INNOVATIVE SCHOOL-LEVEL QUANTITATIVE CHEMISTRY EXPERIMENTAL TECHNIQUE (I): PH MEASUREMENT BY ANTIMONY ELECTRODE

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ABSTRACT

This paper introduces the principles of pH measurement by antimony/copper(II) combination electrodes, use of an innovative mini "salt-plug" and details for the construction of the electrodes and an electronic sensor. Raw e.m.f. signals generated by the combination electrode are amplified by the sensor which is pre-set to give an analogue output voltage of **10 mV per pH**. The voltage displayed by a commercial low-cost digital multimeter (DMM) can be treated as the pH value. The "DMM display" technique works for measurements of conductance and colour intensity as well as pH, provided that suitable sensors are used. *[African Journal of Chemical Education—AJCE 9(3), November 2019]*

INTRODUCTION

Quantitative measurement of pH of aqueous solutions is essentially the measurement of change in e.m.f. of a chemical cell formed by electrodes immersed in the solution. Today, most commercial pH meters employ the H+(aq) ion sensitive glass membrane electrode coupled with a silver/silver chloride reference electrode. However, fabrication of the glass electrode is costly and schools with resource constraints cannot afford multiple sets of pH meter for student use and, needless to say, glass electrodes have limited lifetime and are vulnerable to breakage. In fact, it had been shown, at the beginning of last century [1], that antimony metal in aqueous solution as a half-cell electrode also generates an e.m.f. that depends on the concentration of H+(aq) ions in solution. This offers another means of quantitative measurement of pH [2]. Recently, the antimony electrode was re-discovered as surgical equipment for pH measurement, primarily because of its ability to be miniaturized [3].

pH measurement: Antimony electrode vs Glass electrode

The mechanism of the glass-membrane hydrogen ion sensitive electrode has been well documented. On the other hand, the antimony electrode, because of its drawbacks, was not adopted for advanced scientific measurements. We have no up-dated information on the mechanism of the dependence of half-cell e.m.f. of antimony electrode on concentration of hydrogen ion. However, judging from the pH range most school-based quantitative experiments encounter and considering users' level of instrumental competence, the accuracy of pH measurement by antimony electrode is not a major problem.

Antimony electrode

From standard electrode potential literature, we have the following data [4]:

(A) With reference to standard hydrogen electrode (E□ = 0.000 V)

Medium	**Reduction half equation**	**E$^{\phi}$/V**
Alkaline	$SbO_2^-(aq) + 2H_2O(aq) + 3e^- \rightleftharpoons Sb(s) + 4OH^-(aq)$	-0.639
Neutral or slightly acidic	$Sb_2O_3(s) + 6H^+(aq) + 6e^- \rightleftharpoons 2Sb(s) + 3H_2O(l)$	+0.150
Acidic	$SbO^+(aq) + 2H^+(aq) + 3e^- \rightleftharpoons Sb(s) + H_2O(l)$	+0.204

Clearly, according to the Nernst equation, the half-cell formed by oxidation state (III) species SbO2-, Sb2O3 and SbO+ involves H+ or OH- and generates an e.m.f. which depends on the concentration of H+(aq) over the entire pH range.

Usually, the commercial reference electrode for full cell pH measurement is the Ag/Ag+(aq) reference electrode. For the experiment, we use a less expensive alternative which is a low-cost Cu/Cu2+(aq) half-cell.

(B) With reference to standard copper/copper (II) ion electrode (E□ = +0.340 V)

Medium	**E$^{\phi}$/V, w.r.t. standard hydrogen electrode**	**E$^{\phi}$/V, w.r.t. standard Cu/Cu^{2+} standard electrode**
Alkaline	-0.639	- (+0.340 + 0.639) = - 0.979
Neutral or slightly acidic	+0.150	- (+0.340 - 0.150) = - 0.190
Acidic	+0.204	- (+0.340 - 0.204) = - 0.136

The chemical cell formed during pH measurement is therefore:

$$\overset{-}{Sb(s)} \mid Sb(III) \mid H^+ (aq) \parallel Cu^{2+}\ \overset{+}{(1M)} \mid Cu(s)$$

Theoretically, a chemical cell formed by the Sb/Sb(III) half-cell and a Cu/Cu(II) reference half-cell will generate a potential difference covering the most commonly encountered pH range of 1 to 13, with Cu as the positive pole, from 0.136 V to 0.979 V.

