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Effect of Variables on pH Measurement in Acid-Rain-Like Solutions as Determined by Ruggedness Tests

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Ruggedness Test (RT) experiments were performed to assess the significance of the various main factors which affect pH measurements in low ionic strength aqueous solutions, as well as to establish the presence of interactions between the main factors. Stirring has an adverse effect on the measurement of pH, since it not only increases the random noise but also biases the measured value. Temperature control to the nearest 0.5 °C is sufficient for maintaining measurements accurate to 0.01 pH. Addition of $NaNO_3$ or KCl can not be tolerated in accurate pH measurements. Three small two-factor interactions were also revealed.

Key words: acid rain; glass electrodes; low ionic-strength solutions; main effects; pH measurements; ruggedness tests; two-factor interactions.

Introduction

The evaluation of the performance of a practical pH measuring system is a critical component of quality assurance for such programs as wet deposition monitoring. The purpose for these ruggedness test (RT) experiments, [1,2][1] was to assess the significance of the various main factors which affect pH measurements in low ionic strength aqueous systems, as well as to detect the possible presence of interactions between the main factors.

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RT experiments were conducted using a Plackett-Burman (PB) design, with seven factors and eight different factor combinations per set of measurements. Each factor is used at one of two chosen levels, arbitrarily designated as high (+) and low (−) levels (see table 1). In this design with (N=8) measurements per set, each

Table 1. A Plackett-Burman design for N=8 runs.

	Factor						
Run	A	B	C	D	E	F	G
1	−	−	−	−	−	−	−
2	−	−	+	−	+	+	+
3	−	+	−	+	−	+	+
4	−	+	+	+	+	−	−
5	+	−	−	+	+	−	+
6	+	−	+	+	−	+	−
7	+	+	−	−	+	+	−
8	+	+	+	−	−	−	+

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[1] Figures in brackets indicate literature references.

factor appears an equal number of times (4) in its high level and in its low level. The main effect of any factor, then, is calculated simply as the average of the measurements made at the high level minus the average of the measurements made at the low level of the factor. By conducting 2N measurements (16 in our case) one can also separate the main effects from groups of two-factor interactions.

The RT experiments for the pH experiment system included rather drastic variations in the experimental parameters. Such extreme variations are not usually encountered in the course of controlled pH measurements made within a single laboratory.

These variations are, however, at the upper limits of those encountered in practical pH measurements made in different laboratories. In the RT experiments a considerable efficiency is obtained by the process of changing all variables simultaneously. It is worthwhile to note, however, that RT experiments are seldom made under the conditions of final interest. Nevertheless, RT can be useful for quality assurance in wet deposition monitoring programs, by aiding in the selection of the tolerances of the test conditions. This results in more precise and accurate pH measurements.

Experimental

The measurement process first involved the calibration of a commercial combination glass/reference electrode and a digital pH meter. Calibration was accomplished by setting the slope adjustment of the pH meter to 100% and adjusting the pH meter calibration setting while measuring the pH=4.006 buffer (SRM 185e). Following the above calibration step, the pH=6.863 buffer (SRM 186d) was measured. A strong acid (HCl) reference solution denoted as SA83 1000 series (pH=3.685, prepared and determined in our laboratory in a hydrogen cell without liquid junction), was also measured. At this point the system was ready for the experimental solutions of the RT.

The experiments entailed the measurement of the pH of solutions at selected levels of seven factors. The factors initially chosen were: temperature, stirring during measurement, dilution (0.5 mL distilled H_2O per 20 mL of solution), depth of electrode immersion, pH meter slope setting[2] (90% and 100%), addition of KCl and equilibration time. After a preliminary set of experiments, two things become evident: 1) as expected, the addition of KCl had a pronounced effect on the measured pH, and 2) the magnitude of the effect of slope adjustment between 90 and 100% was so large in comparison to the effects of the other variables that it obliterated all other effects. For this reason it was decided to modify the experimental plan as follows. The slope adjustment on the pH meter was to remain fixed at 100% for all measurements. Hence, slope was no longer a variable factor. Instead of slope, a new factor was introduced: an addition of $NaNO_3$.

