Statistical Analysis of pH Measurements

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Abstract
This paper used three-way Analysis of Variance to investigate precision and accuracy in pH measurements. PH meters were calibrated at 20°C using pH 4, 7 and 10 buffers. Experimental design utilized three acidity levels, three pH electrodes, three potentiometers, and three-fold replication pH measurement. Fisher 5% level F tests revealed that pH variation was statistically significant with respect to acidity (F_{crit} = 4.46 < F_{exp} = 2.63x10^4) but insignificant in regard to both potentiometer (F_{crit} = 4.46 > F_{exp} =1.19) and electrode (F_{crit} = 4.46 > F_{exp} = 1.18). All two-way interactions were statistically insignificant: acidity/potentiometer (F_{crit} = 3.84 > F_{exp} = 0.141), acidity /electrode (F_{crit} = 3.84 > F_{exp} = 1.537), and electrode /potentiometer (F_{crit} = 3.84 > F_{exp} = 0.869). The 95% level confidence intervals for pH, 3.976 ≤ pH ≤ 4.019, 6.976 ≤ pH ≤ 7.025, and 10.033 ≤ pH ≤ 10.081, agreed with standard buffer pH, 4.00, 7.00 and 10.06 at 20°C. Errors in pH in order of increasing pH were – 0.0475%, 0.0106% and – 0.0328%. Coefficients of variation in order of increasing pH were 1.391, 0.918 and 0.593.

Key Words: pH measurement, accuracy, precision, Analysis of Variance

1. Introduction

Because acidity level is an important property of aqueous solutions, the pH meter is one of the most used instruments in the quantitative analysis laboratory. In order to determine if pH depended differently upon samples, three pH meters and potentiometers were calibrated at 20°C using standard pH 4, 7 and 10 buffers, and used to determine pH of three unknowns of different acidity levels. The collected data was subjected to analysis of variance (ANOVA) to identify significant pH variability. The dependent variable was pH, and independent variables were potentiometers, electrodes and sample acidity.

2. Materials, instruments and experimental procedure

Three potentiometers, three electrodes, three standard buffers of pH 4, 7 and 10, a Celsius thermometer and de-ionized H_2O were used. Data collection consisted of the following steps.

a. Calibrate pH meters with electrodes
b. Measure pH of each unknown three times with each pH meter.
c. Switch electrode/potentiometer combinations and repeat steps a and b.
d. Repeat steps c until each of the three electrodes and three potentiometers have been used.

3. Calculations

Availability of computer programs for statistical and other types of calculations were key to the successful of completion of this research project.

3.1 ANOVA Calculations

The independent variables (called factors) were potentiometers, electrodes and acidity levels. The dependent variable was measured mean pH. The number of potentiometers a = 3, number of acidity levels b = 3, and number of electrodes c = 3. The twenty-seven pH means given in Table 1 were obtained using three-fold replications. The dependent variables $X_{i,j,k}$ were these twenty-seven pH sample means $<X>$ and sample standard deviations S_X. Data analysis proceeded as follows. First the grand mean $<X>_{...}$, sample standard deviation S_X and its number of degrees of freedom, DF_X were calculated.

$$<X>_{...} = 1/abc \sum\sum\sum X_{i,j,k} = 7.021, \quad S_X = 165.805, \quad DF_X = 26$$

This was an average over three main factor variables $X_{i,j,k}$, potentiometers, acidity levels and electrodes. The S_X had 26 degrees of freedom, DF_X = a x b x c -1. Next, partial means (sums over two indices) and sample standard deviations were calculated. Here, the presence of the two dots indicates that averages over the levels of two specific factors, as indicated by the position of the two dots, were calculated.

