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Estimation of measurement uncertainty of routine pH measurement in selected chemical laboratories

Estimation of uncertainty of pH measurement

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A **procedure for estimation of measurement uncertainty of routine pH measurement using pH meter with pH range -2 to 16, three-point calibration, easy recall of calibration point and slope data, temperature compensation and combination glass electrode based on the ISO method is presented. The uncertainty of pH strongly depends on the pH meter itself. Buffers of different ions (NH_3/NH_4Cl, CH_3COOH/CH_3COO^-) at specified pH-values are prepared gravimetrically according to the Henderson Hasselbach equation. Both calibrations and measurements were performed at 25±1.0 °C on the same day. The pH-values of the buffer solutions were close to the expected values but notable uncertainties were also found. Basic statistical calculations and the law of propagation of uncertainty in a spreadsheet model will be used for analysis of uncertainty. The uncertainty of pH measurements will be compared to manufacturers' specifications. In essence, *interval* and *confidence level* are needed, in order to quantify uncertainty. This investigation was performed to provide adequate confidence that pH meters performed satisfactorily and corresponded with laboratory requirements. This approach is used to solve quality related problems in the industry as well ensuring product quality in the industry and to improve knowledge about quality assurance. The study is proposed to be used by assessing organizations, Quality Assurance specialists/ managers/ officers and analytical staff, both in industry and the academic world. It provides principles from which assessing organizations such as accreditation (the ISO/IEC standard 17025) or certification bodies could specify assessment criteria.**

Keywords: pH meter; Henderson Hasselbach equation; uncertainty; accuracy; corrective actions;

I. INTRODUCTION

Measurement of pH is a common and important analytical tool in the modern laboratory (Barron, Ashton, & Geary, n.d.), and it is considered an activity operation in the laboratory. Laboratory operations require the use of tools, equipments and procedures which ought to provide reliable and accurate data to make quality of the products certain (Williams Chairman et al., n.d.). The accuracy of these equipments depends on the uncertainty of the results measurements. Taking pH meter into attention, the uncertainty of its results is reliant on the pH meter itself as analytical measurements of the pH meter made from one chemical laboratory pH meter are not consistent with those made from another and this compromises quality of products and reliability on the equipment. Reliability is assured by consistent monitoring. Monitoring involves a full range of planned practices designed to ensure that quality control measures are being properly implemented which is referred to as Quality assurance. Control measures referring to practices that apply to analytical test like the use of blank samples, certified standard solutions, check samples from both within the lab and from outside, blind samples, quality manuals, replicate analyses, and control charts (Williams Chairman et al.).

The purpose of this research is to estimate uncertainty of the pH meters as one of the simple measurements in chemical and research laboratories; its value is an important quality control parameter and like in any test of physical properties, there is an obvious requirement for reliability of measurement results, which is associated with notable uncertainties. The experiments were conducted at the chemistry laboratories using the Department pH meter (Basic 20) and the pH meter (thermo scientific Orion star) of the Department of Biology and Biotechnology.

II. Experimental Procedure

A. Apparatus

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pH meters

Most measurements were performed by a Basic 20 pH meter. The meter has a large graphic display with resolution of 0.01 units in the pH measurement mode and 0.1 in temperature. It has a measuring uncertainty (±1digit), ≤0.01 in pH measurement and ≤0.2 in temperature. The meter is capable of measuring pH ranges from -2 to 16 by two measuring modes: by stability or in continuous mode. The calibration is programmable with validity between 0 h and 7 days and the meter gives an automatic recalibration warning. Calibration involves automatic recognition of technical buffers pH 2.00, 4.01, 7.00, 9.21, 10.90 values at 25ºC with 1, 2 or 3 buffers selectable inside the range. It has magnetic stirrer as the key to precise and repeatable measurements. This instrument has ambient conditions such; working temperature 5...40 °C, storage temperature -15...55 °C and Relative humidity < 80% (not condensed).

Another meter that was used is the thermo scientific Orion star. The meter has a large, informative screen; it has parameter specifications such as operating temperature 0-50℃, pH range -2 to 16, with resolution 0.1 or 0.01, relative accuracy being ±0.01 and up to three calibration points with easy recall of calibration point and slope of data.

B. *Materials*

Water bath at 25 degrees Celsius, pH meter (thermo scientific Orion star A111, basic 20), analytical balance, 250ml Erlenmeyer flask, 100ml beaker, weighing boat, spatula, top pan balance, thermometer.