All subsequent experiments were conducted using the following seven factors: 1) temperature; 2) stirring; 3) dilution; 4) immersion depth; 5) addition of $NaNO_3$; 6) addition of KCl; and 7) equilibration time.
The various designated factors were adjusted to values dictated by the PB design, and the pH of the experimental solutions was measured at 1, 5 and 10 min after the immersion of the electrode into the solution. Table 2 shows an example of the measurement scheme. Only the

Table 2. One example of measurement scheme using solution No. 99-5.

Measurement No.	Temp. °C	Stirring	Dilution 0.5 mL H_2O per 20 mL soln	Immersion Depth	$NaNO_3$ 0.034 mol/L	KCl 0.068 mol/L	Equilibration Time		
							1 min	5 min	10 min
1	30	No	No	Bottom	No	No	2.905	2.904	2.912
2	30	No	Yes	Bottom	Yes	Yes	3.021	3.012	3.015
3	30	Yes	No	Top	No	Yes	2.981	3.006	3.006
4	30	Yes	Yes	Top	Yes	No	2.946	2.964	2.965
5	25	No	No	Top	Yes	No	2.993	2.996	2.999
6	25	No	Yes	Top	No	Yes	3.057	3.055	3.060
7	25	Yes	No	Bottom	Yes	Yes	3.045	3.049	3.050
8	25	Yes	Yes	Bottom	No	No	2.938	2.946	2.949

Reference Solution	Before the Experiment	After the Experiment
pH 4.01 Buffer	4.005	3.977
pH 6.86 Buffer	6.820	6.810
SA83 1000	3.610	3.634

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[2] On a pH meter, the slope setting is equivalent to setting a gain factor, namely mV/pH. 100% slope corresponds to the theoretical Nernstian slope of 59.157 mV/pH at 25 °C, and 90% slope corresponds to 53.241 mV/pH.

underlined pH measurements in the last two columns at the right of the table were used in the RT. The other pH measurements were obtained as a matter of routine, but were only used for background information. (One of the conclusions from this background information is that an equilibration time of 1 min is inadequate for stable pH measurements.) Following the completion of a set of pH measurements on each experimental solution, the pH values of the strong acid reference solution SA83 1000, and the pH 4.01 and 6.86 buffers, were remeasured.

The measurements were conducted in 30 mL borosilicate glass beakers. For each experiment a beaker containing exactly 20 mL of the appropriate solution was placed into a constant temperature bath that was thermostated to the nearest 0.1 °C. The solution in the beaker was allowed to come to thermal equilibrium with the bath. At this point a calibrated combination glass/reference electrode was immersed into the beaker. For the purpose of the experiment, this immersion time was designated as $t=0$. The values displayed digitally by the pH meter were recorded at the appropriate time intervals. The readability of the pH meter was 0.001 pH.

The RT experiments were performed on six different solutions (see table 3) which can be conveniently subdivided into three groups. The first group of solutions (solutions 99-1 and 99-2) was prepared from coulometrically standardized H_2SO_4. In addition to sulfuric acid, solution 99-1 also contained approximately 2 ppm by weight of other anions and cations, while solution 99-2 contained approximately 10 ppm of other ions. The second group of solutions (99-3 and 99-4), consisting of two reference HCl solutions, was prepared in 1983 in our laboratory. These solutions were not intentionally spiked with any foreign ions. The third group (99-5 and 99-6) consisted of two freshly prepared pure HCl solutions, containing no added contaminants. The last column of table 3 lists our reference pH values for the test solutions. For the sulfuric acid solutions (99-1 and 99-2) coulometrically determined concentrations along with the mean activity coefficient from the Debye-Hückel equation were used to calculate the reference pH values. The mean activity coefficient value for these two solutions is 0.927. The pH values of solutions 99-3 and 99-4 were accurately measured in a hydrogen cell without liquid junction. The pH values of solutions 99-5 and 99-6 were calculated, using the coulometrically determined hydrogen ion concentrations and tabular values of activity coefficients [3].