3.2 Dependence of pH variability upon potentiometers

Averages over acidity levels and electrodes, $\{<X>\} = \{<X>_{i..}\} = \{1/bc\sum\sum X_{i,j,k}\}$, and standard deviations S_X were calculated for each potentiometer level. Nine, N = bxc, values of mean pH were used to calculate $<X>$ and S_X. This S_X had degrees of freedom, DF_X = bxc –1 = 8. $<X>$ and S_X for the potentiometers are presented in Table 2. Using the $<X>$ and S_X given in Table 2 with One-Way ANOVA provided between groups variance S_{BG}^2 and within groups variance S_{WG}^2. Variance S_{BG}^2 had degrees of freedom, DF_{BG} = a -1 = 2, and variance S_{BG}^2 had degrees of freedom, DF_{WG} = a (bc -1) = 24. Fisher quotients, $F_{Exp} = S_{BG}^2 / S_{WG}^2$ were calculated and compared to 5% level critical F quotient values taken from Fisher's Statistics Table[1]. One-Way ANOVA for pH variability related to potentiometer gave experimental Fisher quotient $F_{Exp} = (S_{BG}/S_{WG})^2 = 6.067x10^{-4}$, critical $F_{Crit} = 3.4$ for a 5% level F_{test}, within groups $S_{WG} = 2.638$ and between groups $S_{BG} = 0.0497$.

3.4 Dependence of pH variability upon acidity levels

One-Way ANOVA analysis for pH variability for acidity level was similar to that for the potentiometer factor. The averages $\{<X>\} = \{<X>_{\bullet j \bullet}\} = \{1/ac\sum\sum X_{i,j,k}\}$, and standard deviations S_X calculated over potentiometers and electrodes are given in Table 3. One-way ANOVA for this pH variability in the acidity levels gave $N_X = ac = 9$, $DF_X = ac - 1 = 8$, $DF_{BG} = b-1 = 2$, and $DF_{WG} = b(ac-1) = 24$. For denominator, $S_{WG} = 0.06025$ and numerator, $S_{BG} = 9.202$, Fisher F quotient, $F_{Exp} = (S_{BG}/S_{WG})^2 = 2.26810^{+4}$ and $F_{Crit} = 3.4$.

3.5 Dependence of pH variability upon electrodes

Averages over acidity and potentiometers factor levels, $\{<X>\} = \{<X>_{\bullet\bullet k}\} = \{1/ab\sum\sum X_{i,j,k}\}$, and standard deviations S_X calculated for each electrode are given in Table 4. One-way ANOVA of variability related to these electrodes gave $N_X = ab = 9$, $DF_X = ab - 1 = 8$, $DF_{Num} = DF_{BG} = c - 1 = 2$, $DF_{Denom} = DF_{WG} = c(ab - 1) = 24$, $S_{WG} = 2.628$, $S_{BG} = 0.06683$, $F_{Exp} = (S_B/S_W)^2 = 6.466x10^{-4}$ and $F_{Crit} = 3.4$.

3.6 pH variability with respect to potentiometer and acidity

Next, more partial means (sums over single indices) were calculated. Here, the presence of the single dot indicates that an average over the c = 3 levels of the electrode factor variable, as indicated by the position of the dot, were calculated. The required averages, $\{<X>_{i,j\bullet}\} = \{1/c \sum X_{i,j,k}\}$, over three electrodes were calculated. The calculated pH means and Two-Way ANOVA analysis results are given in Table 5. Three Fisher F quotients were calculated, F_A for potentiometer, F_B for acidity level and another F_{AB} for potentiometer/acidity level interaction. These experimental F quotients, numerator and denominator degrees of freedom and Fisher critical F quotients at 5% probability are given in Table 5.

3.7 pH variability with respect to potentiometer and electrodes

Two-way ANOVA analysis for pH variability arising in potentiometers and electrodes was similar to that for potentiometers/acidity levels. From the averages, $\{<X>_{i,\bullet,k}\} = \{1/b \sum X_{i,j,k}\}$ determined for b = 3 acidity levels were calculated Fisher F quotients, F_A for potentiometer, F_C for electrode level and F_{AC} for potentiometer/electrode level interaction. These experimental F quotients, numerator and denominator degrees of freedom, and 5% level critical Fisher quotients are given in Table 6.

