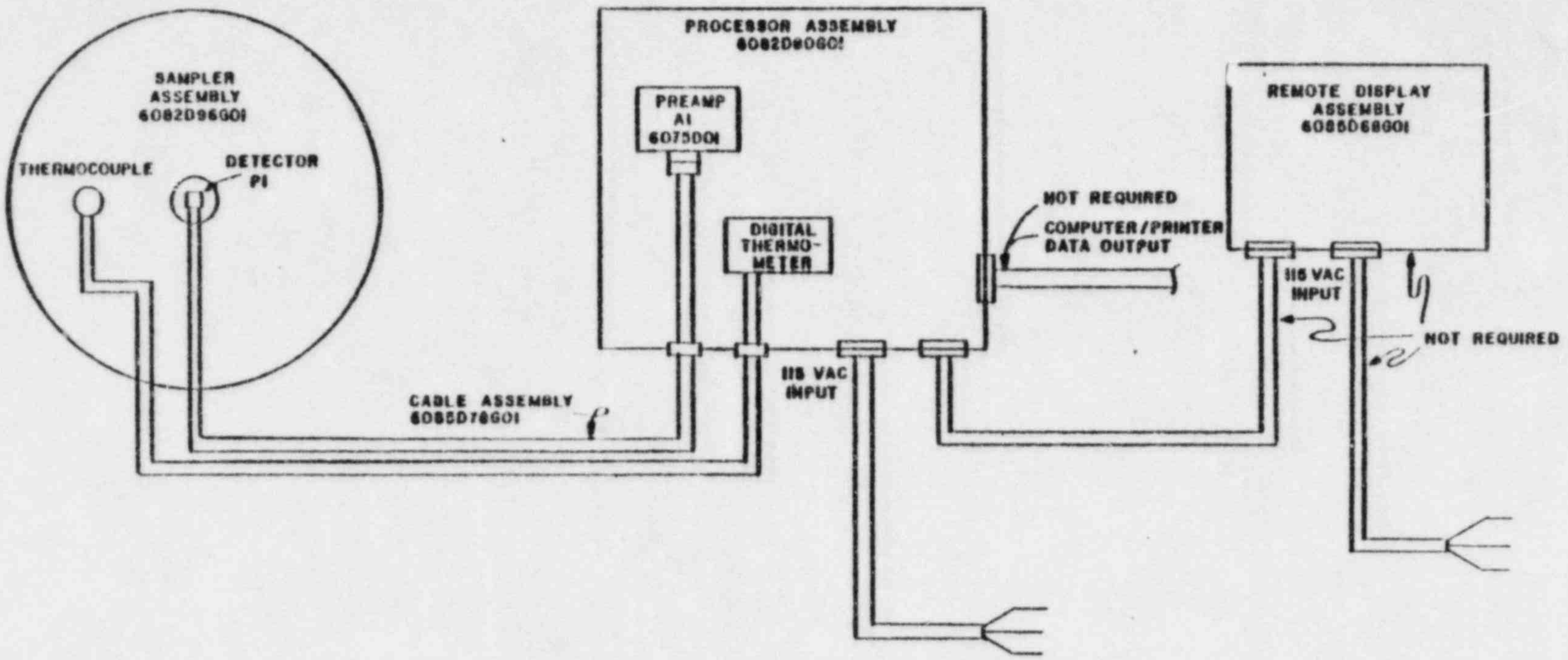


FIGURE 3-2
WESTINGHOUSE MARK V BORON ANALYZER

Processor Enclosure

The processor enclosure is a wall-mounted, louvered, NEMA 12 enclosure containing the components that control operation of the BCMS, Mark V analyzer. Operator controls and indicators are contained on the control panel which is accessed by opening the hinged front door of the cabinet. Also contained in the process enclosure is the preamplifier with bias control to discriminate against detection of noise. For maintenance and troubleshooting purposes, the control panel is hinged to allow access to the microcomputer power supplies, preamplifier, card cage, terminal boards, and test point assemblies.

The electronic processor enclosure may be located hundreds of cable feet away from the sampler tank provided the preamp is removed and located within 20 feet of the tank. It receives the fission count rate and temperature from the sampler tank assembly, processes it, displays the calculated boron concentration (in measure mode) on the local display, and serially transmits the concentration data to the remote display assembly and plant computer. The electronic processor enclosure contains a microcomputer made up of a single-board central processing unit (CPU) board, complementary metal-oxide semiconductor random-access memory (CMOS RAM) board with battery backup, and input/output (I/O) expansion board.

Remote Display Assembly

The remote display assembly displays the boron concentration in ppm at a location (usually in the control room) remote from the processor enclosure. Measuring approximately 7.75 inches wide, 4.5 inches high, 9.62 inches deep, and weighing 10 pounds, the unit can be installed up to 1000 feet from the processor enclosure.

Concentration data calculated by the processor enclosure is transmitted serially over a twisted shielded pair. The remote display assembly contains the circuits that receive, decode, and present the data on a four-digit light-emitting-diode (LED) display.

TEST DESCRIPTION

GENERAL

The irradiation testing was performed at the hot cell test facility at Georgia Tech. Testing to investigate reliability characteristics of the Mark V boron analyzer was performed at this same location. Testing to determine reproducibility of the boron analyzer was also performed at Georgia Tech.

IRRADIATION TESTING

The radiation source was provided by eight, 8 x 13 inch frame assemblies containing a total of 53,000 curies ^{60}Co (6,600 curies per frame). Radiation source from the one liter primary coolant sample tank under accident conditions will be around 40,000 curies for reactor coolant with activity of 4 Ci/cc. Radiation levels were increased or decreased by placing one or more of these frame assemblies around the sampler tank assembly as shown in Figure 3-3. The radiation level for maximum radiation testing was measured by placing a dosimeter at the detector location in a second sampler tank assembly. Geometry was held constant for the second sampler tank and the tested sampler tank assembly in the irradiation testing performed. A second tank was required to determine radiation dosage because the dosimeter was placed in the position that would have been occupied by the detector tube during irradiation testing. Testing was performed at a maximum radiation level of 3.45×10^5 R/hr, determined by dosimetry. The level of 3.45×10^5 R/hr required the use of the eight frame radiation sources that were available. A radiation level with the second sampler was determined for only this one configuration because most of the irradiation experiments were performed at the maximum achievable level. Estimated radiation levels for the Westinghouse boron analyzer for reactor coolant with an activity of 4Ci/cc are around the maximum radiation levels achieved in this test work.