C. *Chemicals*

- Ammonia solution (NH_4OH),Rochelle chemicals, Assay min.25%, 070515AM
- Ammonium chloride (NH_4Cl), Merck (Pty) Ltd, Assay 99%, Uni lab SAAR1122700EM
- Acetic acid (CH_3 COOH), Rochelle chemicals, Assay 99.5%, 090215AA
- sodium acetate ($CH_3COONa.3H_2O$), Merck (Pty) Ltd, Assay 99- 101.0 %
- Three standard buffer solutions (pH 4, 7 and 9)
- Electrode storage solution (3M KCl)

D. *Preparing the buffer solutions*

Pre lab calculations

In this experiment, mole ratio were assigned and expected pH values calculated with Henderson-Hasselbach equation, and having the number of moles, the required mass were calculated using equation ($moles = \frac{mass\,(g)}{molarmass\,(gr}$) and buffer solution was then prepared. There were two sets of acid-base pairs available in the lab. These are:

1. Acetic acid (CH_3CO_2H, K_a = 1.8 × 10^{-5}) and sodium acetate ($NaC_2H_3O_2$).
2. Ammonium chloride (NH_4Cl, K_a for NH_4^+ = 5.6 × 10^{-10}) and ammonia solution (NH_3).

E. *Procedure*

The buffers were prepared by calculating the mass ratio of acid to base that will produce the assigned pH, and then mixed the calculated amounts of the two compounds with enough deionised water to make 250 mL. Amount of the buffer component needed we measured accurately on an analytical balance (i.e. NH_4Cl) and top pan balance (under a fume hood for NH_3), and dissolved in a small quantity of water in the beaker, the solution was transferred quantitatively into a 250 ml volumetric flask and filled to the mark with distilled water. Then the solution was mixed homogenously by tilting the capped flask upside down a few times. The buffer solution was kept at temperature of 25.0 ±1.0 degree Celsius.

pH meters were set under fume hood, then standardized using three buffers (three-point calibration). The three standardization buffers used were pH 4.01 buffer, a pH 7.00 buffer, and a pH 9.00 buffer (at 25 °C) according to the manufacturer's instructions. About 25 ml of buffer solution was poured into a small beaker and measured the pH. At all

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times the electrode was rinsed off with demonized water when transferring it between different solutions. The pH-values of the solutions were close to the expected value but not exactly the same.

III. RESULTS

IV. Table 1: quantification of uncertainty using interval and confidence level at various calculated pH values of NH_3/ $NH_4Cl$and CH_3CO_2H/ $NaC_2H_3O_2$buffer measured with thermo scientific Orion star thermometer at 25±0.1 °C

a. Parameter of measured pH ↓	b. Calculated pH values c. NH_3/ NH_4Clbuffer				d. Calculated pH values e. CH_3CO_2H/ $NaC_2H_3O_2$ buffer		
f.	g. 11.25	h. 10.25	i. 9.25	j. 6.75	k. 4.75	l. 3.75	m. 2.75
Mean	*11.071*	*10.21*	*8.907*	*6.464*	4.70	3.354	2.264
SD	*0.0304*	*0.022*	*0.26*	*0.085*	0.15	0.023	0.026
F	0.00019	0.124	0.37	0.015	0.0088	0.016	0.94
t	*2.26*	*2.26*	*2.26*	*2.26*	2.16	2.78	2.78
CI	*0.022*	*0.027*	*0.18*	*0.061*	0.089	0.029	0.032

NB;t<0.05= significance difference, (t>0.05) = no significance difference
; SD- standard deviation
F – F test
t- T Test/ student's t
CI- confidence Interval @ 95%

Table 2: quantification of uncertainty using interval and confidence level at various calculated pH values of NH_3/ $NH_4Cl$and CH_3CO_2H/ $NaC_2H_3O_2$buffer measured with Basic 20 thermometers25±0.1 °C

n. Parameter of ↓ measured pH	o. Calculated pH values p. NH_3/ NH_4Clbuffer				q. Calculated pH values r. CH_3CO_2H/ $NaC_2H_3O_2$ buffer		
	11.25	10.25	9.25	6.75	4.75	3.75	2.75
Mean	*11.52*	*10.44*	*8.99*	*6.15*	*4.65*	*3.50*	*2.51*
SD	*0.13*	*0.037*	*0.19*	*0.014*	*0.071*	*0.097*	*0.025*
F	0.00019	0.12	0.37	0.015	0.0088	0.016	0.94
T	*2.26*	*2.26*	*2.26*	*2.26*	*2.16*	*2.78*	*2.78*
CI	*0.093*	*0.015*	*0.13*	*0.010*	*0.041*	*0.12*	*0.03*

NB;t<0.05= significance difference, (t>0.05) = no significance difference
; SD- standard deviation
F – F test
t- T Test/ student's t
CI- confidence Interval @ 95%

V. Statistical Analysis of Experimental Data

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We reasonably anticipate that the uncertainty is dependent on the pH meter itself, and (Leito, Strauss, Koort, & Pihl, 2002) states that the uncertainty of pH depends on the pH value itself. Uncertainty with two decimal places was used deliberately in order to detect small differences in uncertainty introduced by the pH meter as (Meinrath & Spitzer, 2000) made it obvious that a result is meaningless without statement of the associated measurement uncertainty.