Table 3. List of solutions used in ruggedness test.

Solution No.	Solution Description	pH [@ 25 °C]
99-1	Simulated acid rain (H_2SO_4)	4.293
99-2	Simulated acid rain (H_2SO_4)	3.586
99-3	SA83 1000 (HCl)	3.685
99-4	SA83 2000 (HCl)	4.303
99-5	HCl 1.0008×10^{-3} mol/kg	3.015
99-6	HCl 1.026×10^{-5} mol/kg	4.989

Results and Discussion

The results of the experiments were presented and statistically analyzed in our earlier publications [1,2]. For the sake of convenience, the summary data of the observed main effects and two-factor interactions, which were presented in [2], are again introduced as tables 4 and 5. Some additional reduction of data has been performed in presenting these tables. For reasons

Table 4. Main effects of various factors on pH of strong acid solutions as revealed by the ruggedness test.

Solution	Electrode No.	*A* Temp	*B* Stirring	*C* Dilution	*D* Immersion Depth	*E* $NaNO_3$	*F* KCl	*G* Equil. Time
HCl	1	0.045	−0.010	0.010	0.005	0.030	0.085	0.000
H_2SO_4	1	0.025	−0.015	0.015	0.000	0.060	0.115	0.005
HCl	2	0.032	−0.025	0.015	−0.015	0.025	0.020	−0.010

Legend to Factor Levels

Factor	+	−
A	25 °C	30 °C
B	Stirred	Not stirred
C	0.5 mL dilution/20 mL	No dilution
D	1 cm to top	3 cm to top
E	$NaNO_3$	None added
F	KCl	None added
G	10 min	5 min

Table 5. Two-factor interactions as revealed by the ruggedness test.

Solution	Electrode	AE/BF/DG	AB/EF/CG	AF/BE/CD
HCl	1	0.005	−0.020	0.005
H_2SO_4	1	0.020	−0.040	0.020
HCl	2	0.015	0.015	0.020

The letter designation of factors in table 5 is the same as in table 4. The following is the legend to the two factor interactions:

AE: Temp. with $NaNO_3$
BF: Stirring with KCl
DG: Immersion depth with time

AB: Temp. with Stirring
EF: $NaNO_3$ with KCl
CG: Dilution with time

AF: Temp. with KCl
BE: Stirring with $NaNO_3$
CD: Dilution with immersion depth

which shall be discussed later, the results for the low ionic strength solution 99-6 are excluded from these tables. Two different combination glass/reference electrodes were used in the RT experiments. The electrode numbers are given in column 2 of tables 4 and 5. The choice of two different electrode pairs was not by design. The first electrode was broken in use.

Temperature is the first main effect listed in table 4. For electrodes 1 and 2, and for the HCl and H_2SO_4 solutions, the temperature effect in going from 30 °C to 25 °C is moderately large, about +0.035 pH. The calculated effect of the change in temperature from 30 °C to 25 °C, based strictly on the change of the Nernstian response factor, should result in a pH increase of +0.017. The observed change is of the correct sign, but the magnitude per five degrees is somewhat larger than predicted. Two possible sources of explanation for the apparently excessive temperature effect may be: 1) temperature gradients across the combination glass/reference electrode; and 2) temperature response of the residual liquid junction potential. Both of these effects are difficult to calculate theoretically. Thus for practical pH measurements, one must empirically determine the overall temperature effect. The RT experiments, in fact, performed this task.

