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Modification in pH measurements for getting accurate pH values with different pH meters irrespective of aging and drifts in the meters

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Abstract: pH meters are widely used to measure the pH of water, solutions and environmental samples. Accurate results of pH values can help to understand the course of reactions in various chemical and biochemical processes. Normally the pH meters are set for three buffers nearer to 7.0, 9.2 and 4.0 pH values. Linearity is established in this range and the measurements will be accurate. If there is any drift, control knobs are provided to standardize the meter with pH buffers. However due to aging of the meter or electrode, the meter may not be set to the theoretical values of the pH buffers using the control knobs. In such situations, it is necessary to get accurate results independent of the drift in the meter. For this, certain modifications in procedure are proposed and the laboratories can still maintain the accuracy in results. While measuring pH values in the field, the recommended procedure can be followed assertively without concerning for the condition of the meter. Experiments were conducted using Hanna and Radiometer pH meters which were very aged. The meter readings were noted for three pH buffers (viz. 4.0, 7.0 and 9.2) by turning the control knobs and bringing the readings to the nearest of the theoretical values of the pH buffers. The pH of nine other buffers and 20 natural water samples were measured and calculations were used to arrive at their correct pH values. The modification proposed is particularly useful to measure the pH values in rural labs and in the field where service support is not readily available.

Key words: pH, pH electrode, pH buffer, pH meter, pH measurement, pH error, pH accuracy, aging of pH meter, pH meter drift.

Introduction

pH value or range is of immense importance for any chemical reaction. A chemical shall be highly effective at a particular pH. Chemical coagulation, disinfection, water softening and corrosion control are governed by pH adjustment. In anaerobic treatment below pH 5.0, acids accumulate and the process is severely affected. Shifting of pH beyond 5 to 10 upsets the aerobic treatment of the wastewater. Dewatering of sludges, oxidation of cyanides and reduction of hexavalent chromium need a favorable pH range. High values of pH hasten the scale formation and reduce germicidal potential of chlorine.

A practical pH scale is based on use of combined glass electrodes together with pH buffers[1]. Artur Dybko, et.al have reported about a pH sensor that exhibits a linear working range within 6.9-9.5 which can cover typical changes of water[2]. Wen-Yaw Chung.et.al discuss about a two-point calibration based on standard pH 4 and 7 buffers for measurement of correct pH value[3].

pH buffer solutions are the reference of our pH measurements and the pH result can be as good as the pH buffers used for calibration[4]. Cheng K L, et.al. discuss about some commonly encountered errors in pH meter calibrations. For purposes of greater accuracy it is necessary to carry out a portion of the calibration curve near the sample pH using known buffers. In strong acid, strong alkaline and neutral regions, the pH meter show non-linear deviations[5].

Each pH electrode used for measurements is slightly different and its characteristics changes with aging. pH meter calibration procedure calls for use of two or three pH calibration buffers of exactly known pH. Some pH meters recognize buffer automatically and perform calibration on its own or knobs are used to set the meter for each pH buffer. Here linear dependence between pH and electrode voltage is assumed[6].

The pH meters need periodic calibration and each time the meter is calibrated, the meter assigns a new set of values to the voltage measured in milli volts. Initially the drift will be small but as the electrode ages the drift exceeds -30 to -35mV and the electrode becomes unstable. A pH meter should be calibrated at a minimum of two points and the common points are values of pH 7.01 and 4.01 or 7.01 and 10.01. If the user wants to measure a solution which has value between 3.00 and 4.00, he should calibrate at 3.00 and 7.01 rather than 4.01 and 7.01. Further certain precautions like proper rinsing, dabbing the bottom of the sensitive glass with a soft paper tissue, etc. are required. If an electrode is dirty or clogged with oil, grease, debris, etc. it will still yield a digital result. The reading more than likely will not be correct. The electrode when not in use should be immersed in a solution whose salt concentration is same as that inside the electrode[7].

Some factors like asymmetry potential of glass electrode, liquid junction potential of cell and clogging of glass electrode diaphragm lead to systematic errors in pH measurement results[8].

