

TESTING OF DISSOLVED OXYGEN  
ANALYZERS FOR POST-ACCIDENT ANALYSIS  
APPLICATION

(Revised March 26, 1984)

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SUMMARY AND CONCLUSIONS

This report gives the results of testing of the Orbisphere Model 2606 Dissolved Oxygen Analyzer with the Orbisphere Model 2110 High Sensitivity Oxygen Detector for post-accident analysis applications. The L&N Model 7931 Dissolved Oxygen Receiver and Probe and the YSI Model 54 Dissolved Oxygen Analyzer were used as reference analyzers. These testing results demonstrate the following:

- The Orbisphere Model 2606 Analyzer/Model 2110 Probe is suitable for post-accident dissolved oxygen analyses. The testing was conducted with demineralized water, PWR simulated reactor coolant, and PWR simulated sump water with air, oxygen, nitrogen, and hydrogen gas blankets to simulate accident conditions.
- The L&N Model 7931 Analyzer is not suitable for post-accident dissolved oxygen analyses. Hydrogen causes a negative interference, resulting in erroneous readings. However the L&N model 7931 Analyzer is well suited for PWR feedwater applications.
- The YSI Model 54 Analyzer is not sufficiently accurate to cover dissolved oxygen levels below about 0.1 ppm, although this testing program does not indicate that post-accident matrix environment affects instrument response.

Accordingly, NUS recommends that the Orbisphere Model 2606-2 Analyzer/Model 2110-2 Probe be used in post-accident applications. These testing results confirm that the Orbisphere meets the Reg. Guide 1.97 (Revision 2) range of 0 to 20 ppm and accuracy requirements specified in NUREG 0737 (Section II.B.3, Evaluation Criteria Guidelines).

STONE & WEBSTER ENGINEERING CORPORATION	
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J. O. NO.	12241
SPEC. NO.	2BVS-114A
DATE	4/4/84
BY	RJ Kiernan

MATERIALS USED IN TESTINGDissolved Oxygen Analyzers

The Orbisphere Model 2606 Oxygen Indicating Instrument is a digital readout meter with the following scales:

- (a) 0-20 ppm
- (b) 0-2 ppm
- (c) 0-200 ppb
- (d) 0-20 ppb

Range selection is made automatically by an internal autoranging circuit. Temperature is measured by a thermistor located within the sensor. The sensor is housed in the Model 2950 Flow Chamber. The flow rate must be controlled between 50 and 250 mL/min.

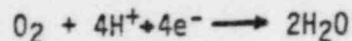
The Model 2110 Sensor must be calibrated because the sensitivity of the instrument depends on the tension in the membrane mounted over the detector. The detector consists of a gold cathode and silver anode. This type of cell is known as a Clark polarographic cell.

The Orbisphere Model 2606-2 Oxygen Indicating Instrument and Model 2110-2 Sensor is marketed for post-accident applications. This instrument and detector are identical to the ones tested except for replacement of plastic with stainless steel in the probe housing.

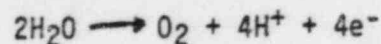
The L&N Model 7931 Dissolved Oxygen Receiver and Probe is an analog readout meter with the following scales:

- (a) 0-20 ppm
- (b) 0-2 ppm
- (c) 0-200 ppb

The probe is easily calibrated in air. When the probe is placed in a sample stream, oxygen diffuses through a membrane and is reduced at the cathode:



An equal amount of oxygen is generated at the anode:



The diffusion continues until the oxygen tension on both sides of the membrane is equal. The electrical circuitry is arranged such that the current necessary to maintain the equilibrium is converted to read out the dissolved oxygen level. No net oxygen, acid, or water is consumed.

The YSI Model 54 Analyzer is a Clark polarographic type instrument with two ranges:

- (a) 0-10 ppm
- (b) 0-20 ppm

This is a field type instrument and was previously installed in the testing apparatus.