3.8 pH variability with respect to acidity and electrodes

Two-way ANOVA for pH variability with respect to acidity and electrodes was similar to that for potentiometer/acidity and potentiometer/electrode. The required averages, $\{<X>_{\bullet j,k}\} = \{1/a \sum X_{i,j,k}\}$, determined over electrodes, and Two-Way ANOVA analysis results are given in Table 7.

3.9 Sum of squared deviations

Next the sums of squared deviations from the grand mean **<X>…** was calculated.

$$SS_T = \sum\sum\sum (X_{i,j,k} - <X>_{\bullet\bullet\bullet})^2 = 165.805$$

Sum of the squares of deviations of $X_{i,j,k}$ from the grand mean, SS_T was divided up into several partial sum of squared deviation contributions, $SS_T = SS_A + SS_B + SS_C + SS_{AB} + SS_{AC} + SS_{BC} + SS_{ABC}$.

$SS_A = bc \sum (\langle X\rangle_{i\bullet\bullet} - \langle X\rangle_{\bullet\bullet\bullet})^2 = 4.892\text{x}10^{-3}$,
$SS_B = ac \sum (\langle X\rangle_{\bullet j\bullet} - \langle X\rangle_{\bullet\bullet\bullet})^2 = 1.652\text{x}10^{+2}$,
$SS_C = ab \sum (\langle X\rangle_{\bullet\bullet k} - \langle X\rangle_{\bullet\bullet\bullet})^2 = 8.428\text{x}10^{-3}$,
$SS_{AB} = c \sum\sum (\langle X\rangle_{i,j\bullet} - \langle X\rangle_{i\bullet\bullet} - \langle X\rangle_{\bullet j\bullet} + \langle X\rangle_{\bullet\bullet\bullet})^2 = 2.005\text{x}10^{-3}$,
$SS_{AC} = b \sum\sum (\langle X\rangle_{i\bullet k} - \langle X\rangle_{i\bullet\bullet} - \langle X\rangle_{\bullet\bullet k} + \langle X\rangle_{\bullet\bullet\bullet})^2 = 1.238\text{x}10^{-2}$,
$SS_{BC} = a \sum\sum (\langle X\rangle_{\bullet j,k} - \langle X\rangle_{\bullet j\bullet} - \langle X\rangle_{\bullet\bullet k} + \langle X\rangle_{\bullet\bullet\bullet})^2 = 7.300\text{x}10^{-2}$,
and
$SS_{ABC} = \sum\sum\sum(X_{i,j,k} - \langle X\rangle_{i,j\bullet} - \langle X\rangle_{i\bullet k} - \langle X\rangle_{\bullet j,k} + \langle X\rangle_{i\bullet\bullet} + \langle X\rangle_{\bullet j\bullet} + \langle X\rangle_{\bullet\bullet k} - \langle X\rangle_{\bullet\bullet\bullet})^2 = 2.850\text{x}10^{-2}$

3.10 Degrees of freedom

Each of these sum of squared-deviations had statistical degrees of freedom. DF_T = abc-1, DF_A = a-1, DF_B = b-1, DF_C = c-1, DF_{AB} = (a-1) (b-1), DF_{AC} = (a-1) (c-1), DF_{BC} = (b-1) (c-1) and DF_{ABC} = (a-1) (b-1) (c-1).

3.11 Three-Way ANOVA Fisher quotients

Calculating the square-root of the variance (SS/DF) gave the corresponding standard-deviations, $S = (SS/DF)^{1/2}$ which were used to calculate experimental Fisher F quotients reported in Table 8 and defined as follows: $F_A = (S_A/S_{ABC})^2$, $F_B = (S_B/S_{ABC})^2$, $F_C = (S_C/S_{ABC})^2$, $F_{AB} = (S_{AB}/S_{ABC})^2$, $F_{AC} = (S_{AC}/S_{ABC})^2$ and $F_{BC} = (S_{BC}/S_{ABC})^2$. Main factor F quotients F_A, F_B and F_C and between-factor interaction F quotients, F_{AB}, F_{AC} and F_{BC} were calculated. Experimental F quotients were compared to the critical F values obtained from Fisher Statistics[1, 2] Tables at chosen 5% probability level according to the above numerator and denominator degrees of freedom used to calculate the experimental F quotients. Each Statistical Null Hypothesis H0 stated that the pH variability was insignificant. The Alternative Hypothesis stated that pH variability was significant. A Null Hypothesis H0 was accepted if $F_{exp} \leq F_{crit}$ and Alternative Hypothesis H1 was accepted if $F_{exp} > F_{crit}$.