Summary of pros and cons in using a glass electrode and an antimony electrode to measure pH

Antimony electrode	Glass electrode
* Almost linear relationship between cell emf and pH, from pH 2 to 12	* True linear relationship between cell emf and pH, from pH 0 to 12, except the acidic and the alkaline error ranges [5]
* Low cell internal resistance. Conventional plug and socket input will suffice.	* Extremely high cell internal resistance. BNC plug and socket input are required
* Slow response, less sensitive to low pH ranges	* Fast response, sensitive to all regions of the linear pH range.
* Readings reproducible and stable	* Today's high-tech high impedance input fabrication enables reproducible and stable readings, but still liable to external interference
* Measurement principle explainable at school level	* Advanced measurement principle
* Sturdy	* Fragile
* Lifetime dependent on mass of electrode	* Limited glass membrane lifetime
* Liable to chemical corrosion	* Resistant to chemical corrosion
* Easy fabrication	* High-tech fabrication needed
* Low-cost	* Expensive

Examination of the advantages and disadvantages between antimony and glass electrodes reveals that the antimony electrode is a better choice than a glass electrode for school use.

Innovative "Salt-plug"

A small piece of freshly prepared filter paper strip wetted with saturated KNO_3 solution is usually employed as a salt bridge for school use. In the experiment, an alternative way is used which involves a small section of wooden toothpick soaked with sat. KNO_3 solution and let dried. A number of such small pieces of home-made instrument are readily available as innovative "salt-plugs". Using them is very simple: First fill the reference electrode glass tubing chamber with 1M

$CuSO_4$ solution, and then insert the “salt-plug” into the opening of the glass tubing chamber. Air bubbles in the chamber are not allowed as they may cause the copper metal and the copper(II) sulfate solution to be out of contact (Fig. 1, 2, 3 and 4). Lower the finished reference electrode, together with the antimony electrode, into the testing solution for pH measurement.

“Salt-bridges” need to be freshly prepared for each measurement. However, “salt-plugs”, after rinsing, can be used repeatedly until the end of the experiment.

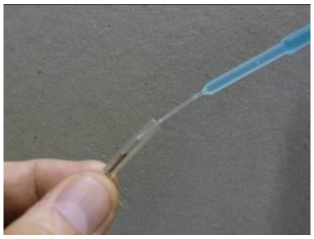


Fig. 1
Use a micro-tip plastic pipette to fill the small chamber with 1M $CuSO_4$ solution

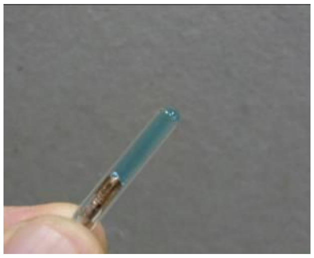


Fig. 2
Solution should be filled to the top of the small tubing. Slight excess as judged by an almost overflow.

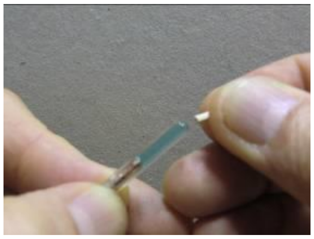


Fig. 3
Insert the “salt plug”

Fig. 4
Prepared copper /copper sulfate electrode with no air bubbles

Practical pH measurement by antimony / copper(II) combination electrode

Theory of measurement

Although the raw cell e.m.f. vs pH graph as shown on page 5 is a straight line, it does not pass through the origin and hence the raw e.m.f. is not directly proportional to pH. The graph shows an OY axis intercept of 0.097 V, and subtraction of this value of voltage from each raw e.m.f. reading will bring the adjusted e.m.f. exactly proportional to pH. That is to say the raw e.m.f. vs pH straight line is converted to one which passes through the origin and achieves a 0 pH (in) / 0 V (out) condition. Even if this has been done, each adjusted reading still has to be amplified by a fixed voltage gain ("one-point" calibration) so as to achieve the desired display of **10 mV per pH** e.g. 35 mV for pH 3.5; 66 mV for pH 6.6 etc.