Calibrating with buffers that lie within the pH measuring range increases the accuracy of the measurement. Stirring during calibration process plays a big role.

By reducing the measurement range with respect to both pH values, it becomes possible to raise the precision of pH measurement, owing to a reduction in the values of pH_{act}-pH_{bf} [9].

Multi-point calibration is recommended if minimum uncertainty and maximum consistency are required over a wide range of unknown pH values[10]. Gunther Meinrath, et. al. have given a statistical analysis of multi-point calibration procedure for practical measurement of pH[11]. Multiple point calibration with linear regression is highly recommended instead of the usual bracketing in cases where a precision of $\Delta pH < \pm 0.02$ is required[12].

Felix Grases.et.al. measured urinary pH using two buffer solutions[13]. A seawater pH measurement with 0.01 pH precision is reported using LED photometer and a pH sensitive indicator with a one-time calibration[14].

Rodinov.et.al. indicated the need to calibrate the pH meter with respect to standard media having electrical conductivity close to that of the medium being monitored[15].

The international initiatives to improve the consistency of the results of measurement for pH have been reported by Petra Spitzer[16].

Hydrogen ion concentration

pH is negative logarithm of the hydrogen ion activity [$pH = - \log a_{H+}$][17].

The activity is the effective concentration of the hydrogen ion that is in solution**.** However the difference between effective and actual concentration decreases when moving toward more dilute solutions in which ionic interaction becomes progressively less important.

The activity of the hydrogen ion (aH^+) is defined by its relation to concentration (C_{H+}) and the activity coefficient (f_{H+})[18].

$aH^+ = f_{H+}C_{H+.}$

If the activity coefficient is unity, then activity is equal to concentration. This is nearly the case in dilute solutions, where the ionic strength is low[19].

The factors that normally affect the activity coefficient are the temperature T, the ionic strength u, the dielectric constant $\in$, the ion charge Z_i, the size of the ion in angstroms a^o, and the density of the solvent d. All of these factors are characteristics of the solution which relate the activity to the concentration by two main effects (viz: salt effect and medium effect). Because of these influences, a sample pH value cannot be extrapolated to another temperature or dilution[20].

Potential error

Error in potential measurement can result in pH error[21]. The table below shows that a small milli volt error can cause large pH error.

Error mV	pH	Δ C/c (%)
1	0.017	3.9
4	0.068	15.6
16	0.270	62.3
32	0.541	124.6

Since the resistance of glass bulb in the electrode is very high, the meter used for pH measurement should have very high impedance. The bias current and electronics will vary with temperature and as well aging of components in the system. This can induce a significant error in the system.

In the pH versus milli volt graph the point where no change in potential is observed with respect to change in temperature is called the iso potential point. In practice this point may not lie exactly at 7.0 pH.

Temperature compensation

If the temperature compensation control is left at the standardization temperature and the sample is at a different temperature, the correct sample pH can be calculated with the formula

$pH = 7 - [T_1/T_2 (7- pH_o)]$
where, pH_o - observed pH
T_1 - Temperature of standardization
T_2 - Temperature of sample.

Both automatic and manual temperature compensation are provided on most pH meters. The ATC probe requires time to come to equilibrium with the sample, which may be greater than the time required for electrode to equilibrate[22].

Meter calibration

The pH meter is calibrated using either single point standardization with 100 % slope or two points calibration with the first point for standardization combined with the second point for a span adjustment through use of a slope control. If the sample pH values are over a pH range and a high degree of accuracy is required, a slope adjustment becomes necessary. At high pH values the electrode response of most electrodes is not ideal, the closer the sample pH value is to be the standardization point, less error will be observed[23].

Electrode errors

The resistance of glass electrodes depends on the glass composition; the hydrated conditions of the bulb, the bulb configuration or thickness, and the temperature with a high resistance glass membrane, a noisier reading and a pH error are more likely. High resistance can also be caused by decrease in temperature. The resistance of glass membrane approximately doubles for every 7°C decrease in temperature.