4. Discussion

This paper investigated accuracy and precision of pH measurement using standard buffers (4, 7 and 10), three potentiometers, three pH electrodes, three acidity levels and ANOVA methods.

4.1 ANOVA results

The ANOVA analysis determined the significance of both main and interaction effects upon measured pH variability for the potentiometer, acidity and electrode factors. One-Way, Two-Way and Three-Way ANOVA were used.

4.1.1 Main effects

The main factor variables were potentiometers, acidity levels and electrodes.

Potentiometers

Averaging over both acidity levels and electrodes revealed that pH variability introduced by changing potentiometers was quite small: $\{\langle X\rangle_{i\bullet\bullet}\} = \{1/bc \sum\sum X_{i,j,k}\} = \{7.033, 7.034, 6.997\}$. In the ANOVA analysis potentiometer was referred to as Factor #A, and its statistical Null Hypothesis H0 was accepted because observed variations in mean pH with respect to potentiometers were not significant: One-Way ANOVA ($F_{exp} = 0.0 < F_{Crit} = 3.4$), Two-Way ($F_{exp} = 1.07$ and $0.0 < F_{Crit} = 3.55$), and Three-Way ($F_{exp} = 1.19 < F_{Crit} = 4.46$).

Acidity levels

Averaging over both potentiometer and electrode levels revealed that pH variability introduced by changing the acidity levels was quite large: $\{\langle X\rangle_{\bullet j \bullet}\} = \{ 1/ac \sum\sum X_{i,j,k} \} = \{3.998, 7.007, 10.066\}$. The ANOVA analysis was for acidity level Factor variable B. The Alternative Statistical Hypothesis H1 for variability in acidity level was accepted. Observed variations in mean pH with respect acidity level were significant: One-Way ($F_{Exp} = 2.27x10^{+4} > F_{Crit} = 3.4$), Two-Way ($F_{Exp} = 2.90x10^{+4}$ and $2.04x10^{+4} > F_{Crit} = 3.55$), and Three-Way ($F_{Exp} = 2.63x10^{+4} > F_{Crit} = 4.46$).

Electrodes

Averaging over both acidity levels and potentiometers revealed that pH variability introduced by changing electrodes was insignificant: $\{\langle X\rangle_{\bullet\bullet k}\} = \{1/ab \sum\sum X_{i,j,k} \} = \{7.007, 7.010, 7.046\}$. The ANOVA analysis referred to this variable as Factor C, and its statistical Null Hypothesis was H0 accepted. Observed variations in mean pH with respect to electrodes were insignificant: One-Way ($F_{Exp} = 0.0 < F_{Crit} = 3.4$),
Two-Way ($F_{Exp} = 1.49$ and $0.0 < F_{Crit} = 3.55$) and Three-Way ($F_{Exp} = 1.181 < F_{Crit} = 4.46$).

4.1.2 Interaction effects

The three interactions examined were potentiometer/electrode, potentiometer/acidity, and acidity/electrodes.

Potentiometer/acidity interaction

Accept Null Hypothesis H0. Interaction effects upon variations in mean pH with respect to potentiometers and acidity level were insignificant: Two-Way ($F_{Exp} = 0.139 < F_{Crit} = 2.96$) and Three-Way ($F_{Exp} = 0.141 < F_{Crit} = 3.84$).

Potentiometer/electrode interaction

Accept Null Hypothesis H0. Interactions effect upon variations in mean pH with respect to potentiometer and electrode were insignificant: Two-Way ($F_{Exp} = 0.0 < F_{Crit} = 2.96$) and Three-Way ($F_{Exp} = 0.869 < F_{Crit} = 3.84$).