Voltage gain is calculated as follows (referring to the graph of Fig.5, 6):

Consider pH 7.00: Adjusted voltage = (0.46 – 0.097) V = 0.36V. This value of voltage has to be amplified to 0.70V. Voltage gain = 0.70/0.36 = 1.94

An electronic device (sensor) is needed to do both jobs, i.e. (i) raw e.m.f. subtraction and (ii) voltage amplification. The circuit of the sensor will be described in details later. The treatment reatment of raw cell e.m.f. so far can be summarized as follows:

pH	Raw e.m.f./V	Adjusted e.m.f./V
2	0.21	(0.21 – 0.097) = 0.11
4	0.31	(0.31 – 0.097) = 0.21
7	0.46	(0.46 – 0.097) = 0.36
10	0.61	(0.61 – 0.097) = 0.51
13	0.80	(0.80 – 0.097) = 0.70

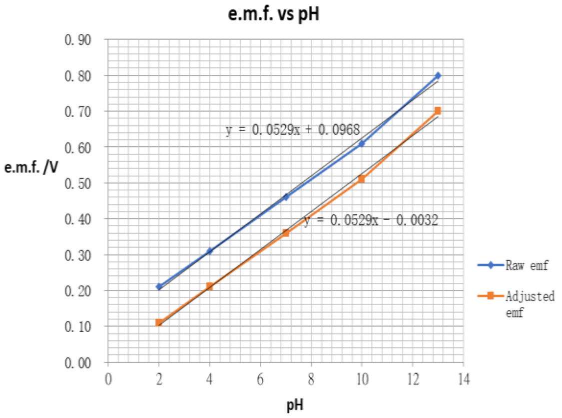


Fig.5 Raw and adjusted e.m.f.

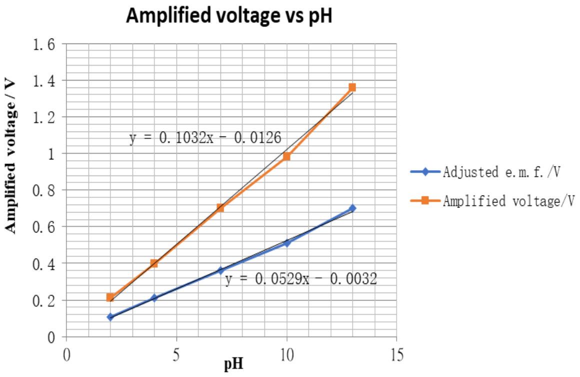


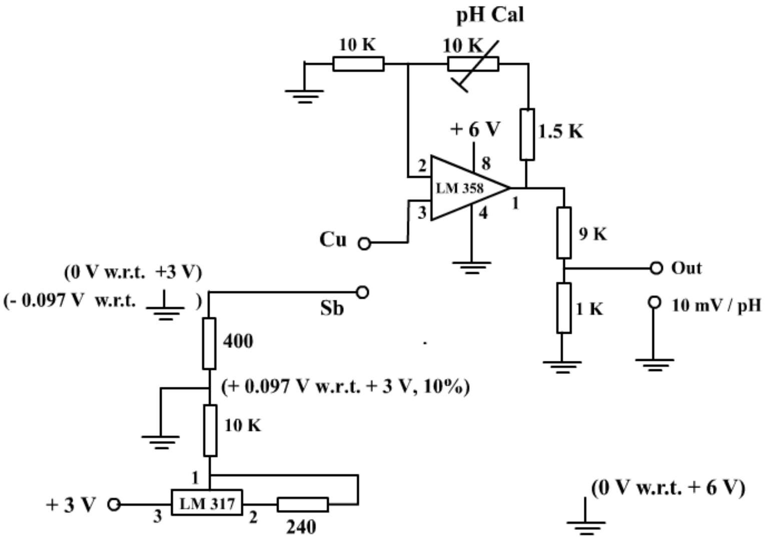
Fig.6 "One-point calibration" with amplified voltage plotted against pH