Absorption of proteins to the surface of the glass electrode disturbs the exchange capacity of the electrode and this can cause asymmetry potential. The magnitude of this potential varies with the pH of the solution in contact with the glass, with age, with temperature, with membrane configuration and with time. Although the electrode asymmetry potential may change slightly on day to day use, it is compensated through use of the standardization control of the pH meter. When the rate of change becomes a source of error in long-term measurements or the magnitude exceeds the capacity of the standardization control to compensate then this potential becomes a problem. It should be noted that the asymmetry potential of the glass electrode affects the iso potential point.

Another error caused is the result of sodium ion penetrating into silicon oxygen network of glass. This is called sodium ion error. Cations other than hydrogen ions contribute to the electrode potential and can give rise to measuring errors.

When the milli volt per pH unit is greater than normal value it is called as acid error. The magnitude of this error depends on pH, temperature, exposure time and size of anions in test solution.

Rejuvenation of electrodes is necessary when a lag in response, undue sensitivity to physical movement of the electrode, a short span between two buffers, or abnormal potentials (an inability to calibrate the pH meter with the standardization control). When the above indications are noted it may be due to the pH meter.

Characteristics of pH buffer

The primary parameters which will qualify a particular solution as a buffer are the buffering capacity, the effect dilution has on the buffer, the pH change with temperature, shelf life, growth of mould and absorption of CO_2.

Errors in pH measurement

Apart from the sources of errors discussed above, while making pH measurement the following difficulties are encountered and relative errors are caused:

1. The meter could not be adjusted to the set buffer values.
2. If three buffers are used for standardization, the slope is different for the two ranges covered by the buffers.
3. Improper functioning of Temperature compensation control.
4. Inadequate rinsing of electrode during measurement of pH of successive samples.
5. Scratches caused to the electrode due to rubbing with filter/tissue paper after rinse with distilled water.
6. Error in buffer (due to poor chemicals or wrong preparation)

Normally in developing countries, the service back up facilities available for the District or Provincial laboratories is not satisfactory and no remedial measure could be immediately taken. Till the meter is rectified the testing of samples could not be suspended. The following procedure can eliminate most of the errors and can yield correct pH results for samples even with a poorly functioning pH meter/pH electrode and could be followed till the pH meter is rectified or replaced.

Modification in pH measurement

The recommended procedure is as follows:

1. The meter is standardized always with three buffers preferably 7.0, 9.2 and 4.0. If the meter could not be set to the theoretical values, then record the actual values displayed for the buffers. However the respective knobs should be adjusted to get a closer pH value to the theoretical value.
2. The buffers and samples should be always taken in duplicate (one as ‘Rinse’ and another as ‘Test’). One is labeled for rinsing. Another is labeled for actual test measurement.
3. Two beakers with distilled water should be taken for at least two rinsing before measurement of actual pH for samples and buffers.

Actual measurement

After switching on the instrument and waiting for the warm up time, the electrode is dipped in $d.H_2O_{RinseI}$ and $d.H_2O_{RinseII}$. Then it is dipped in $pHBuffer7.0_{Rinse}$ and $pHBuffer7.0_{Test}$. While the electrode is in $pHBuffer7.0_{Test}$, adjust the control knob and set the meter reading to 7.0 or as closer to 7.0 as possible. Record the meter reading. The readings for $pHBuffer9.2_{Test}$ and $pHBuffer4.0_{Test}$ is also recorded after dipping them in the respective $Buffer_{Rinse}$ solutions. Now the sample readings are measured by successively dipping in the samples (each sample taken in duplicate and labeled as ‘Rinse’ and ‘Test’). The readings should be recorded only when the electrode is dipped in the ‘Test’ solutions.

Calculation

Calculations are now made as follows:

If the pH value for sample is greater than the observed pH value of 7.0 buffer,
pH of sample = [7.0 + (((pH observed for sample - pH observed for 7.0 buffer)/(pH observed for 9.2 buffer – pH observed for 7.0 buffer)) * 2.2)]
Else,
pH of sample = [7.0 – (((pH observed for 7.0 buffer – pH observed for sample)/(pH observed for 7.0 buffer – pH observed for 4.0 buffer))*3.0)]
The pH values for control I & II are also calculated as above. The results for samples are accepted only if the calculated values for ControlI and ControlII do not have a variation of ± 0.1 pH.