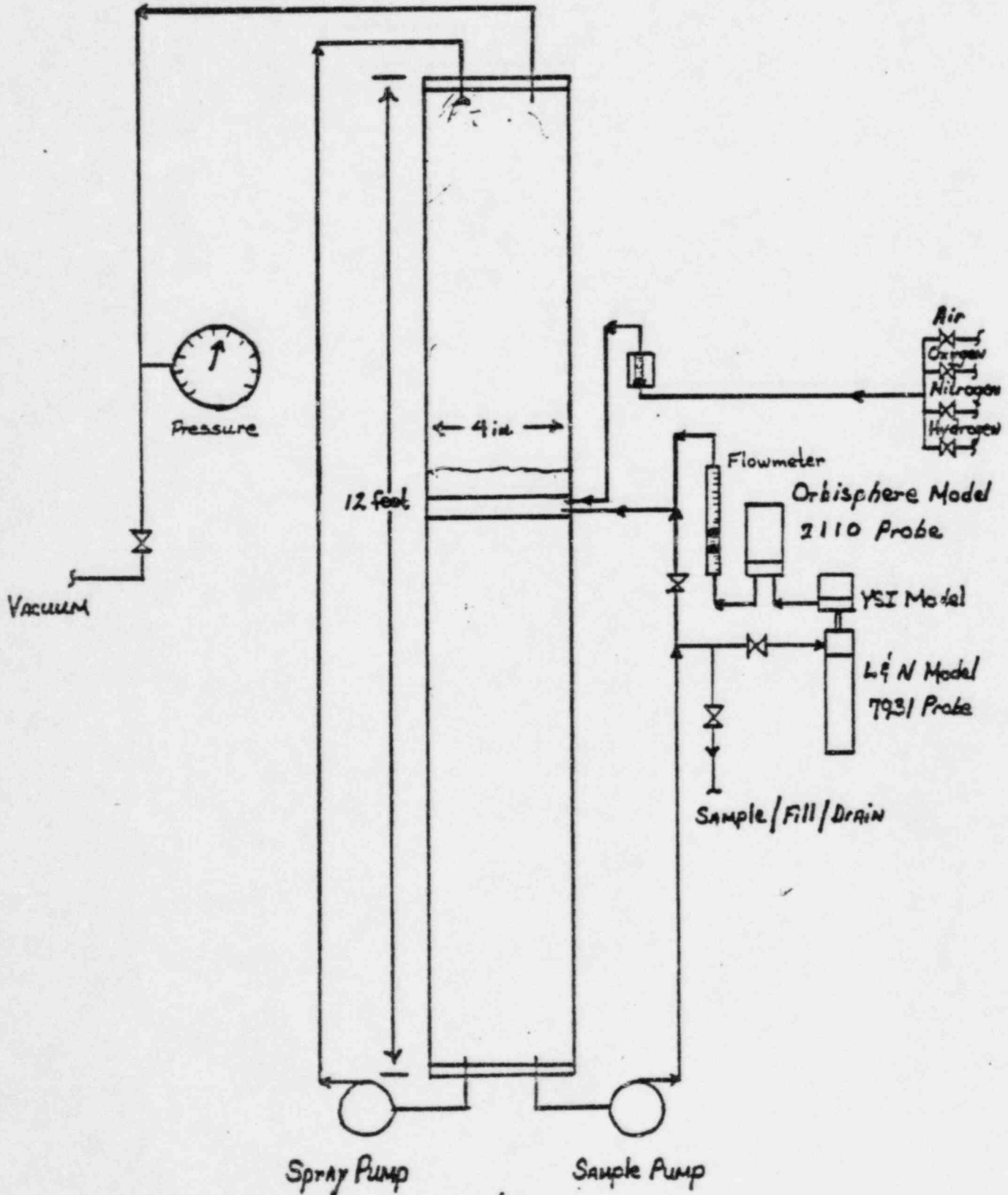
#### TESTING APPARATUS

Figure 1 illustrates the testing apparatus. Pumps circulate liquid to either the analyzers or sample tap and to the top of the apparatus. The liquid is discharged into a four-inch diameter glass column to obtain equilibrium with the gas above the liquid. The gas blanket can be changed by placing the system under vacuum followed by displacement with air, nitrogen, oxygen, or hydrogen as appropriate for a test. Flow can be throttled to the analyzer loop as necessary.

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SUBJECT Oxygen Analyzer Testing Checked By \_\_\_\_\_

**Figure 1: Dissolved Oxygen Analyzer Testing Apparatus**





CHEMICAL REFEREE TESTS

The Winkler dissolved oxygen analysis was the referee chemical method for dissolved oxygen levels above approximately 0.1 ppm. This method is based on the reaction of dissolved oxygen reacting with an equivalent amount of dispersed divalent manganous hydroxide to form manganese (IV) oxyhydroxide. Manganous sulfate solution is first added to a sample collected in a 300 mL BOD bottle. A potassium hydroxide/potassium iodide reagent is next added. After the manganese (II) hydroxide/manganese (IV) oxyhydroxide has settled, sulfuric acid is added. Free iodine is liberated in direct proportion to the original dissolved oxygen level. The iodine is titrated with standardized sodium thiosulfate solution, using Thyodene indicator. The estimated precision is  $\pm 0.05$  ppm, and the estimated accuracy is approximately  $\pm 0.1$  ppm for oxygen levels above approximately 0.3 ppm.

The CHEMetrics comparator method is based on breaking a sealed tube, containing reagents under vacuum, in a flowing sample stream. The sample is forced into the tube by atmospheric pressure. The color developed is compared to standards supplied with the kit to determine the dissolved oxygen level. Kits and comparator standards are as follows:

<u>CHEMetrics Kit</u>	<u>Range</u>	<u>Standards for Comparison</u>
Model 0-100	0-100 ppb	0, 10, 20, 30, 40, 60, 80, 100 ppb
Model 0-1	0-1 ppm	0.0, 0.5, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0 ppm
Model 0-12	0-12 ppm	1, 2, 3, 4, 5, 6, 8, 10, 12 ppm

Samples showing colors between two comparator standards are estimated as the average of the two standards.

TESTING METHOD

The testing protocol consisted of calibrating the instruments and then testing the following matrix conditions:

<u>Matrix</u>	<u>Composition</u>
A	Demineralized water with air/nitrogen/oxygen blanket to vary oxygen levels.

<u>Matrix</u>	<u>Composition</u>
B	Demineralized water with hydrogen blanket to vary oxygen levels.
C	PWR reactor coolant with simulated fission products with air blanket.
D	PWR reactor coolant with simulated fission products with hydrogen blanket.
E	PWR sump water with simulated fission products with hydrogen blanket.

The initial calibration consisted of using air-saturated water in a flowing system and adjusting meter responses to the value obtained by the Winkler analysis. However, the YSI could not be adjusted to referee analyses. Since the Orbisphere read 2.58 ppm relative to 1.91 ppm by the Winkler analysis during the initial testing on February 28, 1984, all instruments were then air-calibrated. The Orbisphere still gave high readings. The flowmeter was not properly calibrated and the flow rates were in excess of 250 mL/min. as recommended by the manufacturer. The flowmeter was then calibrated and the flow rate was adjusted to 124 mL/min. for the remainder of the test. On February 29, 1984, the flow rate through all probes was set at 124 mL/min. The Orbisphere and L&N probes were calibrated relative to Winkler analysis results. Thus, the first valid Orbisphere data were obtained on February 29. The L&N instrument is not flow sensitive and thus, valid data were collected on February 28. All testing results are summarized in Table 1.