pH	Adjusted e.m.f./V	"One-point" calibration	Amplification ratio	Amplified voltage/V	Attenuated (output) voltage/mV	Interpreted pH
2	0.11	---	---	(0.11 x 1.94) = 0.21	21	2.1
4	0.21	---	---	(0.21 x 1.94) = 0.41	41	4.1

7	0.36	0.70V	0.70/0.36 = 1.94	(0.36 x 1.94) = 0.70	70	7.0
10	0.51	---	---	(0.51 x 1.94) = 0.99	99	9.9
13	0.70	---	---	(0.70 x 1.94) = 1.36	136	13.6

Buffer solutions of pH 2, 4, 7, 10 and 13 are used for calibration. A 0.100 M NaOH solution can be regarded as a pH 13 buffer solution.

Sensor circuit and description



(Measured cell e.m.f. = Cu/Sb cell e.m.f. - 0.097 V)

Fig.7 Sensor circuit

(i) Power supply

The sensor circuit employs two power supplies. One (3 V) for the adjustable voltage regulator LM 317 [6] to generate a negative voltage reference, and the other (6 V) for the V_{cc} of Op Amp LM 358 [7]. They are readily supplied by using three button-type 3 V lithium batteries, two of which are connected in series to obtain 6 V (Fig. 10). Adjustable voltage regulator LM 317 is used because the chip can handle low input voltages (i.e. 3V). Linear dual Op Amp LM 358 is chosen for the amplification stage because this IC needs only a single power supply (i.e. it does not need a negative power supply).

(ii) Negative voltage reference

Adjustable voltage regulator LM 317 is connected by peripheral resistors to output a regulated voltage. The 400 Ω resistor (or suitable adjustment) taps a reference voltage of + 0.097 V. This positive voltage reference source is then connected to the ground of the power supply (6 V) of Op Amp LM 358. In this way, the separate ground terminal (3 V) which generates the reference voltage becomes - 0.097 V. By applying this negative voltage, raw e.m.f.s are “set” and “corrected” for direct proportionality.

Pin 3 of LM 358 (non-inverting input) is connected to the positive pole (Cu) of the Sb/Cu (II) chemical cell used for pH measurement. The negative pole (Sb) is connected to the - 0.097 V reference voltage source. This results in summing the two voltages [8], i.e E_{cell} and -0.097 V and the effective e.m.f. of the Sb/Cu chemical cell becomes (E_{cell} – 0.097) V. Theoretically, the effective e.m.f. straight line graph should pass the origin. This adjusted e.m.f. (blue line, Fig. 6) is then amplified by a resistor network at pin 2 and pin 1 so that the final voltage displayed by the DMM is directly proportional to pH e.g. 100 mV per pH (red line, Fig. 6).

(iii) Amplification of adjusted e.m.f. and “one-point” calibration

Adjusted e.m.f. is fed to the non-inverting input (pin 3) of LM 358. A resistor network between pin 2 and pin 1 amplifies it by a ratio gain which is controlled by adjusting the variable 10 kΩresistor.

Immerse the antimony combination electrodes in a pH 7 buffer solution. Set the DMM's display range at 2000 mV FS. Turn the knob of the variable resistor, i.e. adjust the 10 kΩ variable resistor, until a voltage of 70 mV is displayed. A display of 70 mV is interpreted as a value of pH 7.0. In this way, voltage output of the sensor is literally directly proportional to pH. The position of the knob is then fixed and the sensor is said to be calibrated – "One-point" calibration. (Fig.6, Fig.16). After this calibration procedure, the instrument is ready for pH measurement.

