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STONE & WEBSTER ENGINEERING CORPORATION

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TESTING OF L&N 7075-3 pH RECEIVER AND ELECTRODE PREAMPLIFIER AND MERIDIAN pH ELECTRODE FOR PASS APPLICATIONS

SUMMARY AND CONCLUSION

This report gives testing results of an L&N 7075-3 pH Receiver and Electrode Preamplifier and Meredian pH Electrode for use in post-accident sample systems (PASS). The testing protocol involved setting up the system with two buffers followed by standardizing the system with 7.00 buffer. Buffers covering 1.00 to 13.00 were used to test the system for accuracy. PWR simulated reactor coolant and sump water with matrix fission products were used to verify system performance.

The NRC gives a pH range for PASS applications of 1.0-13.0 (1). The accuracy requirement is ± 0.3 pH unit between pH 5.0 and 9.0 and ± 0.5 pH unit for other ranges (2). This testing shows that the L&N system meets this requirement.

(1) Reg. Guide 1.97, Revision 2
(2) NUREG 0737 (Section II.B.3, Evaluation Criteria Guidelines)

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MATERIALS USED IN TESTING

The L&N Meredian general purpose combination pH electrode (No. 117489) was connected to the L&N 7075-3 pH Receiver and Electrode Preamplifier. Because a temperature compensator was not used, a 720.5 ohm resistor was connected between terminals "TM" and "TA" on the preamplifier unit. The electrode was mounted in an L&N 7775 Meredian Insertion-Type Electrode Mounting.

The following commercial buffers were used in the test:

pH	Ingredients	Fisher No.	Lot No.
1.00	KCl + HCl	So-B-140	735878-18
3.00	$HOCOC_6H_4COOK$+HCl	So-B-97	735442-24
5.00	$HOCOC_6H_4COOK$+NaOH	So-B-102	735444-24
7.00	KH_2PO_4+NaOH	So-B-109	733683-24
9.00	H_3BO_3+KCl+NaOH	So-B-114	734920-24
11.00	NaOH+Glycocoll+NaCl	So-B-142	735447-24

A pH 13 buffer was not commercially available, but was prepared in the NUS laboratories. The pH 13 buffer was 660 mL 0.2M sodium hydroxide, 250 mL 0.2M potassium chloride diluted to 1000 mL.

TESTING METHOD

The pH electrode was soaked in water for nearly two days before testing. The L&N system was buffered with the pH 3.00 buffer using the "Standardize" control. When the electrode was removed from a solution; the "Standardize" control was pulled out to place the system in "Standby" to ensure that the electrode would not become polarized. The L&N system was then buffered with the pH 11.00 buffer, but the "Span or Slope Adjust" (R41) was used for this adjustment. The pH 7.00 buffer was then used, and the instrument was set with the "Standardize" control if required. All readings were taken under static conditions.

Table 1 gives testing results for the buffers. After the first test on January 31, the meter read low for the pH 11.00 and 13.00 buffers. This indicates a possible need to reset the isopotential point, which cannot be easily adjusted with the L&N meter. All subsequent measurements were made after using the pH 5.00 and 9.00 or 3.00 and 11.00 buffers to initially set up the system, followed by a final adjustment with the pH 7.00 buffer. Since the measurements were made at 25 $\pm$ 1°C, no temperature corrections to the measured values were necessary.

As a control, three laboratory pH meters were used: Orion 701, Orion 901, and Fisher Accumet 750. These meters were set up using the pH 5.00 and 11.00 buffers.

The test continued over a four day period using the buffers. PWR post-accident matrix solutions were also tested. A reactor coolant matrix with 2000 ppm boron as boric acid and simulated fission products and a sump water with 2000 ppm boron as boric acid, sodium hydroxide, and simulated fission products were tested. These results are also given in Table 1.

EVALUATION OF TESTING RESULTS

Table 2 gives a statistical evaluation of the testing results. The required accuracy between pH 5 to 9 is ± 0.3 pH unit. For the range 1 to 5 and 9 to 13 the required accuracy is ± 0.5 pH unit.

Two means were used to evaluate the testing results. The first method tests for possible bias by a linear regression. The equation

$$M = a + b \cdot S$$

shows possible bias, where "M" is the measured buffer pH, "S" is the standard buffer value, "a" is the bias, and "b" is the slope. A perfect system would have values of 0 and 1.00 for "a" and "b", respectively. The L&N meter shows a slight positive bias of +0.09, which is reasonable considering that the readout is no better than ± 0.1 pH unit. However, the Orion 701 and Accumet 750 meters showed biases outside the readout, which is ± 0.01 pH unit for these digital instruments.

