



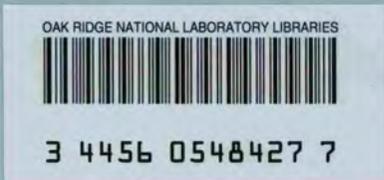
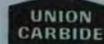
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PRELIMINARY REPORT ON THE MODEL 904 HIGH TEMPERATURE pH METER

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This report describes the modifications necessary to adapt the Model 904 pH Meter manufactured by Canadian Aviation Electronics Ltd. to laboratory use. Included also are the pH data that have been obtained so far with the modified instrument.

The Model 904 pH meter is designed to operate at temperatures up to 200°C and at pressures up to 200 psi. When installed for routine measurement of pH in an industrial process, the liquid flow enters at the bottom of the bomb or chamber containing the electrode assembly and exits through the side. A system of valves must be provided to control the flow and permit calibration of the system. Since hot process solution flows through the bomb it is unnecessary to provide external heating. In the laboratory adaptation the orifices in the bomb were capped and the bomb was heated in a silicone oil bath. The top of the bomb could not be immersed in the silicone oil since the calomel reference electrode, which is external to the bomb, is maintained at 25°C. Cooling of the reference electrode was accomplished by pumping water at 25°C around the reference electrode and back to a constant temperature bath. Nitrogen gas at a pressure 20 psi greater than the pressure in the bomb was applied to the KCl solution around the calomel electrode to prevent solution backing up through the capillary opening at the bottom of the salt bridge connecting the calomel electrode with the solution to be measured. This differential was maintained automatically by means of a regulator supplied with the pH meter. In all the experiments herein described the glass electrode used was a Beckman amber glass high temperature electrode (recommended by the manufacturer). A glass H-tube was used to contain the solution in the bomb.

In setting up the equipment it was found necessary to:

1. Ground terminal No. 12 in the amplifier to the case.*

* Refer to the wiring diagram in the instruction manual for the instrument.



2. Ground the shells of V_1 and V_2 (pin No. 1).
3. Tighten all ground connections on the transmitter chassis.
4. Check V_1 socket for loose-pin connections.
5. Clean SW1 A and B contacts (especially after use).
6. Use 2-wire shielded cable for the recorder signal connections and ground the shield to the recorder ground at the recorder end only.
7. Run the ground lead from the case ground through the armored cable to the bomb and ground at the bomb.
8. Make the ground connection to earth or water pipe from the bomb only.
9. Convert a standard Brown recorder to a 0-100 mv instrument, since the transmitter output is 100 mv full scale.

When these points had been taken care of, the pH meter operated in accordance with the specifications furnished by the manufacturer. The amplifier is stable as far as zero drift is concerned and very few electronic difficulties have been encountered. However, if the front of the amplifier has been opened it is necessary to wait several hours before the circuitry again comes to temperature equilibrium as evidenced by stable pH readings.

In the laboratory adaptation of the Model 904 pH meter several troublesome factors arose that would not be encountered in the industrial use of the instrument:

1) It is inconvenient to make and break the pipe connections every time the solution is changed in the bomb.

2) Heating by means of an oil bath is not very satisfactory: oil gets on the electrodes after the bomb has been opened to change solutions. (Perhaps heating would better be accomplished with an air bath.)

3) Since frequent glass electrode changes must be made a better type of connector should be used in the cable. (Gold plating the contact surfaces may help with the present connectors). Soldered connections would be best, but it is difficult to make shielded soldered connections.

4) It has been found that frequent cycling over wide temperature ranges is hard on the glass electrodes: only 2-3 runs can be made with a given glass electrode between the extremes of 25° and 200°C.

For checking the instrument it would be desirable to construct a battery box to mock up the electrode system. With such a box it would be easy to differentiate between electrode and electronic difficulties.