Approximately three liters of simulated PWR reactor coolant and three liters of simulated PWR sump water were tested in the apparatus illustrated in Figure 1. This was insufficient sample for full testing. The reactor coolant contained approximately 2000 ppm boron as boric acid at a pH of approximately 5.5, whereas the sump sample contained boric acid at the same level but sufficient caustic to increase the pH to about 9.3. Sampling was compromised because of insufficient sample. The CHEMetrics method was also affected by the high pH sump water as shown in Table 1. The Winkler method was slightly modified as noted in Table 1 because of the matrix pH.

Additional testing on simulated PWR reactor coolant was conducted on March 21-22, 1984 and on simulated PWR sump water on March 23, 1984. All test data are summarized in Table 1.

TABLE 1

## SUMMARY OF TESTING RESULTS

Date	Matrix	Cover Gas	ppm Chemical Analysis		Model 2606 Orbisphere	Model 7931 L&N
			Winkler	CHEMetrics		
2/28/84	Demin. Water	Air-N <sub>2</sub>	-----	0.010	(1)	0.007
			-----	0.25	(1)	0.28
			0.289	-----	(1)	0.26
			0.145	-----	(1)	0.14
			-----	0.04	(1)	0.041
			0.067	0.1	(1)	0.081
			0.231	0.2	(1)	0.230
			0.752	-----	(1)	0.70
			2.33	-----	(1)	2.80
			7.30	-----	(1)	8.70
			2/29/84	Demin. Water	Air	6.67
Air	0.617	-----			0.611	0.565
Air-N <sub>2</sub>	-----	0.060			0.056	0.060
-----	0.148	0.15			0.141	0.140
-----	0.703	0.7			0.734	0.66
Air	6.78	7.			6.87	6.70
Air-O <sub>2</sub>	12.65	-----			12.95	12.90
3/1/84	Demin. Water	Air-N <sub>2</sub>	3.22	-----	3.11	3.12
		Air-O <sub>2</sub>	8.63	-----	8.43	8.70
		-----	17.6	-----	16.16	17.0
		-----	16.0	-----	15.25	16.1
		-----	19.7	-----	18.70	19.6
		H <sub>2</sub>	5.73	-----	5.37	0.140(6)
		H <sub>2</sub>	1.52	-----	1.497	0.034(6)
3/2/84	PWR Reactor Coolant Matrix	Air	7.13	-----	7.05	7.10
		Air	7.17	-----	6.93	6.90(3)
		H <sub>2</sub>	2.20	-----	2.06	0.080(3)
		-----	0.45	-----	0.370(6)	0.016(3)(4)(6)
		-----	-----	0.10(5)	0.051(6)	0.006(4)(6)



TABLE 1 (Cont)

## SUMMARY OF TESTING RESULTS

Date	Matrix	Cover Gas	ppm Chemical Analysis		Model 2606 Orbisphere	Model 7931 L&N
			Winkler	CHMetrics		
3/3/84	PWR Sump Matrix	H <sub>2</sub>	(a) 0.35	-----	-----	-----
			(b) 0.32	-----	0.293	0.014(6)
			0.13	-----	0.112	0.008(6)
			-----	0.15(5)	0.039(6)	0.006(6)
3/21/84	PWR Reactor Coolant Matrix	Air	(a) 0.48	-----	-----	-----
			(b) 0.44	0.8(5)	0.402	0.017(6)
3/22/84	PWR Reactor Coolant Matrix	Air	7.44	-----	7.44	7.45
		Air + O <sub>2</sub>	19.78	-----	19.79	19.90
3/23/84	PWR Sump Matrix	Air + O <sub>2</sub>	15.78	-----	15.72	16.60
			11.15	-----	11.07	11.00
		Air + H <sub>2</sub>	1.53	-----	1.44	-----
		H <sub>2</sub>	0.49	-----	0.463	-----
		H <sub>2</sub>	0.21	-----	0.184	-----
		Air + H <sub>2</sub>	0.73	-----	0.700	-----
		H <sub>2</sub>	0.365	-----	0.336	-----
		Air	7.46	-----	7.49	7.49
3/23/84	PWR Sump Matrix	Air + O <sub>2</sub>	16.16	-----	15.35	16.40
			18.90	-----	18.59	19.10
		H <sub>2</sub>	10.04	-----	10.08	-----
		H <sub>2</sub>	4.32	-----	4.31	-----
			1.39	-----	1.40	-----
			0.878	-----	0.873	-----
			0.608	-----	0.599	-----
			0.395	-----	0.380	-----
			0.267	-----	0.259	-----

TABLE 1 (Cont)

## SUMMARY OF TESTING RESULTS

NOTES:

- (1) Flow rate was greater than 300 mL/min. - Orbisphere and YSI are flow sensitive. The Orbisphere should be set between 50 and 250 mL/min.
- (2) Once the flowmeter was calibrated, the flow rate was set to 124 mL/min. for all subsequent tests. YSI could not be calibrated against Winkler.
- (3) Because of boric acid, 4 mL of KI/KOH reagent and 2.5 mL of 1:1 H<sub>2</sub>SO<sub>4</sub> were used for the Winkler analysis versus 2 mL of each.
- (4) Insufficient sample for proper purge.
- (5) CHEMets are apparently affected by matrix.
- (6) Data was not used in statistical evaluation.