The fission count rate was determined as a function of boron concentration and/or radiation level in the sampler assembly. Count rate was determined in the absence of radiation to determine a base level, followed by testing with exposure to high and intermediate radiation levels. The ^{60}Co frames were added or removed to change

GEOMETRY OF IRRADIATION ASSEMBLY
FOR Ⓦ MARK X SAMPLER TANK ASSEMBLY
53,000 CI TOTAL RADIATION SOURCE

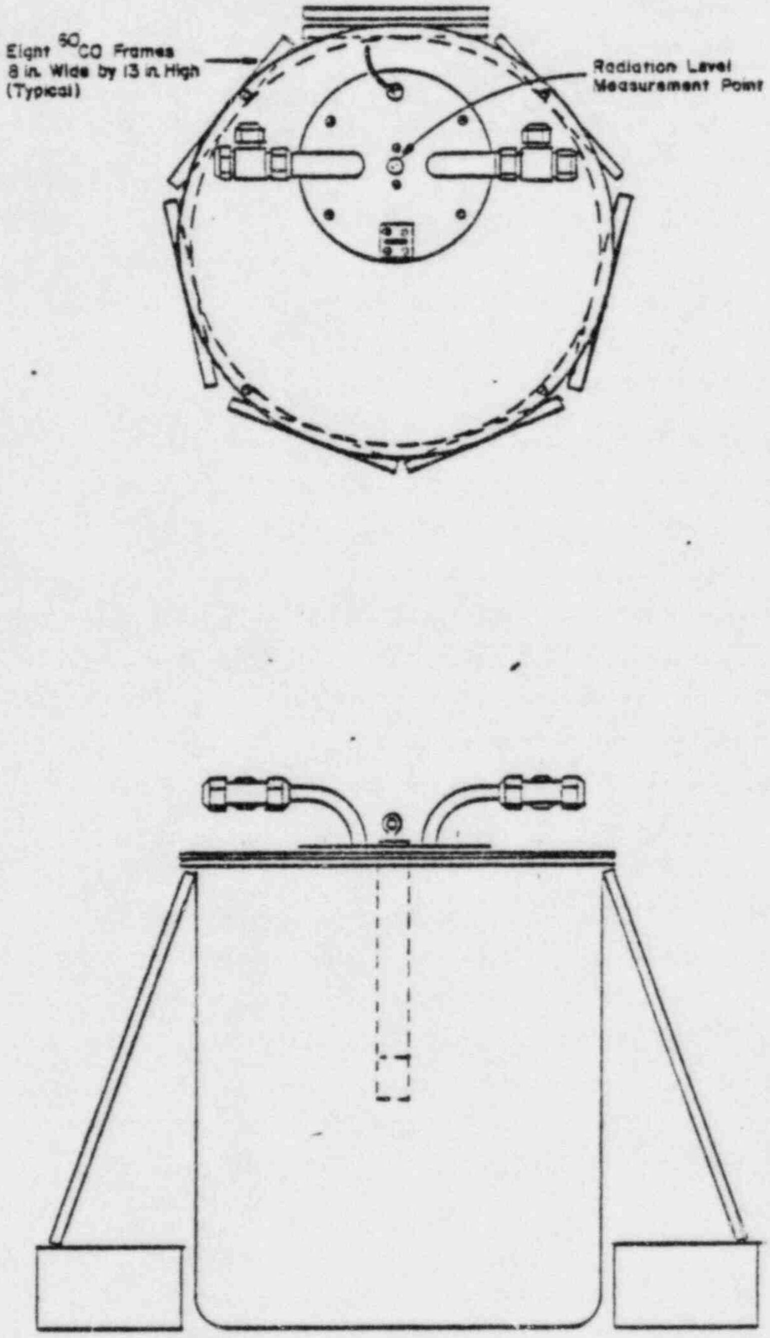


FIGURE 3-3

the radiation levels. Results are based on the fissioning rate rather than ppm readout because the main objective of this test was to determine the effect of high radiation levels on the detector equipment. Evaluation of this equipment can best be performed by monitoring the fission rate during testing under irradiation.

All testing involving radiation exposure was performed in a hot cell under no-flow conditions. The tank sampler tank was rinsed three times with the reference boron solution when concentration was changed.

TEST RESULTS

IRRADIATION TEST RESULTS

Prior to installation of the sampler assembly in the hot cell, the boron analyzer was operated overnight with pure water in the sampler tank. An average fissioning rate frequency of 476.83 counts/second was determined for the 30,000 second overnight run. This compares to an average count rate of 476.16 counts/second for a series of eighteen, 100 second count periods made prior to starting the irradiation tests. This series of 100 second count periods varied from a low of 473.56 to a high of 479.28 counts/second. The data are presented in Table 3-1.

Initial radiation under testing was performed with pure water in the sample tank. The count rate increased by almost 3 percent from an average of 474.96 counts/second to an average of 487.96 counts/second when exposed to a radiation level of 3.45×10^5 R/hr. Moving the connector cable so that is was further removed from the radiation source had no effect on count rate based on the average of 487.44 determined for six, 100 second count periods. The count rate returned to the base level obtained in the preirradiation testing when all radiation sources were removed. Data obtained from the irradiation testing performed with pure water are presented in Table 3-2.

Testing performed with 5140 ppm boron solution in the sampler tank showed the same behavior as was observed with irradiation testing performed with pure water in the tank. In the absence of radiation, the count rate for the 5140 ppm boron solution was 125.98 counts/second for a 100 second count period. This increased by about 3 percent to 129.49 counts/second when exposed to a radiation level of 3.45×10^5 R/hr (eight ^{60}Co frames). Four ^{60}Co frames were removed leaving a total of four ^{60}Co frames around the sampler assembly. This reduced the count rate from 129.49 counts/second to an average of 128.19 counts/second or about 1.5 to 2 percent above the base level obtained in the absence of radiation. The count rate returned to the original base level when all radiation sources were removed. Data obtained with the irradiation testing performed with 5140 ppm boron solution are presented in Table 3-3.

TABLE 3-1

BASE LEVEL FISSIONING COUNT RATE FOR THE WESTINGHOUSE MARK V BORON ANALYZER (PURE WATER RESULTS)

Run Time Sec.	Counts Per Sec.
30,000	476.83
100	474.91
100	473.83
100	475.86
100	475.71
100	473.56
100	476.89
100	474.64
100	479.28
100	478.11
100	475.82
100	476.57
100	475.43
100	474.84
100	477.36
100	479.11
100	478.61
100	475.53
100	474.95

$\bar{x}$ = 476.17

σ = ±1.73

2σ = ±3.46

TABLE 3-2

EFFECT OF IRRADIATION WITH PURE WATER IN THE WESTINGHOUSE MARK V BORON ANALYZER

Zero Radiation			3.45×10^5 R/hr			3.45×10^5 R/hr$^{(1)}$		
Run Time Sec.	Counts Per Sec.	Temp. °C	Run Time Sec.	Counts Per Sec.	Temp. °C	Run Time Sec.	Counts Per Sec.	Temp. °C
600$^{(2)}$	475.69							
			100	490.93	25			
			100	491.67	25	100	487.83	26
100	474.20	23	100	486.93	25	100	488.47	26
100	476.45	23	100	487.93	25	100	485.49	26
100	475.02	23	100	487.07	25	100	490.71	26
100	474.04	23	100	485.22	26	100	488.61	26
100	474.87	23	100	485.98	26	100	483.51	27
$\bar{x}$	475			488			487	
σ	± 0.95			2.45			2.55	
2σ	± 1.90			4.90			5.10	

---

(1) The cable which connects the sampler tank to the electronic processor enclosure was moved further away from the radiation source for this test sequence. This was to determine if count rate is affected by high radiation level exposure of the cable.

(2) Not included in standard deviation.

Testing was also performed with 2570 ppm boron solution in the sample tank. The same behavior was observed as was noted with the pure water and 2570 ppm boron solutions. The count rate increased about 3 percent from 206.73 to 212.29 counts/second. These data are presented in Table 3-4.