Acidity/electrode interaction

Accept Null Hypothesis H0. Interactions effect upon variations in mean pH with respect to electrodes and acidity levels were insignificant: Two-Way ($F_{Exp} = 1.92 < F_{Crit} = 2.96$) and Three-Way ($F_{Exp} = 1.54 < F_{Crit} = 3.84$)

4.2 Accuracy of pH measurement

The 95% level confidence intervals for measured pH, namely $3.976 \leq pH \leq 4.019$, $6.976 \leq pH \leq 7.025$, and $10.033 \leq pH \leq 10.081$, agreed well with the standard buffer pH, namely 4.00, 7.00 and

10.06 at 20°C. The determined errors in pH (in order of increasing pH) were - 0.0475%, 0.0106% and - 0.0328%.

4.3 Precision of pH measurement

The mean pH, <X> and its sample standard deviation S_X were used to calculate coefficients of variation, CV = 100 S_X/<X>. In order of increasing pH the CVs were 1.391, 0.918 and 0.593, respectively.

5. Conclusion

ANOVA statistical methods provided convenient methods to identify significant changes in pH. Fisher 5% level F_{tests} analysis of the data indicated that pH variation was definitely significant with respect to acidity level ($F_{crit} = 4.46 < F_{exp} = 2.63x10^4$) but not so with respect to potentiometer ($F_{crit} = 4.46 > F_{exp} = 1.19$) and electrode ($F_{crit} = 4.46 > F_{exp} = 1.18$). Acidity/potentiometer ($F_{crit} = 3.0 > F_{exp} = 0.50$), acidity/electrode ($F_{crit} = 3.84 > F_{exp} = 1.53$), and potentiometer/electrode ($F_{crit} = 3.84 > F_{exp} = 0.869$) outcomes revealed absence of statistically significant interactions. Accuracy and precision of pH measurement indicated that the instruments were producing reliable acidity data. The 95% level confidence intervals for measured pH, namely $3.976 \leq pH \leq 4.019$, $6.976 \leq pH \leq 7.025$, and $10.033 \leq pH \leq 10.081$, agreed well with the standard buffer pH, namely 4.00, 7.00 and 10.06 at 20°C. Percent error in measured pH (in order of increasing pH) were-0.0475%, 0.0106% and - 0.0328%. Finally, coefficients of variation for pH precision (in order of increasing pH) were 1.391, 0.918 and 0.593, respectively.

Table 1. Mean pH versus potentiometer, electrode and acidity level

Pt#	El#	Level #1	Level #2	Level #3
1	1	3.963	6.963	10.167
1	2	4.047	7.023	10.077
1	3	4.053	7.007	10.000
2	1	3.993	6.993	10.013
2	2	4.023	6.927	10.103
2	3	4.013	7.147	10.097
3	1	3.910	6.967	10.097
3	2	3.923	6.953	10.017
3	3	4.053	7.023	10.023

Table 2. pH dependence on the potentiometer factor

	$Pt_{\#1}$	$Pt_{\#2}$	$Pt_{\#3}$
N_X=bc	9	9	9
DF_X = (bc-1)	8	8	8
<X>	7.033	7.034	6.996
S_X	2.625	2.653	2.635

Table 3. pH dependence on the acidity level factor

	$pH_{\#4}$	$pH_{\#7}$	$pH_{\#10}$
N_X=ac	9	9	9
DF_X = (bc-1)	8	8	8
<X>	3.998	7.000	10.066
S_X	0.0547	0.0696	0.0559

Table 4. pH dependence on the electrode factor

	$El_{\#1}$	$El_{\#2}$	$El_{\#3}$
N_X=ab	9	9	9
DF_X = (ab-1)	8	8	8
<X>	7.007	7.010	7.046
S_X	2.658	2.628	2.599