## EVALUATION OF TESTING RESULTS

### Statistical Evaluation

Table 2 summarizes valid testing results for the Orbisphere and L&N analyzers. Data for the Orbisphere, which were obtained when the instrument was not calibrated properly, have not been included in Table 2. Table 3 gives the results of a statistical evaluation of the Table 2 data. The first evaluation determines the equation for "best fit" straight line:

$$Y = mX + b$$

where "Y" is the analyzer reading, "X" is the chemical analysis referee result, "m" is the slope and "b" is the intercept. Since the NRC gives separate accuracy statements for 0 to 0.5 ppm and from 0.5 to 20 ppm, the statistical evaluation also considers these ranges. Table 3 also gives the mean difference between the chemical analyses and the corresponding analyzer readings. The mean difference is given in ppm for the 0 to 0.5 ppm range and in percent for the 0.5 to 20 ppm range. The predicted range for the population mean difference can be used to determine if the instruments meet NRC accuracy requirements. As shown in Table 3, NRC accuracy requirements are met by the Orbisphere. The requirement for the 0 to 0.5 ppm range is  $\pm 0.05$  ppm, whereas this testing shows an upper limit of 0.035 ppm. The accuracy requirement for the 0.5-20 ppm range is  $\pm 10\%$ , whereas this testing shows an upper limit of 3.60%.

The L&N analyzer meets NRC accuracy requirements for samples not containing hydrogen, but full matrix testing with hydrogen shows that this analyzer cannot be used in post-accident or normal reactor coolant applications. However, the L&N analyzer should provide good service for PWR feedwater applications.

Figures 2 and 3 show the data and line of "best fit" for the Orbisphere for the two ranges. It can be seen in each figure that the data are very close to the line of "best fit" indicating a high correlation coefficient. It can also be observed that the probe is not biased by any of the three matrices in which it was tested.

TABLE 2  
SUMMARY OF DATA USED IN STATISTICAL EVALUATION

Analyzer	Matrix (1)	Range	ppm Dissolved Oxygen		Absolute Difference
			Instrument Reading	Chemical Test	
Model 2606 Orbisphere	A	0-0.5	0.056	0.060	0.004
	A		0.141	0.150	0.009
	D		0.184	0.210	0.026
	D		0.336	0.365	0.029
	D		0.463	0.490	0.027
	E		0.112	0.130	0.018
	E		0.259	0.267	0.008
	E		0.293	0.33(2)	0.037
	E		0.380	0.395	0.015
	E		0.402	0.460	0.058
					<u>ppm</u>
					<u>%</u>
	A	0.5-20	0.611	0.62	1.47
	A		0.734	0.70	4.63
	A		3.11	3.22	3.54
	A		6.65	6.67	0.30
	A		6.87	6.78	1.31
	A		7.05	7.13	1.13
	A		8.43	8.63	2.37
	A		12.95	12.70	1.93
A	15.25		16.00	4.92	
A	16.16		17.60	8.91	
A	18.70		19.70	5.35	
B	1.497		1.52	1.54	
B	5.37		5.73	6.70	
C	6.93		7.17	3.46	
C	7.44		7.44	0	
C	11.07		11.15	0.72	
C	15.72		15.78	0.38	
C	19.79		19.78	0.05	
D	0.700		0.73	4.29	
D	1.44		1.53	6.25	
D	2.06	2.20	6.80		
E	0.599	0.608	1.50		
E	0.873	0.878	0.57		
E	1.40	1.39	0.71		
E	4.31	4.32	0.23		
E	10.08	10.04	0.40		

TABLE 2 (Cont.)

## SUMMARY OF DATA USED IN STATISTICAL EVALUATION

Analyzer	Matrix (1)	Range	ppm Dissolved Oxygen		Absolute Difference	
			Instrument Reading	Chemical Test		
Model 2606 Orbisphere	F	0.5-20	7.49	7.46	0.40	
	F		15.35	16.16	5.28	
	F		18.59	18.90	1.67	
Model 7931 L&N	A	0-0.5	0.007	0.01	0.003	
	A		0.041	0.04	0.001	
	A		0.060	0.06	0	
	A		0.081	0.07	0.011	
	A		0.140	0.15	0.010	
	A		0.140	0.15	0.010	
	A		0.230	0.23	0	
	A		0.260	0.29	0.030	
	A		0.280	0.25	0.030	
	A		0.5-20	0.565	0.62	9.73
	A			0.66	0.70	6.06
	A			0.70	0.75	7.14
	A			2.80	2.33	16.79
	A			3.12	3.22	3.21
A	6.67	6.67		0		
A	7.70	6.78		1.19		
A	7.10	7.13		0.42		
A	8.70	7.30		16.09		
A	8.70	8.63		0.80		
A	12.90	12.70	1.55			
A	16.10	16.00	0.62			
A	17.00	17.60	3.53			
A	19.60	19.70	0.51			
C	6.90	7.17	3.91			



TABLE 2 (Cont.)