Further testing was performed to determine if exposure of the connector cable to very high radiation levels would affect the count rate. The connector cable was clamped between two ^{60}Co frames (1/2 inch gap) to obtain exposure level estimated to be in the range of 10^6 to 10^7 R/hr. Radiation measurements made in connection with other irradiation experiments performed indicate that radiation levels between the two frames are on the order of 10^6 R/hr with 3 to 4 inches gap between the two frames. Since the actual gap was about 1/2 inch, the radiation level would be well over 10^6 R/hr. No effect on count rate was noted from this radiation level based on count rates of 206.58, 209.35, 206.96 and 206.35 counts/second over four, 100 second count periods. The base level count rate for this system (2570 ppm boron) in the absence of radiation was 206.73 counts/second. These data are consistent with the data presented in Table 3-2.

The testing performed indicates that the increase in count rate noted with the high radiation levels is an instantaneous function of radiation levels. That is, the count rate changes as soon as the radiation level increases or decreases. There is no memory effect, nor is there any indication of permanent damage suffered based on about 2×10^7 rads total exposure to the sampler assembly. This is equivalent to over 25 hours operation with an activity level of 4 Ci/cc in the primary coolant.

RELIABILITY TEST RESULTS

After the irradiation testing was complete, the Mark V boron analyzer was operated under steady state conditions for a period of 13 days. This was done in the absence of radiation with 2570 ppm of boron in the sample tank. Initially, data were taken every half hour during the course of an eight hour day. Later, the data were taken on an hourly basis or sometimes on a daily basis. This data is shown in Table 3-5.

The Westinghouse equipment operated very well during the reliability testing. There were no outages or system malfunctions of any kind during this test period. Unfortunately, the data recorded in Table 3-5 represent 1 second count periods rather than the 100 second or 1000 second data intended. However. since the standard deviation is proportional to $\frac{1}{n}$, n being the number of samples, we can infer a standard deviation for 100 second and 1000 second counting intervals of 1.02 and 0.32 respectively.

TABLE 3-3

EFFECT OF IRRADIATION WITH 5140 ppm IN THE WESTINGHOUSE MARK V BORON ANALYZER

Zero Radiation			3.45×10^5 R/hr			2×10^5 R/hr(1)		
Run Time Sec.	Counts Per Sec.	Temp. °C	Run Time Sec.	Counts Per Sec.	Temp. °C	Run Time Sec.	Counts Per Sec.	Temp. °C
600(2)	125.97	32						
			100	130.20	29			
			100	127.79	30			
			100	129.87	30	100	128.85	31
100	125.16	32	100	128.90	30	100	127.68	31
100	124.19	32	100	130.51	30	100	129.86	31
100	126.96	32	100	129.38	30	100	127.27	31
100	127.02	32	100	129.19	30	100	127.92	31-32
100	125.63	32	100	128.99	30	100	127.34	32
100	125.68	32	100	129.83	31	100	128.39	32
100	125.58	32	100	130.25	31	100	128.26	32
$\bar{x}$	126			129			128	
σ	± 0.99			1.62			1.72	
2σ	± 1.98			3.24			3.44	

---

(1) Estimated radiation level of 2×10^5 R/hr

(2) Not included in standard deviation.

TABLE 3-4

EFFECT OF IRRADIATION WITH 2570 PPM BORON IN THE WESTINGHOUSE MARK V BORON ANALYZER

Zero Radiation			3.45×10^5 R/hr		
Run Time Sec.	Counts Per Sec.	Temp. °C	Run Time Sec.	Counts Per Sec.	Temp. °C
600(1)	207.02	32	600(1)	213.20	32
			100	212.83	32
			100	212.72	32
100	206.87	32	100	213.28	32
100	205.97	32	100	211.99	32
100	205.61	32	100	213.25	32
$\bar{x}$	206			213	
σ	± 0.65			0.49	
2σ	± 1.30			0.98	

---

(1) Not included in standard deviation.

TABLE 3-5

STEADY STATE OPERATION FOR 1 SECOND COUNT PERIODS WITH 2570 PPM BORON IN THE WESTINGHOUSE MARK V ANALYZER (BACKGROUND RADIATION)

8-28-81 (1)		8-31-81		9-1-81		9-2-81		9-3-81		9-4-81	
Counts Per Sec.	Temp. °C	Counts Per Sec.	Temp. °C	Counts Per Sec.	Temp. °C	Counts Per Sec.	Temp. °C	Counts Per Sec.	Temp. °C	Counts Per Sec.	Temp. °C
				211	23						
				200	23						
226	24			221	24						
205	23			206	24						
199	23			204	24	202	23				
204	24	228	23	202	23	197	23	217	23		
197	24	215	23	191	24	190	24	204	24		
214	24	219	23	209	24	213	24	212	24		
226	24	217	23	218	24	222	24	198	24	215	24
213	24	207	23	203	23	198	24	209	24	205	24
200	24	214	23	207	24	206	24	215	24	221	24
196	24	201	23	218	24	211	24	214	24	217	24
195	24	210	23	213	24	202	24	200	24	203	24
210	24	219	24	200	24	199	24	191	24	197	24
199	24	215	24	198	24	189	24	204	24	212	24
233	24	201	23	205	24	207	24	202	24	209	24
187	24	209	24	217	24	217	24	196	24	191	24
193	24	214	24	193	24	190	24	194	24	213	24
212	24	212	24	186	24	206	24	196	24	215	24
208	24	208	24	180	24	211	24	199	24	205	24
206	24	217	24	190	24	209	24	211	24	193	24

Total Counts = 102
$\bar{x}$ = 206.16
σ = 10.16

---

(1) The system was operated, however, there was no data taken over the weekend.

DISCUSSION OF RESULTS AND CONCLUSIONS

DISCUSSION

Results of the irradiation tests indicate that the Westinghouse Mark V boron analyzer would perform well under post-accident conditions. Count rate increases, and thus the ppm boron readout decreases with increasing radiations levels, however, the effect is a predictable one. For exposure levels in the range of 2 x 10^5 R/hr and 3.45 x 10^5 R/hr (maximum achievable radiation level) the fissioning count rate increases by about 1.5 percent and 3 percent, respectively. Linear extrapolation of this data indicates that the fissioning count rate would increase by about 5 percent for a radiation field of 5 x 10^5 R/hr. Extrapolation is based on results of other irradiation tests which indicate a linear relationship to radiation levels of 7.1 x 10^5 R/hr. A radiation level of 5 x 10^5 R/hr is anticipated in the Westinghouse Mark V analyzer with a primary coolant activity of 10 Ci per cc.

An increase in count rate resulting from high radiation levels will not give an equivalent percent decrease in apparent boron concentration. The change in boron indication will be slightly less than the percent change in count rate. Even assuming a linear relationship between change and count rate and decrease in indicated boron concentration, the accuracy of this instrument is equivalent to, or better than the accuracy that can be achieved with other methods of on-line or wet-chemical analyses available for use during accident conditions. Consequently, no corrective factor would need be applied to results of this analyzer during operation in a high radiation environment.

The temperature correction system was not operated during this work. However, temperature was not a factor in the results since temperature did not vary by more than a few degrees in any one test. The intent was to determine the relative change that may result from high radiation levels rather than measure absolute values. Testing performed with the Combustion Engineering Boronometer indicate that a 5-10 degree change in temperature has no significant effect on count rate.