The absolute values of the differences between the measured values and the actual values were evaluated for pH ranges: 1.00 - 13.00, 5.00 - 9.00, and 1.00 - 5.00, and 9.00 - 13.00 to test for accuracy requirements given by the NRC. The L&N meter shows an overall deviation as follows:

pH Range	Expected Uncertainty, $\bar{x} + 2\sigma$
1.00 - 13.00	0.40
5.00 - 9.00	0.29
1.00 - 5.00 and 9.00 - 13.00	0.47

These results confirm the suitability of the L&N system for PASS applications. (Normally, analytical uncertainty is given at the one sigma level. Since this was not defined in NUREG 0737, the two sigma values are used here).

Table 1 matrix testing results also confirm the suitability of the L&N system. For example, the PWR reactor coolant matrix varies between 5.4 and 5.5. The overall uncertainty of ± 0.29 for this pH range covers the two values of 5.64 and 5.48 measured with the Orion 901 system. The sump matrix also verifies suitability of the L&N system: an uncertainty of 0.47 applied to the measured values of 9.3 - 9.4 covers the 9.74 - 9.32 values measured with the Orion 901, although the 9.74 value is suspect.

TABLE

pH TESTING RESULTS FOR BUFFERS AND PWR MATRIX

Date	Time	pH Meter	Temp °C	pH1	pH3	pH5	pH7	pH9	pH11	pH13	PWR RCS Matrix	PWR Sump Matrix	Buffer(1)
1-31-84	1030	L&N	25.7	1.1	2.9	5.0	7.0	8.9	10.6	12.4	------	------	3-11
	1715	Orion 701	26.0	0.90	2.84	4.91	7.01	9.00	10.94	12.87	------	------	3-11
2-1-84	1500	L&N	25.6	1.1	3.0	5.2	7.4	9.3	11.0	13.0	------	------	3-11
	1650	Orion 701	26.0	0.79	2.74	4.84	6.95	8.98	11.0	12.92	------	------	3-11
2-2-84	0855	L&N	25.0	0.90	2.7	5.0	7.1	9.0	11.0	12.8	5.4	9.3	5-9
	1100	L&N	25.0	1.1	2.8	5.0	7.1	9.0	10.8	12.9	5.5	9.4	5-9
	1315	L&N	25.2	1.0	3.0	5.0	7.1	8.9	11.0	12.6	5.5	9.2	3-11
	1630	Orion 901	26.0	1.00	3.00	5.20	7.39	9.45	10.98	13.57	5.64	9.74	3-11
	1655	Orion 901	26.0	1.10	2.96	5.04	7.10	9.03	11.03	12.95	5.48	9.32	5-9
2-3-84	1030	L&N	25.0	1.1	2.9	5.0	7.1	9.0	11.0	12.7	5.5	9.3	3-11
	1315	L&N	25.4	1.1	2.9	5.0	7.0	9.0	11.0	12.5	------	------	------
	1645	Accumet 750	26.0	1.25	3.07	5.20	7.27	9.24	11.02	13.10	------	------	5-9
	1700	Accumet 750	25.0	1.11	2.95	5.06	7.12	9.11	10.81	12.99	------	------	5-9

NOTE: (1) This was the buffer pair used to set up the instrument prior to a series of measurments. The pH 7.00 buffer was used for a final meter adjustment of the L&N system.

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TABLE 2

STATISTICAL EVALUATION OF pH METER TESTING

			|S-M|					
	pH 1-13		pH 1-13		pH 5-9		pH<5>9	
Meter	a	b	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
L&N	.088	0.982	0.114	0.147	0.071	0.110	0.146	0.164
Orion 701	-0.172	1.011	0.095	0.081	0.055	0.061	0.125	0.084
Orion 901	0.029	1.014	0.144	0.187	0.202	0.181	0.101	0.192
Accumet 750	0.162	0.990	0.129	0.087	0.167	0.082	0.100	0.083

S = Standard buffer pH

M = Measured buffer pH

$\bar{X}$ = Average difference, $\frac{|S-M|}{n}$

σ = Standard deviation

M = a + b·S