## SUMMARY OF DATA USED IN STATISTICAL EVALUATION

NOTES

(1)	<u>Matrix</u>	<u>Composition</u>
	A	Demineralized water with air/nitrogen/oxygen blanket
	B	Demineralized water with hydrogen blanket
	C	PWR reactor coolant with air blanket
	D	PWR reactor coolant with hydrogen blanket
	E	PWR sump water with hydrogen blanket
	F	PWR sump water with air/oxygen blanket
(2)	Average of 0.346 and 0.322 ppm	

**TABLE 3**  
**STATISTICAL EVALUATION OF TEST RESULTS (1)**

Analyzer	Range	m(2)	b(2)	No. of Data Points (n)	Mean Difference(3)	Std. Dev. of Mean Difference(4)	Predicted Range for Population Mean Difference(5)
							$0.0231 \pm \frac{0.0162}{\sqrt{10}} \times 2.262$
Orbisphere Model 2606	0-0.5 ppm	0.9263	-0.0020	10	0.0231 ppm	$\pm 0.0162$ ppm	0.0115-0.0347 ppm
							$2.6486 \pm \frac{2.5004}{\sqrt{29}} \times 2.048$
	0.5-20 ppm	0.9683	0.0714	29	2.6486%	$\pm 2.5004\%$	1.6977-3.5995%
							$0.0106 \pm \frac{0.0119}{\sqrt{9}} \times 2.306$
L&N Model 7931 (6)	0-0.5 ppm	0.9767	0.0020	9	0.0106 ppm	$\pm 0.0119$ ppm	0.0015 - 0.0197 ppm
							$4.7700 \pm \frac{5.5111}{\sqrt{15}} \times 2.145$
	0.5-20 ppm	0.9874	0.1594	15	4.7700%	$\pm 5.5111\%$	1.6178 - 7.8222%

**NOTES:**

(1) Table 2 data used

(2) Y - Analyzer reading, ppm  
 X - Chemical analysis, ppm  
 m = Slope  
 b = Intercept, ppm  
 Y = mX + b

(3) Mean difference,  $\bar{X} = \frac{\sum (X-Y)_i}{n}$ (4) Std. Der. Mean Diff.,  $S_{X-Y} = \sqrt{\frac{\sum [(X-Y)_i - \bar{X}]^2}{n-1}}$ (5) Predicted range for population mean difference =  $\bar{X} \pm \frac{S_{X-Y} \times t}{\sqrt{n}}$ 

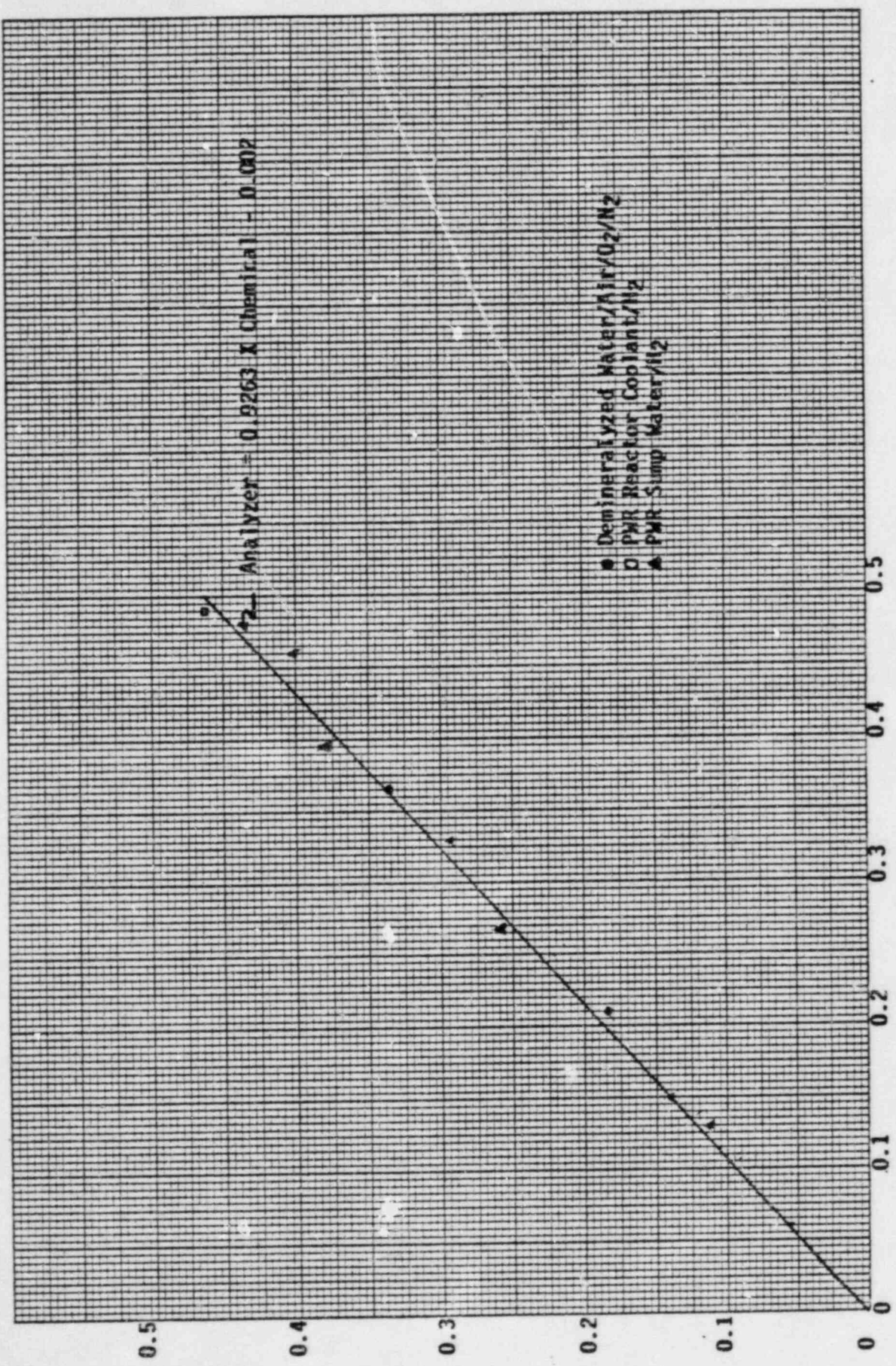
t = 95% probability factor for a specific number of degrees of freedom, n-1

(6) Matrix conditons with hydrogen have not been included.