Table 5. pH dependence on potentiometer and acidity factors

	Acidity levels			
Potentiometers	**4**	**7**	**10**	
#1	4.021	6.998	10.081	**<X>**
	0.0503	0.0311	0.0836	S_X
#2	4.010	7.022	10.071	**<X>**
	0.0153	0.113	0.0501	S_X
#3	3.962	6.981	10.046	**<X>**
	0.0791	0.0370	0.0446	S_X

Two-Way ANOVA for pH variability

	F_{Exp}	F_{Crit}(5%)	DF_{Num}	DF_{Denom}
Potentiometer	1.0667	3.55	(a-1) = 2	ab(c-1) = 18
Acidity	$2.034\times10^{+4}$	3.55	(b-1) = 2	ab(c-1) = 18
Pot/acidity	0.1382	2.96	(a-1)(b-1) = 4	ab(c-1) = 18

Table 6. pH dependence on potentiometers and electrodes

	Electrodes			
Potentiometers	**#1**	**#2**	**#3**	
#1	7.031	7.049	7.020	**<X>**
	3.103	3.015	2.974	**S_X**
#2	7.000	7.018	7.086	**<X>**
	3.010	3.041	3.042	**S_X**
#3	6.991	6.964	7.033	**<X>**
	3.094	3.047	2.985	**S_X**

Two-Way ANOVA for pH variability

	F_{Exp}	F_{Crit}(5%)	DF_{Num}	DF_{Denom}
Potentiometer	$4.708\text{x}10^{-4}$	3.55	(a-1) = 2	ac(b-1) = 18
Electrode	$4.603\text{x}10^{-4}$	3.55	(c-1) = 2	ac(b-1) = 18
Pot/Electrode	$3.367\text{x}10^{-4}$	2.96	(a-1)(c-1) = 4	ac(b-1) = 18

Table 7. pH dependence on acidity levels and electrodes

Acidity levels	**Electrode levels**			
	#1	**#2**	**#3**	
4	3.955	3.998	4.040	<X>
	0.0421	0.0658	0.0231	S_X
7	6.974	6.968	7.079	<X>
	0.0163	0.0497	0.0766	S_X
10	10.092	10.066	10.040	<X>
	0.0771	0.0441	0.0507	S_X

Two-Way ANOVA for pH variability

	F_{Exp}	F_{Crit}(5%)	DF_{Num}	DF_{Denom}
Acidity	$2.902\text{x}10^{+4}$	3.55	(b-1) = 2	bc(a-1) = 18
Electrode	1.488	3.55	(c-1) = 2	bc(a-1) = 18
Electrode/Acidity	1.921	2.96	(b-1)(c-1) = 4	bc(a-1) = 18

Table 8. Three-way ANOVA chart for %5 level Ftest

Factor	SS	DF	F_{exp}	F_{crit}	Significant
$A_{Potentiometer}$	$8.492x10^{-3}$	2	1.192	4.46	No
$B_{Acidity}$	165.723	2	$2.626x10^{4}$	4.46	Yes
$C_{Electrode}$	$8.428x10^{-3}$	2	1.181	4.46	No
AB	$2.005x10^{-3}$	4	0.141	3.84	No
AC	$1.238x10^{-2}$	4	0.869	3.84	No
BC	$2.190x10^{-3}$	4	1.537	3.84	No
Within	$2.850x10^{-2}$	8			
Total	165.805	26			

Table 9. Accuracy and precision of pH measurements [A, B]

Level	<pH>	S_{pH}	CV_{pH}	% Error	95% Confidence interval
#1	3.998	0.05561	1.391	-0.0475	$3.971 \le pH \le 4.021$
#2	7.000	0.06400	0.914	0.0106	$6.975 \le pH \le 7.026$
#3	10.057	0.05961	0.593	-0.0328	$10.033 \le pH \le 10.080$

[A] Mean of 27 pH measurements, S_{pH} sample standard deviation, CV_{pH} coefficient of variation, percent error, 95% level pH confidence interval.
[B] Calibration buffers: pH 4.00, 7.00 and 10.06 at 20 ^{o}C.

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