Excel Formula for calculation

The calculation can be made using a program in ‘EXCEL’.

If, A_1 = Observed pH for 4.00 buffer, B_1 = Observed pH for 7.00 buffer, C_1 = Observed pH for 9.20 buffer and D_1 = Observed pH for sample, then
E_1 = Calculated pH and the formula to be used is:
“=If($D_1>B_1$,(7+(((D_1-B_1)/(C_1-B_1))*2.2)),(7-(((B_1-D_1)/(B_1-A_1))*3)))”

Sample No.	A1	B1	C1	D1	E1

Results of Experiments

Buffer solutions were prepared with buffer tablets pH 7.0, 9.2 and 4.0 for setting (standardization) of pH meter.

Nine other known buffers with values 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 were also prepared as in **Table I**[24].

Table I (Clark and Lubs Buffers at 20^{o}C)

Preparation Of Standard pH	pH
5.3 mL 0.2 N HCl + 25 mL 0.2 N KCl → Diluted to 100 mL	2.0
20.32 mL 0.1 N HCl + 0.1 M $KHC_8H_4O_4$ → Diluted to 100 mL	3.0
0.40 mL 0.1 N NaOH + 50 mL 0.1 M $KHC_8H_4O_4$ → Diluted to 100 mL.	4.0
3.85 mL 0.1 N NaOH + 50 Ml 0.1 M $KHC_8H_4O_4$ → Diluted to 100 mL.	5.0
5.7 mL 0.1 N NaOH + 50 mL 0.1 M KH_2PO_4 → diluted to 100 mL.	6.0
29.63 mL 0.1 N NaOH + 50 mL 0.1 M KH_2PO_4 → Diluted to 100 mL.	7.0
46.80 mL 0.1 N NaOH + 50 mL 0.1 m KH_2PO_4 → Diluted to 100 mL.	8.0
21.30 mL 0.1 N NaOH + 50 mL 0.1M H_3BO_3 → Diluted to 100 mL.	9.0
43.90 mL 0.1 N NaOH + 50 mL 0.1 M H_3BO_3 → Diluted to 100 mL.	10.0

Measurements of pH values for the three standard buffer tablets and nine known buffer solutions were made with HANNA and RADIOMETER pH meters (**Table II**). The measurements were repeated after setting the meters for the three buffer tablets at different values (three different settings). The pHs of the nine buffers were calculated using the above formula. The calculated pHs of known buffers were close to the theoretical values as could be seen in **Table III**.

Table II Observed pH values for known buffers:

Buffer	Meter Setting						Average of observed pH values for known buffers	Variation of extreme values from middle value
	Radio meter	Radio meter	Radio meter	Hanna	Hanna	Hanna		
7.0 9.2 4.0	7.5 10.3 4.65	8.0 10.2 4.92	8.5 10.02 6.12	7.0 9.2 4.8	7.5 9.1 5.01	6.0 7.33 3.90		
Buffer	**Observed pH for Buffers**							
Buffer 2.0	2.74	2.88	4.52	3.32	3.38	2.48	3.22	± 1.02
Buffer 3.0	3.66	3.95	5.31	4.06	4.21	3.25	4.07	± 1.03
Buffer 4.0	4.69	4.94	6.16	4.88	5.02	3.93	4.94	± 1.12
Buffer 5.0	5.62	5.99	6.93	5.52	5.85	4.62	5.76	± 1.16
Buffer 6.0	6.59	6.97	7.79	6.28	6.68	5.28	6.58	± 1.26
Buffer 7.0	7.53	7.99	8.48	6.98	7.43	6.01	7.40	± 1.24
Buffer 8.0	8.71	8.98	9.23	8.01	8.22	6.71	8.29	± 1.26
Buffer 9.0	9.95	9.94	9.85	9.02	8.97	7.21	9.16	± 1.32
Buffer10.0	11.22	11.01	10.63	10.03	9.69	7.80	10.06	± 1.42