The Henderson Hasselbach equation, even though it has limitations as stated by(Po & Senozan, 2001) it was used to calculate pH values. This equation can only be used to calculate pH values that are close to the pK_a of the acid. That gives the reason to use two different buffer solutions with different acids and ionic strength (NH_3/ NH_4Cl and CH_3CO_2H/ $NaC_2H_3O_2$). NH_3/ NH_4Cl buffer (pKa= 9.25) was used to attain higher pH value of 11.25 and CH_3CO_2H/ $NaC_2H_3O_2$buffer (pK_a= 4.) was used to attain lower pH 2.75.

Concurring with (Schmitz, 1994) in common practice we cannot expect to get differences between calculated and measured pH values, but the results show that most of the measured pH values were not equal to the calculated ones. When using acetate buffers, results of both pH meters were observed to be always lower than the calculated ones as reflected by mean values (table1 and table2). This is supported by (Schmitz, 1994) who made a kinetic study in acetate buffers and gave explanation to be caused by the relation between the pH meter reading and the activity of hydrogen ions. For ammonia buffer, pH values measured by thermo scientific Orion were observed to always be lower than the expected values, while for Basic 20, the values were at times lower or higher than expected ones.

Measurements of the pH buffer solutions with Thermo scientific meter were less accurate; for pH 11.25 buffer it gave a pH reading that was less: pH =11.071 0.030, the pH = 10.25 buffer it gave a reading of 10.21±0.22 (table 1) which falls within the 95% confidence interval, so there is a chance that when measurements are repeated tenth times the meter will give out the known answer for pH 10.25. Even though, it cannot be concluded that the Thermo scientific Orion star thermometer is accurate because almost all of the mean values are just outside the 95% confidence interval. Therefore, there is less than 5% chance that when measurements are repeated tenth times it will give out the known answer, as well as the Basic 20 pH meter. We used *t* test to compare mean values with another to decide whether there is a statistically difference between the two pH meters readings. The *null hypothesis* in statistics states that the mean values from two sets of measurements are not different; we reject the null hypothesis if there is less than a 5% chance that the observed difference arises from variations of the meters. Table 1 and 2, *t test* results shows that the mean values from the two meters are different, so we reject the null hypothesis.

Although most of the mean values are not close to the calculated pH values, from calculations of repeatability standard deviation (SD), it is understandable that the measured pH values are close to the mean of the data set, in average, for both the pH meters and thus resulting in precision that does not agree closely with calculated value. This is supported by (Andersen & Alfaloje, 2013) stating that high standard deviation results in low accuracy and vice versa.

VI. CONCLUSION

Both the pH meter readings generally did not agree closely with the calculated pH values, but gave similar readings to each other, so the pH meters appear to be too inaccurate in this research. It is clear that we have seen differences on the pH meter that people did not care much about.

All the calculations were performed using the Henderson Hasselbach equation which has limitations, so for future work we intend to formulate a new equation without limitation. As well it was discovered that the manufacturers claims that their pH meter can measure within the range -2 to 16, so in future

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we are going to use sodium hydrogen sulphate/ sulphuric acid buffer with hydrogen sulphate (HSO_4^-) pK_a equal to 2 to try reach lower pH, if possible down to pH = -1, then use acid with pK_a equal to 11 to reach higher ranges in the pH scale.

The measurements we repeated tenth times, but for future work we intend to repeat it several times.

VII. TABLES AND FIGURES

Table 3: The assigned moles ratios and the calculated expected pH values of NH_3/ NH_4Clbuffer components used

Trial	*Assigned mole ratios*		*Expected*	*Calculated masses (g)*	
	NH_3	*NH_4Cl*	*pH*	*NH_3*	*NH_4Cl*
1	*100/100*	*1/100*	*11.25*	*35.05*	*0.5349*
2	*1/100*	*100/100*	*7.25*	*0.3505*	*53.49*
3	*1/100*	*1/100*	*9.25*	*0.3505*	*0.5349*
4	*10/10*	*1/10*	*10.25*	*35.05*	*5.349*
5	*1/10*	*10/10*	*8.25*	*3.505*	*53.49*
6	*0.001*	*0.316*	*6.75*	*0.03505*	*16.9028*

Table 4: The assigned moles ratios and the calculated expected pH values of CH_3CO_2H /$NaC_2H_3O_2$ buffer components used

Trial	*Assigned mole ratios*		*Expected*	*Calculated masses(g)*	
	CH_3CO_2H	*$NaC_2H_3O_2$*	*pH*	*CH_3CO_2H*	*$NaC_2H_3O_2$*
1	*100/100*	*1/100*	*2.75*	*60.05*	*1.3608*
2	*1/100*	*100/100*	*3.75*	*60.05*	*13.608*
3	*1/100*	*1/100*	*4.75*	*0.6005*	*1.3608*

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Figure 1: Basic 20 pH meter

Figure 2: Thermo scientific Orion star pH meter

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