Experimental Results

The Model 904 pH meter is so designed that the output signal of the transmitter is a voltage proportional to the current flow through the feedback resistors; and since the feedback resistors contain the temperature sensitive resistance bulb in the bomb, the output voltage is a function of both the electrode potential difference and the temperature. The value of the resistor in the bomb is said to be so chosen that it compensates for the temperature coefficients of the various junction potentials in the system, for the Soret potential in the salt bridge, and for the $\frac{RT}{nF}$ coefficient of the pH value. Hence one can compare directly the pH values of solutions at various temperatures.

To determine whether the pH meter was operating properly, a series of runs was first made with .0100 m HCl over the temperature range 30° to 130°C. As shown in Table I the observed pH change was 0.04 pH unit; this change is just what one would expect from the change in the activity coefficient of the HCl over this temperature range, although this close agreement is fortuitous

in view of the accuracy of the instrument. It was observed in a series of four runs using fresh aliquots of 0.1 m H_2SO_4 that the maximum deviation of any point from the mean line through all the points was 0.1 pH unit, with the average deviation about ± 0.07 pH unit. Hence, from these runs it appeared that the instrument was operating within the manufacturer's specifications of ± 0.1 pH unit. Moreover, the built-in temperature compensation appeared to cancel all effects (within the accuracy of the instrument) in the runs with HCl solutions except the actual change in the thermodynamic activity of the HCl.

In Table I are summarized the average values of the pH readings so far obtained with the Model 904 instrument.

Table I

The pH Values of HCl, H_2SO_4 , and UO_2SO_4 Solutions as a
Function of Temperature

	m	t ^o C	pH	t ^o C	pH	Δt	ΔpH
HCl	0.0100	30	2.13	130	2.17	100	0.04
H_2SO_4	0.00490	30	1.76	180	1.93	150	0.17
"	0.04615	30	1.28	180	1.62	150	0.34
"	0.09740	30	0.96	180	1.21	150	0.25
UO_2SO_4	0.13	30	2.68	180	1.66	150	-1.02
"	1.1	30	1.76	180	1.81	150	0.05
* $\text{UO}_2\text{SO}_4 + \text{H}_2\text{SO}_4$		30	1.22	180	1.83	150	0.61

* UO_2SO_4 solution which read pH 2.68 at 30^oC, to which was added sufficient H_2SO_4 to bring the pH reading down to 1.22 at 30^oC.

From Table I several observations may be made:

1) The 0.01 m HCl solution behaved as expected: the observed pH change was exactly that predicted on the basis of the decrease of the activity coefficient with increase in temperature.

2) All three H_2SO_4 solutions increased in pH with temperature. The increase is to be expected since the bisulfate dissociation constant decreases with increasing temperature.

3) The pH value of the more dilute UO_2SO_4 solution decreased by about one pH unit presumably due to hydrolysis of the UO_2SO_4 . The pH value of the more concentrated UO_2SO_4 solution changed little with temperature; of course, at a lower pH (i.e. higher acidity) more moles of acid must be formed or removed for a given pH change because of the logarithmic relation between acidity and pH. The pH readings of the two UO_2SO_4 solutions (of widely different concentration) were about the same at 180°C , indicating a larger change of hydrolysis with temperature at the lower concentration.

4) When H_2SO_4 was added to the more dilute UO_2SO_4 solution the mixed solution behaved about the same as a pure H_2SO_4 solution of the same initial pH. This implies that the change in bisulfate acid constant is more important than the change in hydrolysis of the uranium under these conditions, although the actual situation obtaining involves a complex series of equilibria.

If further laboratory experiments are to be performed with the Model 904 pH meter it would be very desirable to modify the experimental set-up to obviate the troublesome factors previously mentioned in this report. It would also seem desirable to test the pH meter by measuring continuously the pH of a UO_2SO_4 solution in a circulating loop at $180\text{-}200^\circ\text{C}$. The instrument has proved very satisfactory in the pulp and paper industry where it is used to follow continuously

the pH of acid bisulfite solutions in digestors at 180-200°. The manufacturers see no reason why the instrument should not operate at temperatures as high as 250°C.

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