FIGURE 2

Orbisphere Model 2606 Dissolved Oxygen Analyzer

Response: 0-0.5 ppm



Chemical Analysis

PPM Dissolved Oxygen

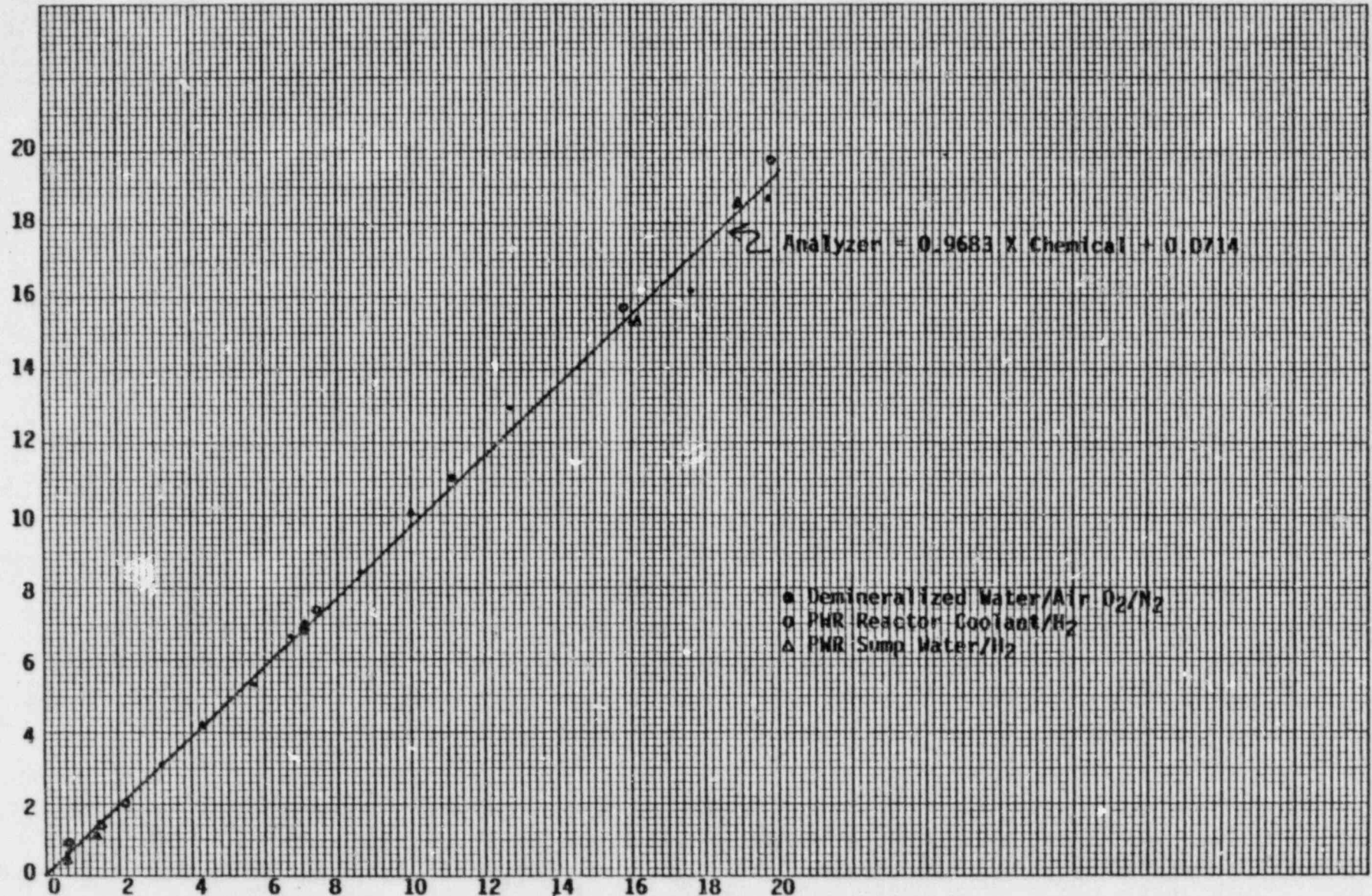


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FIGURE 3

Orbisphere Model 2606 Dissolved Oxygen

Analyzer Response: 0.5 to 20 ppm



Chemical Analysis  
PPM Dissolved Oxygen

### Other Considerations Affecting Results

When changing oxygen levels from high (e.g., several ppm) to low (e.g., less than 100 ppb), the analyzers may require three hours or longer for a stable response. Because of the limited time available for this testing and of the concern to simulate power plant conditions, the stabilization period generally did not exceed two hours except for two occasions in which the testing apparatus was allowed to remain operating overnight.

Another consideration is the sampling technique used for low oxygen levels when testing PWR matrix solutions. Normally, the BOD bottle is allowed to overflow at least three bottle volumes. The mouth of the bottle is normally maintained under liquid during sampling and white reagents are being added. Sufficient matrix solutions were not available to allow this technique. However, Table 1 data show that chemical results in these few cases are only slightly high.