Table III Calculated pH values for known buffers:

Buffer	Meter Setting						Average of calculated ph values for known buffers	Variation of extreme values from theoretical value
	Radio meter	Radio meter	Radio meter	Hanna	Hanna	Hanna		
7.0 9.2 4.0	7.5 10.3 4.65	8.0 10.2 4.92	8.5 10.02 6.12	7.0 9.2 4.8	7.5 9.1 5.01	6.0 7.33 3.90		
Buffer	**Calculated pH for Buffers**							
Buffer 2.0	1.99	2.01	1.98	1.98	2.06	1.97	2.00	± 0.06
Buffer 3.0	2.96	3.06	2.98	2.99	3.04	3.07	3.02	± 0.07
Buffer 4.0	4.04	4.02	4.05	4.11	4.01	4.04	4.05	± 0.11
Buffer 5.0	5.02	5.04	5.02	4.98	5.01	5.03	5.02	± 0.04
Buffer 6.0	6.04	6.00	5.97	6.02	6.01	5.97	6.00	± 0.03
Buffer 7.0	7.02	6.99	6.97	6.97	6.92	7.02	6.98	± 0.03
Buffer 8.0	7.95	7.98	8.06	8.01	7.99	8.01	8.00	± 0.06
Buffer 9.0	8.93	8.94	8.95	9.02	9.02	9.00	8.98	± 0.05
Buffer10.0	9.92	10.01	10.08	10.03	10.01	9.98	10.01	± 0.08

20 natural water samples were also taken for the experiment. The observed and calculated values are recorded in **Table IV** and **Table V** respectively. The calculated values for each sample by different settings were almost same and the variations did not vary beyond ± 0.07 pH.

Table IV pH measurement – Observed readings for 20 natural water samples

Buffer	Meter Setting					
	Radiometer	Radio meter	Radio meter	Hanna	Hanna	Hanna
7.0	7.5	8.0	8.5	7.0	7.5	6.0
9.2	10.3	10.2	10.02	9.2	9.1	7.33
4.0	4.65	4.92	6.12	4.8	5.01	3.90
Sample No.	**Observed pH Readings for Samples**					
Sample1	9.02	9.14	9.33	8.17	8.33	6.71
Sample2	9.04	9.12	9.29	8.16	8.35	6.69
Sample3	9.39	9.59	9.56	8.55	8.62	6.92
Sample4	9.54	9.60	9.61	8.57	8.66	6.98
Sample5	9.46	9.57	9.60	8.52	8.59	6.93
Sample6	9.18	9.30	9.35	8.24	8.44	6.77
Sample7	9.38	9.39	9.50	8.44	8.55	6.89
Sample8	9.61	9.61	9.68	8.68	8.74	7.01
Sample9	10.18	10.22	10.05	9.20	9.13	7.33
Sample10	9.45	9.56	9.53	8.53	8.61	6.94
Sample11	9.69	9.71	9.68	8.76	8.76	7.05
Sample12	9.23	9.27	9.35	8.29	8.43	6.75
Sample13	9.08	9.23	9.31	8.20	8.38	6.71
Sample14	8.87	9.05	9.24	8.01	8.25	6.6
Sample15	8.75	9.00	9.17	7.97	8.22	6.62
Sample16	9.17	9.30	9.41	8.25	8.47	6.76
Sample17	9.14	9.17	9.34	8.22	8.41	6.75
Sample18	9.18	9.19	9.39	8.26	8.45	6.78
Sample19	8.86	9.06	9.18	8.00	8.25	6.61
Sample20	9.47	9.54	9.56	8.52	8.62	6.93

Table V Calculated pH values for samples:

Buffer	Meter Setting						Average pH for Sample	Variatio nin pH
	Radiometer	Radio meter	Radio meter	Hanna	Hanna	Hanna		
7.0	7.5	8.0	8.5	7.0	7.5	6.0		
9.2	10.3	10.2	10.02	9.2	9.1	7.33		
4.0	4.65	4.92	6.12	4.8	5.01	3.90		
Sample No.	**Calculated pH for Samples**							
1	8.19	8.14	8.20	8.17	8.14	8.17	8.17	±0.03
2	8.21	8.12	8.14	8.16	8.17	8.14	8.16	±0.05
3	8.49	8.59	8.52	8.55	8.54	8.52	8.53	±0.05
4	8.60	8.60	8.61	8.57	8.60	8.62	8.60	±0.03
5	8.54	8.57	8.59	8.52	8.50	8.54	8.54	±0.05
6	8.32	8.30	8.23	8.24	8.29	8.27	8.28	±0.05
7	8.48	8.39	8.45	8.44	8.44	8.47	8.45	±0.05
8	8.66	8.61	8.71	8.68	8.71	8.67	8.67	±0.05
9	9.11	9.22	9.24	9.20	9.24	9.20	9.20	±0.07
10	8.53	8.56	8.49	8.53	8.53	8.55	8.53	±0.04
11	8.72	8.71	8.71	8.76	8.73	8.74	8.73	±0.03
12	8.36	8.27	8.23	8.29	8.28	8.24	8.28	±0.07
13	8.24	8.23	8.17	8.20	8.21	8.17	8.20	±0.04
14	8.08	8.05	8.07	8.01	8.03	7.99	8.04	±0.05
15	7.98	8.00	7.97	7.97	7.99	8.03	7.99	±0.03
16	8.31	8.30	8.32	8.25	8.33	8.26	8.30	±0.04
17	8.29	8.17	8.22	8.22	8.25	8.24	8.23	±0.06
18	8.32	8.19	8.29	8.26	8.31	8.29	8.28	±0.02
19	8.07	8.06	7.98	8.00	8.03	8.01	8.03	±0.05
20	8.56	8.54	8.53	8.52	8.54	8.54	8.54	±0.02

Stability of readings

It is noted that the time taken to attain stability of reading varies in each measurement (**Table IV**). It differs from meter to meter and also setting to setting. There is also no correlation between the electrical conductivity and time for stability.

Table VI pH Measurement – Time in seconds to get stable pH readings

Buffer		**Meter Setting**					
		Radio meter	**Radiometer**	**Radio meter**	**Hanna**	**Hanna**	**Hanna**
7.0		7.5	8.0	8.5	7.0	7.5	6.0
9.2		10.3	10.2	10.02	9.2	9.1	7.33
4.0		4.65	4.92	6.12	4.8	5.01	3.90
Sample No.	**E.C for sample (micS/ cm)**	**Time for Stable Reading (Seconds)**					
Sample1	730	7	21	90	9	13	3
Sample2	1397	45	38	28	11	14	3
Sample3	2152	20	26	26	11	10	4
Sample4	1350	9	20	28	13	13	12
Sample5	1256	17	18	24	10	12	10
Sample6	1782	14	22	25	9	10	21
Sample7	390	21	37	40	8	16	9
Sample8	590	18	22	27	20	15	10
Sample9	980	8	19	28	11	8	13
Sample10	240	37	50	90	10	16	20
Sample11	550	15	24	24	8	22	18
Sample12	4400	19	26	31	10	13	16
Sample13	220	17	60	12	7	15	17
Sample14	2152	26	35	24	13	22	22
Sample15	5226	18	21	27	14	14	17
Sample16	1828	17	12	21	8	8	10
Sample17	3996	23	22	12	15	17	19
Sample18	2843	14	12	20	13	12	10
Sample19	830	22	40	35	11	15	22
Sample20	725	18	12	30	11	10	17

Conclusion

The experiments clearly showed that the modified procedure for measurement of pH by using three buffers for two ranges with suitable calculation could yield good results without the influence of errors in the meter or electrode. The pH meter or the electrode even if not in proper working condition can give results with ±0.1 pH accuracy and the labs will have adequate time to rectify the problems in the meter without immediately suspending the work.

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