The values for the second main effect, stirring, are about −0.015 pH for solutions 99-1 to 99-5, for the electrodes used in this RT (table 4). Solution 99-6 had such a low strength that stirring caused the results to be very erratic, and hence they were not included in table 4. In previous work [4–6], we observed for a number of different electrodes that stirring had an even greater effect than −0.015 pH. The current RT did not purposely include different electrodes as one of the variables to be studied. We believe that the small stirring effects observed in this RT are not representative of most pH electrode systems. The oscillations observed in the measured pH are caused by periodic disruption of the diffusion gradient at the liquid junction between the filling solution of the Ag, AgCl reference electrode (3.5 mol/L KCl solution) and the test solution. In the less vigorous period of the stirring cycle, the 3.5 mol/L KCl filling solution, diffuses through the ceramic plug and establishes a diffuse concentration gradient in the vicinity of the junction. In the vigorous, convective period of the stirring cycle, when the magnetic stirring bar just passes the ceramic junction region of the reference electrode, the shearing action of the stirrer creates a sharp concentration boundary at the ceramic plug-solution interface. We know that for certain geometries the oscillations of the pH readings are in phase with the rotation of the magnetic stirrer. This phenomenon is much less pronounced in the case of more concentrated acid solutions. The total ionic strength difference at the junction is not as great for the more concentrated solutions, and consequently the fluctuations are attenuated. This phenomenon is also highly dependent on the type and condition of the reference electrode junction.[3]

From both the RT and previous work, we conclude that accurate pH measurements should be performed on quiescent solutions. Of course, stirring prior to the measurement is required for homogenization of the test solution.

The third observed main effect of +0.015 pH is caused by dilution. On the basis of the 2.5% concentration change due to dilution, the calculated pH showed increase by 0.011 pH. Dilution is one of the few pH measurement effects which can be clearly calculated from theory. Excellent agreement with the RT measurements is obtained.

As can be seen, in table 4, the fourth factor, the electrode immersion depth produces little effect. No significant difference in pH values as a function of the electrode immersion depth of 1 and 3 cm could be detected.

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[3] In the course of publishing this study, there appeared a new article [7] reporting the behavior of nine different glass electrodes with different reference electrodes and different junctions. This new study also showed large and variable liquid junction effects. The general conclusions reached are complementary to our study.

The fifth and sixth main effects are due to addition of neutral salts (0.033 mol/L $NaNO_3$ and 0.067 mol/L KCl). These effects are quite pronounced. For electrode 1, we observed that the addition of KCl has a greater effect than the addition of $NaNO_3$. It should be noted that the molar concentration of the added KCl is exactly twice that of $NaNO_3$. As one would expect from theory, and as observed for electrode 1, the additions of salts have a greater effect on the H_2SO_4 than on the HCl solutions. The presence of doubly charged sulfate ion is to a large extent responsible for the different behavior of the two acids, since activity coefficients for chloride and sulfate at a given ionic strength are quite different. For electrode 2, the $NaNO_3$ salt effect is qualitatively similar to that observed for electrode 1. The KCl salt effect, however, is much smaller. All of the observed salt effects are the result of many experiments and were reproducible over the extended (two month) period of the RT experiments [2]. Nevertheless, the observed salt effects are not in close agreement with the effects calculated from the Debye-Hückel equation. It is obvious that the glass/reference electrodes are not behaving ideally.

In attempting to rationalize the differences in the observed salt effects with electrodes 1 and 2, a limited number of auxiliary experiments were conducted a year later with electrode 2. These experiments indicate that the apparent salt effects had changed appreciably. We conclude that the use of added salts to low ionic strength solutions for pH measurements is an unacceptable practice.

The seventh factor, G, namely equilibration time was measured at three levels, 1, 5 and 10 min after the immersion of the electrode into the test solution. The analyses of two sets of data (1 and 5 min; 5 and 10 min) show that 1 min is not sufficient time for equilibrium condition to be established. Therefore, the data which are considered and discussed here for the ruggedness tests refer to 5 minute and 10 minute equilibration times as the two levels of factor G. Little difference is observed between the 5- and 10-min equilibration times.

In summary, we conclude that the following three main effects are of practical importance: 1) temperature, 2) stirring, and 3) the addition of $NaNO_3$ and KCl.

Besides the observed large main effects, there are three sets of moderate size two-factor interactions (2FI), summarized in table 5. Our intent is to examine such 2FI and ascribe, if possible, some physical interpretation to these interactions. These 2FI are of the same magnitude, on the order of 0.020 pH.