It is of interest that the increase in count rate resulting from irradiation effects is essentially a constant (as percent of count rate)

It is of interest that the increase in count rate resulting from irradiation effects is essentially a constant (as percent of count rate) for the three conditions tested (pure water. 2570 and 5140 ppm boron).

The data indicate that the standard deviation for boron concentration is acceptable with respect to post-accident or normal conditions. High radiation levels have no significant effect on deviation as indicated below:

Boron Concentration mg/l	Standard Deviation No Radiation				Standard Deviation 100 Sec. Count			
	100 Sec Count		1000 Sec Count		3.45×10^5 R/hr		2×10^5 R/hr	
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
0	476	1.73	-	-	-	-	-	-
0	475	0.95	-	-	488	2.45	-	-
0	-	-	-	-	487	2.55	-	-
2500	206	0.65	-	-	213	0.49	-	-
2500	206	1.02	206	0.32				
5000	126	0.99	-	-	129	0.81	128	0.86

CONCLUSIONS AND RECOMMENDATIONS

- The Westinghouse Mark V boron analyzer is acceptable for use under post-accident conditions. It should be possible to obtain an analysis within 5 or 10 minutes with this system. Concerning its use for normal power operations, the accuracy is probably acceptable.
- Count rate increases, and thus the ppm boron readout decreases with increasing radiation levels, however, the effect is a predictable one and accuracy is still quite acceptable.
- For maximum anticipated exposure levels of 5×10^5 R/hr (10 Ci/cc activity level), the fissioning count rate will increase by about 5 percent. This 5 percent increase in count rate will result in a small error relative to the accuracy required for post-accident conditions.
- The increase in count rate from irradiation is essentially a constant (as percent of count rate) for the three conditions tested (pure water, 2570 and 5140 ppm boron). The increased count rate does not linger when the radiation field is removed.

Section 4

SUMMARY OF RESULTS - CE BORONOMETER

The Combustion Engineering (CE) boronometer performed well, both at radiation levels of 10^6 R/hr and under steady state conditions in the absence of radiation. A 53,000 curie ^{60}Co radiation source was used to achieve the 10^6 R/Hr levels in the high radiation level test work. The boronometer operated at integrated dose of about 2 X 10^7 rads. This corresponds to 20 hours of operation at maximum radiation levels anticipated under radiation conditions. It is expected that the system would remain operational at higher exposure levels based on known characteristics of the system. However, prudent considerations would dictate that radiation exposure be minimized by flushing the sample vessel when the required boron concentration information has been obtained during post-accident conditions.

The system can also be used to monitor boron concentration during normal power operations. The instrument provides readout of the fission rate of the enriched uranium in the fission chambers. Fission rate is inversely proportional to the boron concentration in the sample tank surrounding the neutron source. The boron concentration is derived from the fission count rate by a mathematical curve fitting routine performed by a microcomputer. Use of the boronometer would not eliminate the need for periodic check analyses performed using the boron-mannitol titration. However, it would provide a continuing check against sudden changes in boron concentration and would reduce exposure to personnel.

BACKGROUND INFORMATION

TEST PURPOSE

Testing was performed to determine if the CE boronometer would suffer radiation damage or reduction in accuracy when operated at radiation levels anticipated under post-accident conditions. Testing was also performed to establish accuracy and reliability of the equipment when operated under conditions as anticipated during normal operations. Testing was performed on a preproduction model in the latter stages of development.

SYSTEM DESCRIPTION

General

The boronometer consists of a sampler, preamplifier and signal processor. The system used in this test included a strip chart recorder. This is not part of the normal equipment package, however, its use is recommended to improve statistics and show trending. Performance specifications for these components are listed in Tables 4-1, 4-2 and 4-3. Schematic design of the sampler which contains the neutron source and fission chambers is shown in Figure 4-1. Only those components shown in this figure are in the high radiation field. Overall schematic system design is shown in Figure 4-2. Predicted delay time due to mixing is shown in Figure 4-3.

Operation of the boronometer is based on the principle of neutron absorption by ^{10}B. A small flow of primary coolant containing boron passes through a tank which holds an americium-beryllium source in the center of the tank. Neutrons from this source are thermalized and pass through the primary coolant to cause fissioning of the 93 percent enriched uranium contained in the four fission chambers. Location of the fission chambers relative to the neutron source is shown in Figure 4-1. The counting rate of the fission chambers is inversely proportional to the ^{10}B concentration in the primary coolant, due to the neutron absorption characteristics of ^{10}B. Signals from the fission chambers (neutron detectors) are accepted by the preamplifier box which amplifies and transmits the signals to the signal processor.

TABLE 4-1

PERFORMANCE SPECIFICATIONS FOR THE BORONOMETER

Neutron Detectors	Four fission chamber neutron detectors
Thermistor	Contains one thermistor for temperature compensation control
Pressure Drop	0.04 psid at 1.0 GPM, 0.01 psid at 0.5 GPM, 0.0004 psid at 0.1 GPM
Construction	Designed to ASME B31.1 power piping code, rated at 200 psig and 250°F. All wetted parts are 300 series austenitic stainless steel. Standard inlet and outlet connection are 1/2 inch, Schedule 40 butt weld.
Volume	0.9 gallon
Dimensions	Approximately 12 inches in diameter and 19 inches high.
Weight	Approximately 35 pounds
Neutron Source	2 curie AmBe, double encapsulated, with source handling tool, DOT approved shipping container and vessel padlock.
Ambient Operating Temperature Range	40 to 250°F
Finish	The sampler is constructed of 300 series stainless steel. No finish is applied.

TABLE 4-2

PERFORMANCE SPECIFICATIONS FOR THE BORONOMETER PREAMPLIFIER

POWER REQURIED

Low Voltage ± 15 VDC	100 mAmps
High Voltage. maximum	800 Volts

MAXIMUM RATINGS

Preamplifier Operating Temperature	122°F
Pressure	70 psig
Relative Humidity	95%
High Voltage	+ 800 Volts
Maximum Output Signal Cable Length	500 feet

TYPICAL CHARACTERISTICS

Conversion Gain Input	800 mV/pC
Rise Time each Input (maximum)	50 nSec
Fall Time each Input	200 nSec
Equivalent Noise Charge	2.5×10^{-15} C (rms)
High Voltage in Leakage Current (maximum)	1.4×10^{-4} Amps
Enclosure	All electronics are contained in a 14 gauge steel 20 X 20 X 8 inch NEMA 4 box. The box is finished in gray enamel over phosphatized surfaces.
Cabling to Signal Processor	1 - RG-59/u 1 - 3 conductor No. 16 AWG 1 - 8 conductor No. 16 AWG consisting of four twisted shielded pairs.