When calibrating the Orbisphere for post-accident applications, the following is recommended.:

- a. The probe should be maintained in water at least several hours prior to use.
- b. Air-saturated water should be recirculated through the probe assembly for 30 to 60 minutes. The calibration control knob should be adjusted to either the Winkler chemical analysis results or to the air-saturated value for the particular temperature of the water.
- c. The sample should be circulated through the probe assembly for at least 60 minutes. This may be longer if oxygen levels are low.



EFFECTS OF RADIATION ON ORBISPHERE PROBE

The attachment is a technical note published by Orbisphere which indicates that the Model 2110 sensor is expected to operate for about one year in a radiation field of  $6 \cdot 10^4$  Rads/hour before the electrolyte and membrane must be changed. This assumes that the membrane is made of Tefzel and the electrolyte is 6M KOH solution.

# technical notes

## Measurements of Traces of Dissolved Oxygen in Radioactive Water with the Orbisphere System 2713 Analyzer

by J. M. Hale

The problem often arises, at nuclear reactor or high energy accelerator installations, to determine trace oxygen levels dissolved in radioactive water. These oxygen levels can be as low as several (ug/litre), and their determination therefore demands highly sophisticated, sensitive instrumentation. The Orbisphere System 2713 Analyzer was designed expressly for this type of application, and has earned an excellent reputation for reliable, trouble free service in fossil fueled power plants. Before the system can be implemented for monitoring radioactive water, however, it must be verified that the radiation level to which the oxygen sensor is subjected does not exceed certain design limits. This note discusses the effects of radiation upon the various components of the sensor, presents limiting integrated doses for structural parts and determines servicing frequency for electrolyte and membrane changes as a function of dose. For illustrative purposes, lifetime calculations are performed with assumed average radiation levels of  $10^4$  Rad/h over long periods, and servicing frequencies are deduced for sustained doses of  $6.10^4$  Rad/h.

Because oxygen measurements must be performed on cooled, depressurized water in a flow circuit outside a reactor core the radiation is assumed to consist mainly of  $\gamma$  (electromagnetic) and  $\beta$  (electronic) radiations.

### Structural integrity of materials

The following table lists the materials used in construction of the Orbisphere probe.

Material	Type of stress	Limiting dose Rads	Lifetime at $10^4$ R/hr
Gold	Shear	$10^{11}$	$10^3$ years
Silver	"	"	"
Bronze	"	"	"
316 Stainless steel	"	"	"
Kel-F	"	$2.10^4$	28 months

The metals are of no concern, in respect of the effects of radiation upon their strength, since a very large integrated dose is required to make a noticeable difference to their physical properties.

Plastic materials in general are more subject to alteration by radiation, and Kel-F in particular suffers a rapid deterioration in its mechanical strength when subjected to an integrated dose in excess of  $2.10^4$  Rads. It is an ideal material from the point of view of other requisites, such as chemical resistance and machineability, in the present application. Radiation damaged parts could feasibly be replaced by new ones, provided the sensor did not acquire a dangerous level of radioactivity.

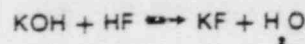
### Gas evolution

Another consideration with fluorinated materials such as Kel-F, is the nefarious effect of gases, notably hydrofluoric acid, resulting from chemical decomposition of the plastic caused by the radiation.

An integrated dose of  $10^4$  Rads produces about 3 ml of HF at normal temperature and pressure per gram of the polymer. At a dose rate of  $6.10^4$  Rad/hr, the Kel-F pieces in the Orbisphere sensor weighing 18 g would therefore produce  $1.5.10^{-4}$  moles HF per hour.

Some of this acid vapor is washed away by the flowing sample water and is therefore of no concern to the operation of the sensor.

That fraction of the vapor which dissolves in the electrolyte in the interior of the sensor is without effect at first, since it is neutralized by potassium hydroxide:



Once the alkali has been removed by this means, however, the accumulation of acid in the electrolyte will lead to a diminished sensitivity of the system towards oxygen. At the above rate of formation of HF, and given the usual concentration (1 M) of KOH in the electrolyte, these considerations suggest that electrolyte renewal will be required sometime after a minimum period of about 30 days, depending upon the rate of diffusion of the vapor out of the solid, and upon the fraction of the vapor which enters the sensor. A most probable frequency of servicing due to this cause of about once every 2 months seems likely. This frequency can be decreased by increasing the quantity of KOH in the sensor. At 6 M, for example, a lifetime of one year should be realizable.

### The Membrane

The membrane of an oxygen sensor is a critical item, in that it determines the accuracy of the measurement.

Any changes of chemical composition, density or crystallinity induced by radiation, might influence the oxygen permeability of the membrane, and hence cause a drift in the sensitivity of the detector and a progressively increasing error of measurement. Another relevant consideration is that the membrane is subjected to tensile stress, and it is this property which usually is most sharply affected by ionizing radiations.

In other applications, a teflon® (registered trademark of Dupont) PFA membrane is employed in the 2713 System. This material is too quickly deteriorated, however, by radiation. A preferred substitute is tefzel® (registered trademark of Dupont) which shares the strength and chemical stability of teflon, but can withstand an integrated dose of  $10^6$  Rad, thus permitting a lifetime of 14 months at the standard dose rate of  $10^4$  R/h.