It can be seen in table 5, that the identified interactions are not unique, but rather they consist of three groups of three possible 2FI: *AE/BF/DG; AB/EF/CG; AF/BE/CD*. The first group consists of the following possible interactions: temperature with $NaNO_3$, stirring with KCl, and immersion depth with time. The first and the third 2FI do not appear to be reasonable candidates. There appears to be no logical reason for an interaction between temperature and $NaNO_3$. For the third 2FI, both the immersion depth and equilibration time are negligible main effects, and therefore the associated 2FI is not considered likely. We attribute the first group's 2FI to stirring with KCl.

The second group consists of temperature with stirring, $NaNO_3$ with KCl, and dilution with time. Temperature with stirring does not appear to be a physically viable interaction candidate, while the interaction due to the two added salts is quite plausible, and shall be discussed shortly. Dilution and equilibration time are negligible main effects, so that we choose to rule out this third 2FI candidate.

The third group 2FI candidates are: temperature with KCl, stirring with $NaNO_3$, and dilution with immersion depth. Here, as with the first group, temperature with salt does not appear to be physically reasonable, and the diluiton and immersion depth are negligible main effects. Thus, we choose stirring with $NaNO_3$ as the likely 2FI. Since these two factors have appreciable, opposing main effects, which by no means bear any simple relationship, it is not surprisingly that a two-factor interaction is observed.

The two-factor interactions observed between the two salts may be partially explained by the ionic strength effect on the mean activity coefficient. The mean activity coefficient is a nonlinear function of the molality, with decreasing slope at higher molalities [3]. Thus, the overall effect of the addition of the two salts is less than additive. Taking out a single factor (main effect) for each of the salts, overcompensates when two salts are added. Thus the opposite sign effect is anticipated. Indeed for electrode 1 (table 5) the $NaNO_3$ and KCl two-factor interaction (2FI) is negative. We do not at present know why the corresponding 2FI for electrode 2 is positive.

For electrode 2 we do note that the main effect for KCl is small and out of line with the other KCl and $NaNO_3$ main effects (see table 4). Since the reference electrode is filled with 3.5 mol/L KCl solution, this suggests that perhaps the difference in the structure of the two liquid junctions of the two reference electrodes is responsible for the observed differences. Since the two electrodes exhibit different main effects, it is not surprising that some of the 2FI for the two electrodes are also different.

From the RT we infer that one must be very cautious in choosing the calibration standards for dilute strong acid measurements. These standards should closely simulate the system of interest because there are a number of unexplained, observed effects which can only be excluded from the measured value through calibration with a similar standard. This aspect of pH measurement is treated in detail in [8].

Having established the magnitude of the influence of the various factors on measured pH, we combined the RT data with calibration data obtained by using the strong acid reference solution SA83 1000. These data are summarized in the table 6. The normalized pH results are in reasonable agreement. The deviations given in the last column of table 6 are generally small. The largest deviation of +0.063 pH is approximately equal to two standard deviations for the between the laboratory component of variability observed in our interlaboratory study [8].

Table 6. Measured normalized pH of five acid solutions.

Solution	pH Normalized to SA83 1000	pH (calc.)	ΔpH
99-1	4.294	4.293	+0.001
99-2	3.557	3.586	−0.029
99-3	3.698	3.685	+0.013
99-4	4.366	4.303	+0.063
99-5	3.028	3.015	+0.013

Conclusions

Stirring has an adverse effect on the measurement of pH of dilute acid solutions. Stirring not only amplifiesthe random noise but also biases the measured values. Moderate temperature control (±0.5 °C) is sufficient for maintaining measurements accurate to 0.01 pH. Addition of neutral salts ($NANO_3$ or KCl) can not be tolerated in accurate pH measurements, as these salts change not only the mean activity coefficients of solutions, but also unpredictably change the electrode behavior and hence the measured pH. The ruggedness tests have revealed, in addition to the above main effects, three 2FI. These 2FI could not be determined from an experiment which changed only one factor at a time.

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