TABLE 4-3

PEFORMANCE SPECIFICATIONS FOR THE BORONOMETER SIGNAL PROCESSOR

Digital Displays	Sample Temperature - °F Detector Count Rate - counts/second Boron Concentration - ppm natural Boron
Analog Outputs	One of the following: 4-20 ma into 0-600 ohms 1-5 ma into 0-2400 ohms 10-50 ma into 0-200 ohms 0 to 10 VDC into 500 ohms Full scale for the above signals can be switched to either 3,000 or 6,000 ppm.
Alarms	High and low alarms, front panel adjustable with indicator lights. Each alarm utilizies a relay with SPDT contacts rated at .1 amp at 120 VAC. Relays deenergized on alarm.
Digital Output	Serial, teletype compatible
Front Panel	The front panel is brushed aluminum with a clear anodized finish.
Ambient Operating	40 to 122°F Temperature
Dimensions	8-3/4" H X 19" W X 16" D, designed for 19" rack mounting
Weight	35 pounds

FIGURE 4-1

SAMPLER FOR THE CE BORONOMETER

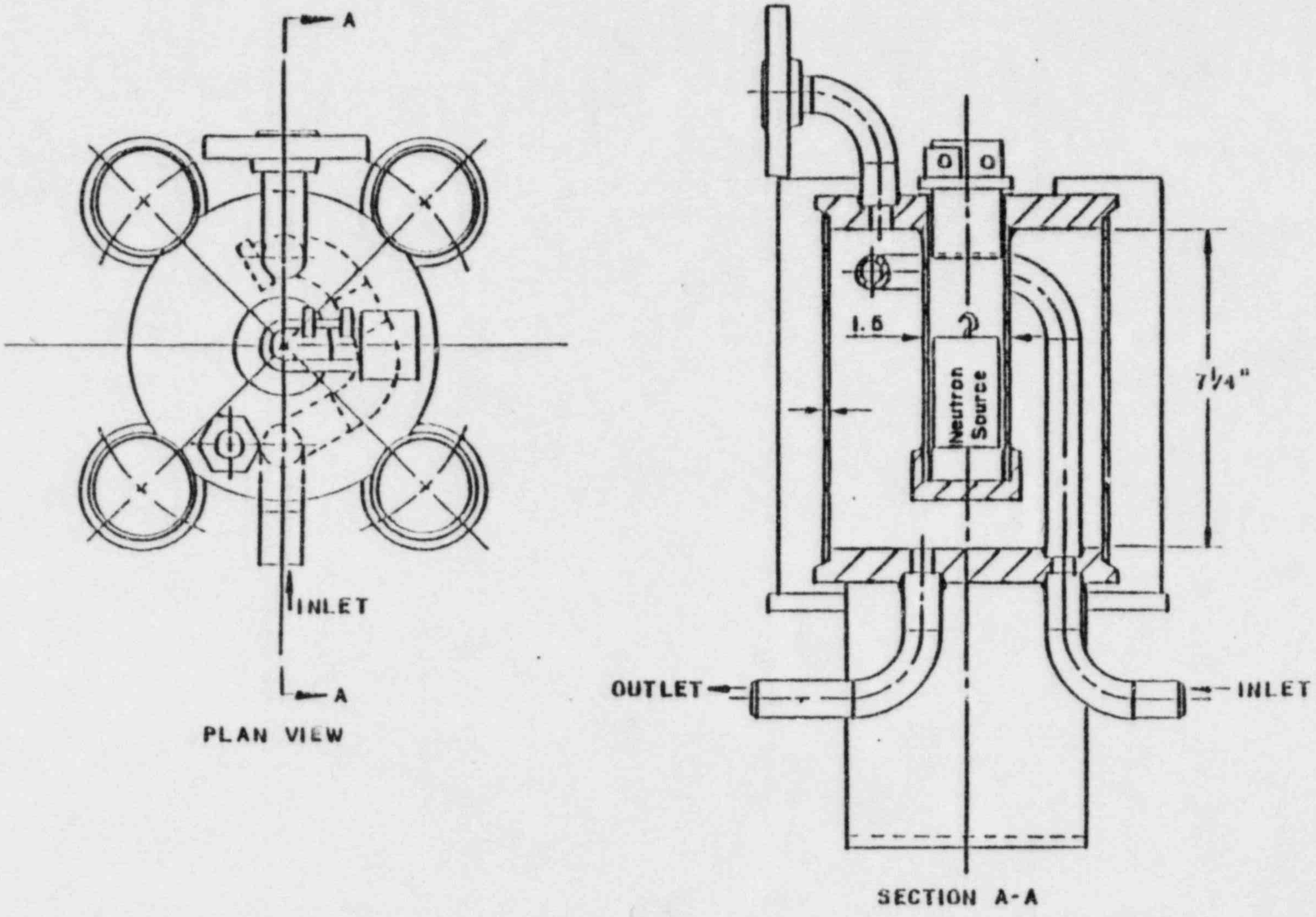


FIGURE 4-2

CE BORONOMETER

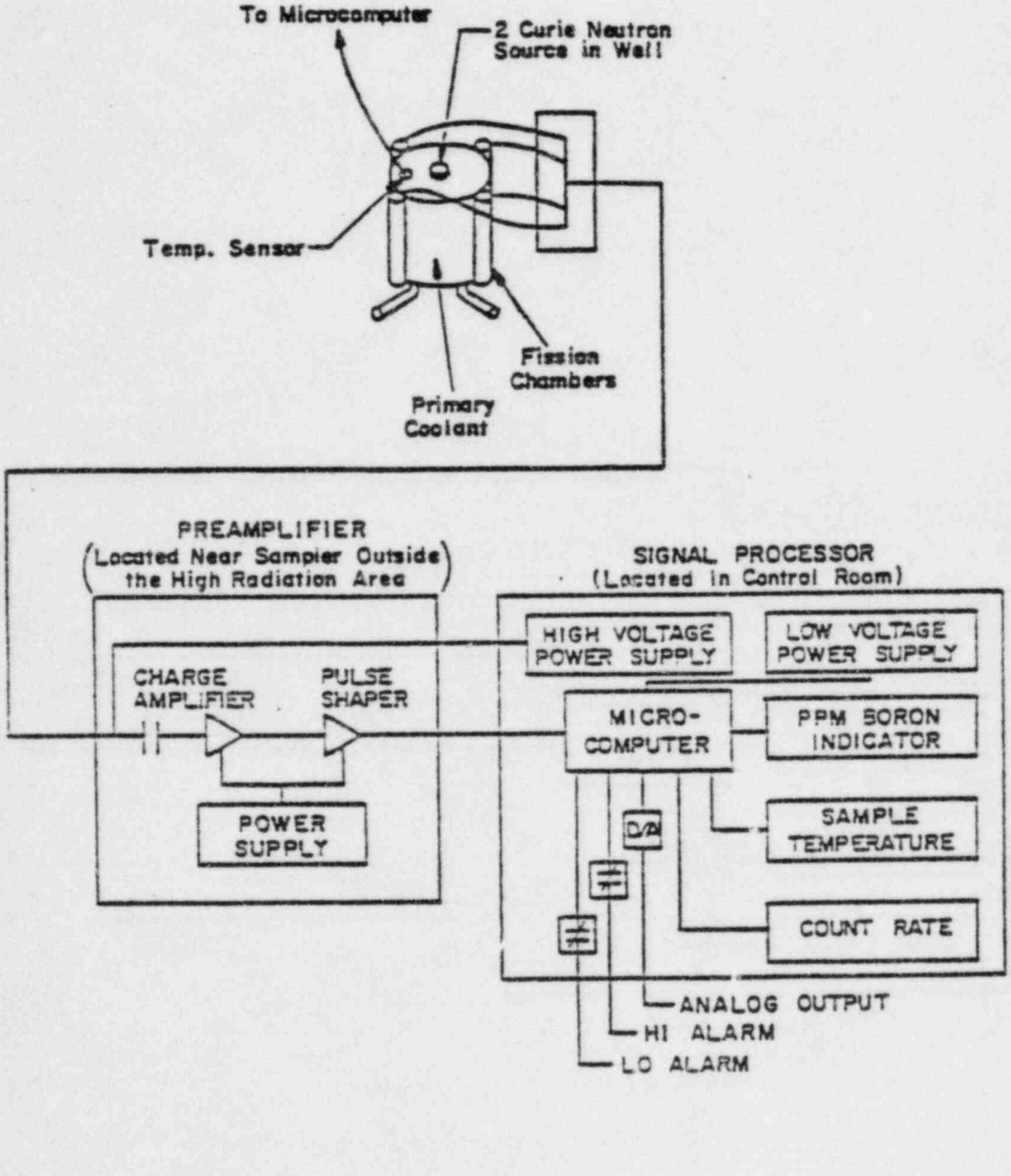