### The Electrolyte

The Orbisphere probe contains about 2 milliliters of an aqueous electrolyte (1MKCl, pH 14). Water is subject to radiolysis in the presence of radiation, with production of hydrogen peroxide and hydrogen gas. These products are both of concern though for different reasons: hydrogen peroxide could be responsible for an erroneously high oxygen measurement, and hydrogen gas, if it were evolved at a rate exceeding the rate of permeation of the gas through the membrane to the exterior, could cause the build-up of pressure in the sensor again interfering with the accuracy of oxygen measurement.

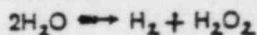
Fortunately, due to certain unique design features of the Orbisphere sensor, the rate of radiolysis of water is not sufficient to pose a problem in practice. The maximum amount of energy absorbed by 2 ml of water irradiated with  $6.10^4$  Rad/hr is:

$$\frac{6.10^4 \text{ (Rads)}}{\text{(hr)}} \cdot \frac{6.242 \cdot 10^{13} \text{ (eV)}}{\text{(Rad g)}} \cdot 1 \text{ (g)} \cdot 2 \text{ (ml)} \\ = 7.5 \cdot 10^{17} \text{ eV/hr}$$

hence the maximum number of water molecules decomposed per hour is:

$$\frac{7.5 \cdot 10^{17} \text{ (eV)}}{\text{(hr)}} \cdot \frac{0.065 \text{ (molecules)}}{\text{(eV)}} \\ = 4.85 \cdot 10^{17} \frac{\text{molecules}}{\text{hr}} = 8.10^{-7} \frac{\text{moles}}{\text{hr}}$$

If the only reaction of significance were assumed to be\*:

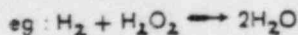


then the maximum rate of evolution of hydrogen would be:

$$\frac{1}{2} \cdot \frac{8.10^{-7} \text{ (moles)}}{\text{hr}} \cdot \frac{22400 \text{ (ml)}}{\text{(mole)}} \\ = 0.009 \text{ ml/hr}$$

In practice, water is highly transparent to  $\gamma$  radiation (penetration depth  $\sim 30$ cm), so that only a small fraction of the order of 5% of the radiation leads to radiolysis in the 1 cm path length in the Orbisphere sensor. This implies a hydrogen evolution rate of only  $0.45 \mu\text{l/hr}$ .

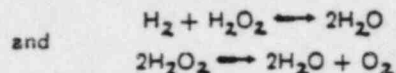
This hydrogen dissolves in the aqueous electrolyte, but its concentration does not increase without limit due to two limiting phenomena. Firstly, various back reactions



naturally lead to a steady state limiting concentration of the hydrogen gas even in a completely closed system.

Secondly, the membrane which encloses the sensor is permeable to the gas, and hence permits its continuous escape to the flowing sample water. In the case of  $1/2$  mil tefzel membrane, for example, the escape rate is about  $30 \mu\text{l}$  per hour, per  $\text{cm}^2$  of membrane, and per one atmosphere difference of hydrogen partial pressure across the membrane. This is sufficiently high to ensure that excess hydrogen pressures do not build up inside the sensor.

As was shown above, hydrogen peroxide could be formed at the rate of  $4.10^{-7}$  moles/hr, when  $6.10^4$  Rads/hr of radiation is completely absorbed in 2ml of water. Various "back reactions" such as

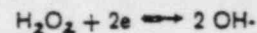


serve to limit the hydrogen peroxide concentration to a steady state value, typically of the order of  $10^{-3}$  molar in pure water.

It must be recognized, however, that most of this hydrogen peroxide has no influence upon measurements with the Orbisphere sensor since it cannot gain access to the cathode.

Peroxide which is formed in the reservoir of the sensor is "trapped" at the guard electrode which surrounds the cathode.

This electrode reduces the hydrogen peroxide to hydroxide ions according to the equation



and these hydroxide ions are totally inactive at the oxygen sensing cathode.

There remain for consideration only those peroxide molecules formed in the thin layer of solution sandwiched between the membrane and the cathode. The maximum rate of formation of these is:

$$\frac{1}{2} \cdot 6.10^4 \cdot 6.242 \cdot 10^{13} \cdot 1 \cdot \pi \cdot (0.316)^2 \cdot 10^{-4} \cdot 0.065 \\ \cdot (6.023 \cdot 10^{23})^{-1} \\ = 6.3 \cdot 10^{-12} \text{ moles/hr}$$

Here  $0.316$  cm is the radius of the cathode and  $10^{-4}$  cm is a typical thickness of the said electrolyte layer.

If all of this hydrogen peroxide is reduced at the cathode, it produces a current of

$$2 \cdot 6.3 \cdot 10^{-12} \cdot \frac{96500}{3600} = 0.34 \text{ nA}$$

This current is to be compared with the sensitivity of the Orbisphere sensor towards oxygen, namely  $2 \text{ nA/ppb}$  at  $20^\circ\text{C}$ .

The hydrogen peroxide produced by radiolysis at the  $6.10^4$  Rad/hr rate, therefore causes a maximum reading error of only  $0.17$  ppb.

### Conclusions

In summary, the materials used in the Orbisphere 2110 sensor are expected to withstand an integrated radiation dose of  $10^6$  Rads without structural failure. Tefzel is a preferred membrane material. Radiolysis of water does not constitute a problem because of unique features of the Orbisphere design, namely the small electrolyte volume, and the protecting influence of the "guard ring" electrode. At  $6.10^4$  Rads/hr continuous operating periods of at least one month are to be expected between electrolyte and membrane changes, and a minor change of electrolyte composition will permit this period to be extended to about one year.