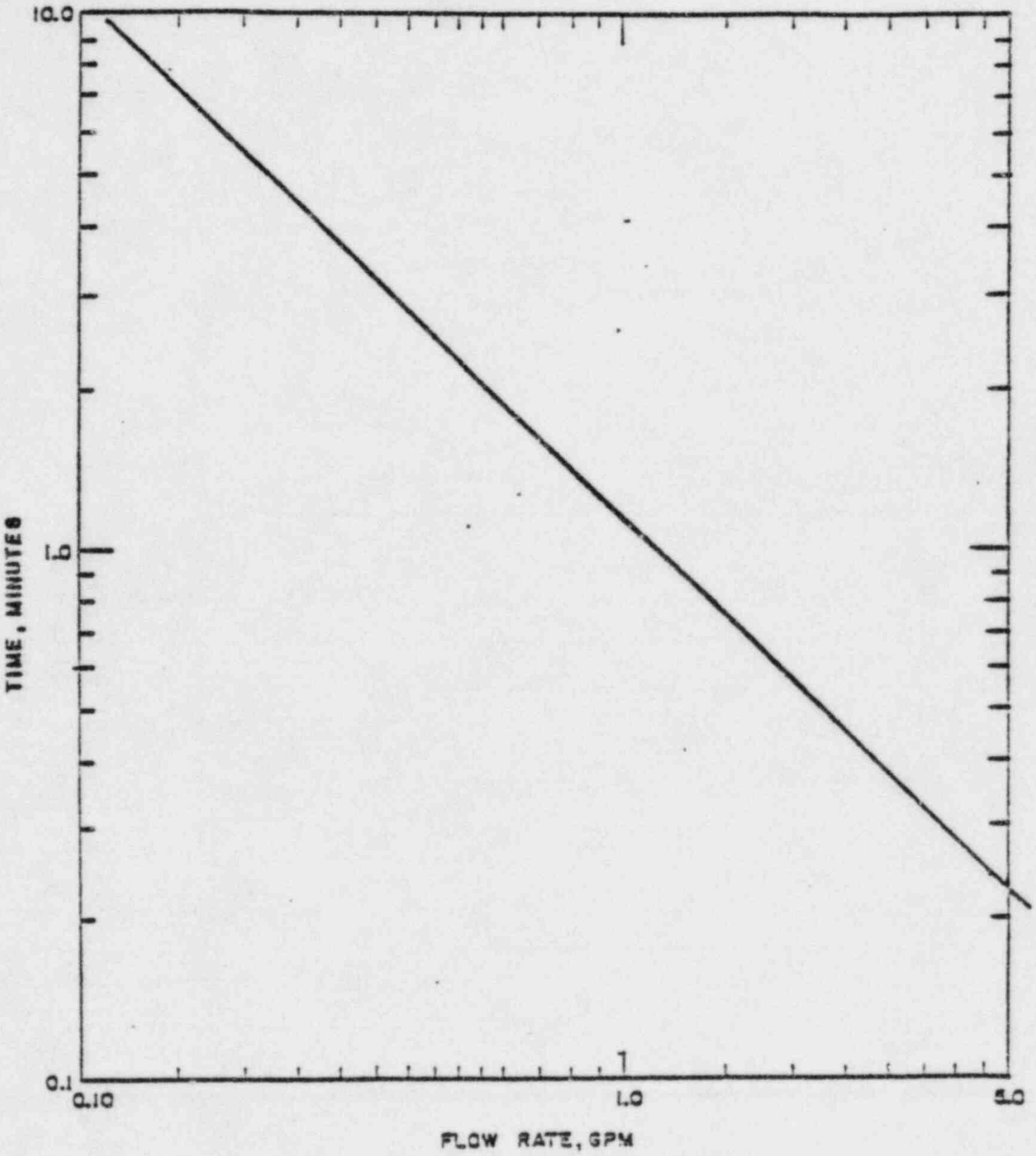


FIGURE 4-3

PREDICTED DELAY TIME DUE TO MIXING
FOR THE CE BORONOMETER



The preamplifier is located remotely outside the high radiation area. The signal processor continuously monitors the signal rate, and through an algorithm stored in a microcomputer in the instrument, converts the count rate to parts per million of boron. Count rates are normally averaged over a time period which can be adjusted over the range of 1 to 999 seconds.

TEST DESCRIPTION

GENERAL

The irradiation testing was performed at the hot cell test facility at Georgia Tech. Testing to investigate reliability characteristics of the boronometer was performed at this same location. No radiation exposure was involved with the reliability testing. Testing to determine accuracy and reproducibility of the boronometer was performed at the CE test facility and witnessed by NUS Check analyses of the boronometer results was performed by CE and NUS using a boron-mannitol titration to determine boron concentration.

IRRADIATION TESTING

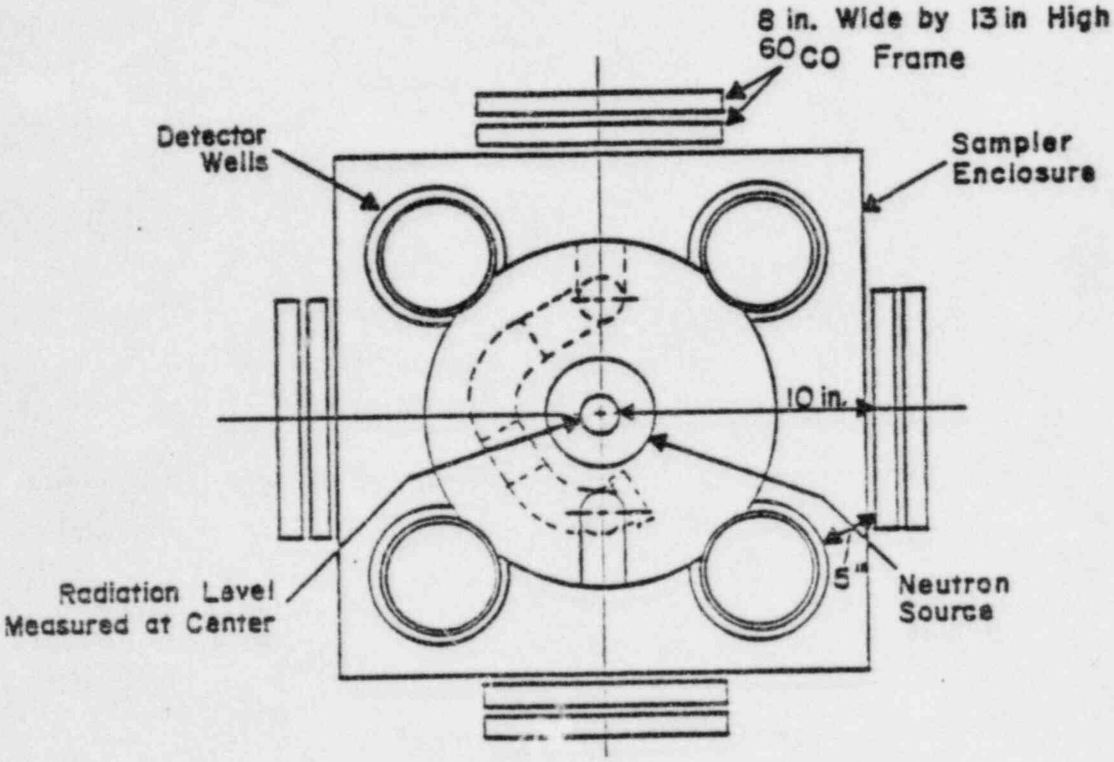
The radiation source was provided by eight, 8 X 13 inch frame assemblies containing a total of 53,000 curies ^{60}Co (6,600 curies per frame). Radiation levels desired were achieved by placing one or more of these frame assemblies around the sampler assembly as shown in Figure 4-4. Radiation levels were measured with dosimetry at the center of the assembly at a point just above the neutron source and estimated elsewhere. Testing was performed at an estimated maximum radiation level of 1 X 10^5 R/hr at the detector tubes. Maximum radiation levels at the center reference point as determined by dosimetry were 7.1 X 10^5 R/hr. The detector tubes were several inches closer to the radiation source than the central reference point, therefore are in a higher radiation level area than is the reference point.

The fission count rate was determined as a function of boron concentration and/or radiation level in the sampler assembly. Count rate was determined in the absence of radiation to determine a base level, followed by testing with exposure to low, intermediate and high radiation levels.

All testing involved radiation exposure was performed in a hot cell under loop flow conditions. Only the sampler assembly was exposed to the radiation source. The remainder of the equipment which includes the preamplifier and the signal processor were installed outside the hot cell. This is the manner in which the equipment would be installed for post-accident or normal operation.

FIGURE 4-4

GEOMETRY OF IRRADIATION ASSEMBLY
FOR BORONOMETER SAMPLER
53,000 Ci TOTAL RADIATION SOURCE



RELIABILITY AND ACCURACY TESTING

In the reliability testing, a boron solution was circulated through the boronometer for a period of seven days while monitoring the fission count rate. This work was performed under normal background radiation levels. Accuracy testing under loop flow conditions was performed at CE using boron solutions containing about 100, 600, 1,800, 3,200 and 5,000 ppm boron.

TEST RESULTS

IRRADIATION TEST RESULTS

Note that the radiation levels noted are measured at the center reference point. Actual radiation levels at the detector tubes which were affected by this radiation, were about 25 to 50 percent higher than the reference point measurements.

Typical results for the fission count rate as a function of boron concentration and radiation levels for discriminator settings of 50 and 60 millivolts are presented in Table 4-4. The results indicate that virtually total discrimination against radiation noise can be achieved. There is no memory effect nor is there any indication of permanent damage based on about 2 X 10^7 rads total exposure to the detector tubes. This is above the exposure levels anticipated under post-accident conditions.

RELIABILITY TEST RESULTS

After the irradiation testing was complete, the boronometer was operated under steady state conditions for a period of seven days. Water containing about 2,960 ppm boron was circulated through the sampler and the fission count rate was recorded on a strip chart recorder. Some noise pickup was evident as is shown in Figure 4-5, demonstrating results of a one day run over this period. However, the system was found to be completely free of noise when the development model preamplifier was replaced with a production model preamplifier.

ACCURACY TEST RESULTS

The boronometer test results for low level boron concentrations are presented in Table 4-5. Note that the data are presented in terms of ppm boron for an approximate curve fit that was used when the data was recorded. This curve has been refined subsequent to the testing reported here to provide the proper ppm indication. Accuracy results for high level boron concentrations are presented in Table 4-6. The deviation from results indicated are acceptable for post-accident analyses.

TABLE 4-4

FISSION COUNT RATE (1) AS A FUNCTION OF RADIATION LEVELS FOR A 50 AND 60 M.V. DISCRIMINATOR SETTING ON THE CUSTOM DESIGNED PREAMPLIFIER WL-24038 (2,960 PPM BORON CONCENTRATION)

	50 M.V. Discriminator Setting				60 M.V. Discriminator Setting				
	Background Radiation	2 X 10^5 R/Hr (2)	4 X 10^5 R/Hr (2)	7.1 X 10^5 R/Hr (2)	Background Radiation	2 X 10^5 R/Hr (2)	4 X 10^5 R/Hr (2)	6 X 10^5 R/Hr (2)	7.1 X 10^5 R/Hr (2)
	208	210	210	204	124	120	120	119	110
	214	214	211	219	121	121	121	121	111
	210	211	214	218	121	124	120	119	114
	209	212	214	225	120	121	119	120	115
	211			205	122	118			118
						120			
Average $\bar{x}$	210	212	212	214	121	121	120	120	114
σ	± 2.3	1.7	2.1	9.3	1.7	2.0	.8	.9	3.2
2σ	± 4.6	3.4	4.2	18.6	3.4	4.0	1.6	1.8	6.4

---

(1) 100 second time interval

(2) Radiation levels at the detector tubes were higher by an estimated value of 25 to 50 percent than indicated here.

TABLE 4-5

BORONOMETER ACCURACY RESULTS FOR LOW LEVEL BORON CONCENTRATIONS

99 ppm Boron(1)

Count Period Seconds		Count Rate(2)	PPM Display
100		314	89
100		315	68
100		314	56
100		310	76
100		314	72
100		311	77
100		314	61
100		315	58
100		310	74
500		314	70
500		314	71
500		315	62
500		314	65
$\bar{x}$		313	69
σ	±	1.8	9.0
2σ	±	3.6	18.0

620 ppm Boron(1)

Count Period Seconds		Count Rate(2)	PPM Display
100		278	504
100		275	603
100		275	653
100		275	679
100		275	697
100		275	688
100		274	690
100		274	710
100		275	697
500		275	684
500		275	695
500		278	671
500		278	667
$\bar{x}$		275	664
σ	±	1.5	55.2
2σ	±	3.0	110.4

---

(1) As determined by chemical analyses

(2) Combined count rate from four fission chambers

At the conclusion of the test, the boronometer was operated briefly while increasing temperature of the solution from 80°F to 117°F. In the half hour testing performed, there was no change in ppm readout beyond the spread noted when temperature was controlled at 80°F. Admittedly, this was a very brief test period, yet it does indicate that minor fluctuation in temperature will have little if any effect on boron readout.

The CE wide range boronometer with BF_3 detectors was also tested by KWU in Germany at GKN for a period of about eight months. They reported that the "measured values, compared to other chemical measurement and evaluation methods were within the specified accuracy of ± one percent (+5 mg/l)." They further recommended the boronometer for use at the KWU site.

The advantages of operating a boronometer for determining boron concentration during post-accident conditions are as follows:

- All operations can be performed remotely. The exposure involved for determining boron concentration would approach zero.
- No chemicals are added to the sample. Sample flow can be pumped back to the primary system reducing the load on the radwaste system.
- It provides a direct measure of boron-10 or neutron poison concentration in the system.
- The system is sealed, thus preventing release of gaseous activity to the environment.
- Analyses results can probably be achieved within a matter of 15 to 30 minutes dependent on flow rate through the sampler.

The disadvantages of operating a boronometer during post-accident conditions as follows:

- The sampler system would have to be shielded since a relatively large volume of coolant is required. About 15,000 curies of activity would need to be transported outside the primary containment to operate this system.
- The system has not been proven under long-term use. However, there is not reason to assume that it would not be reliable. Individual components within the system are off-the-shelf items. Most of the electronics are identical to those used on CE's wide range boronometer and CE has been shipping these units since 1977.

TABLE 4-6

BORONOMETER ACCURACY RESULTS FOR HIGH LEVEL BORON CONCENTRATIONS

1825 ppm Boron(1)			2904 ppm Boron(1)			4928 ppm Boron(1)		
Period Seconds	Count Rate (2)	PPM Display	Period Seconds	Count Rate (2)	PPM Display	Period Seconds	Count Rate (2)	PPM Display
100	234	1921	100	215	2996	100	191	5309
100	234	1915	100	215	2946	100	191	5317
100	234	1921	100	218	2844	100	190	5394
100	235	1904	100	215	2912	100	195	5004
100	234	1861	100	214	2901	100	194	5001
100	231	1899	100	215	2917	100	194	5005
100	234	1897	100	215	2944	100	191	5033
100	234	1915	100	215	2937	100	195	4968
500	234	1915	100	215	2958	100	194	5217
500	230	1951	100	215	2908	100	194	5101
500	231	1944	100	215	2884	100	190	4954
x̄	233	1913	100	211	2981	100	194	4951
σ ±	1.7	24.0	100	214	2934	100	194	4864
2σ ±	3.4	48 0	100	215	2943	100	195	4834
			100	211	3012	100	194	4875
			500	215	2991	100	191	4999
			500	214	3016	100	195	4921
			x̄	215	2943	500	194	5077
			σ ±	1 6	46.7	500	194	5045
			2σ ±	3 2	93.4	500	191 5046	
						x̄	193	5046
						σ ±	1.8	154.1
						2σ ±	3.6	308.2

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(1) As determined by chemical analyses (2) Combined count rate from four fission chambers

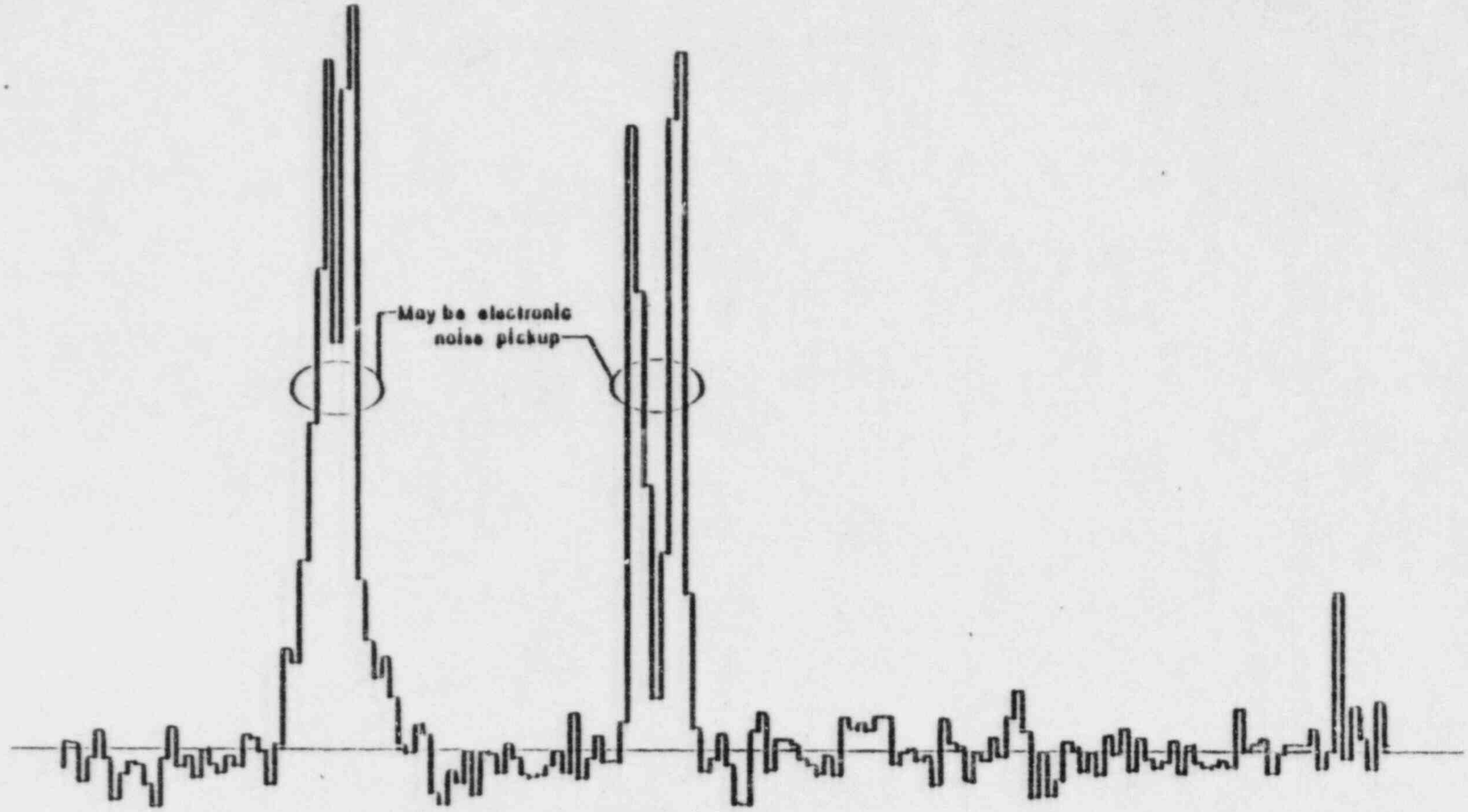

FIGURE 4-5
ONE DAY STRIP CHART RECORDING
OF 2960 ppm BORONOMETER ANALYSES RESULTS
(Background Radiation)

CONCLUSIONS AND RECOMMENDATIONS

- The CE Boronmeter is acceptable for use under post-accident conditons.
- Reproducibility of results is excellent as based on fission count rate, however, conversion of count rate to ppm is somewhat below the accuracy desired for daily operations. CE indicates, however, that the proper curve fit routine in the microcomputer will provide proper ppm indication.
- A 500 second count rate is recommended for determining boron concentrations below 1,000 ppm.
- The use of strip chart recorder is recommended for use with the borononmeter. This will improve statistics and show trending.
- There is some increase in the standard deviation (Table 4-4) from radiation levels in the range of 10^6 R/Hr at the planned discriminator setting of 50 millivolts. The increase is not significant with respect to post-accident analyses requirements.