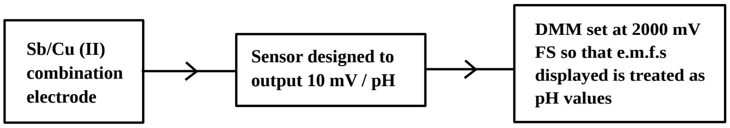


Fig. 8 Flow chart of pH measurement

An attenuating resistor ladder (9: 1) at pin 1(output) of LM 358 sets the final output to the required condition of 10 mV per pH. Absence of this attenuating resistor ladder will result in an output of 100 mV per pH. This is not desirable as the instrument is designed to have a pH accuracy of one decimal place, not 2 decimal places.

(iv) A completed homemade sensor

Using available electronic components, the circuit as shown in Fig. 7 can be soldered onto a semi PCB (Fig. 9 and 10). The fabricated body can be housed in a plastic utility box measuring 10 cm x 6 cm x 2.5 cm (Fig. 10 and 11)

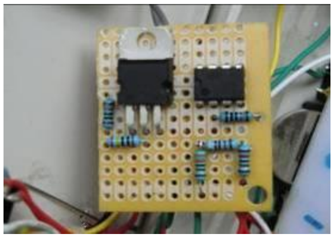


Fig. 9

Electronic components soldered onto a semi PCB

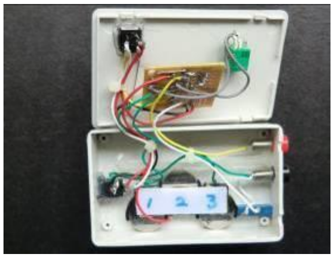


Fig.10

Exposed interior of utility box (three 3V lithium button-type batteries are labeled as 1, 2 and 3)

Fig. 11

Finished utility box with all components installed

Fabrication of copper/copper sulfate reference electrode and antimony electrode

(1) Copper/copper(II) sulfate reference electrode

The copper/copper(II) sulfate reference electrode is constructed by using a short section of glass tube, one end of which is sealed with epoxy glue, leaving a protruded thick copper wire and forming a small chamber for filling with copper(II) sulfate solution (Fig. 12). A small "salt-plug", constructed by using a toothpick bit, replaces a conventional filter paper salt bridge. A "salt- plug" is simply a small section of wooden toothpick soaked in sat. KNO_3 solution and allowed to dry. Air bubbles are not allowed in the chamber, otherwise solution conductance will become unstable (Fig. 13)

Fig.12
Copper electrode
and "salt-plug"

Fig. 13
Finished Cu/Cu(II)
reference electrode

(2) Antimony electrode

Antimony metal of A.R. grade was strongly heated in a crucible (inside a fume cupboard) until it melted (Fig. 14). The molten metal was withdrawn upward, with the help of a pipette filler or syringe into a small glass tube. The hot liquid antimony solidified inside the glass tube and the solid metallic rod was taken out by breaking the glass tubing. The antimony rod formed is brittle and breaking it to yield a small bit is easy. The bit is soldered onto a thick copper rod as lead. The major part is insulated by 2 layers of heat-shrinkable plastic tubing, leaving the two ends for conduction (Fig.15).

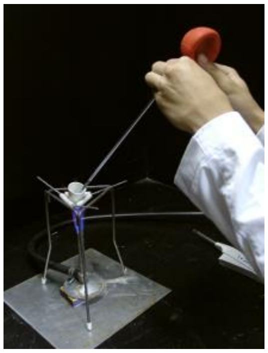


Fig.14
Melting antimony metal
in a crucible

Fig. 15
Fabricated electrode

The antimony electrode and the copper/Cu(II) reference electrode, together with the cable leads, are placed together. The two cables are then fixed by heat-shrinkable plastic tubing to form a complete pH combination electrode (or using any suitable way).

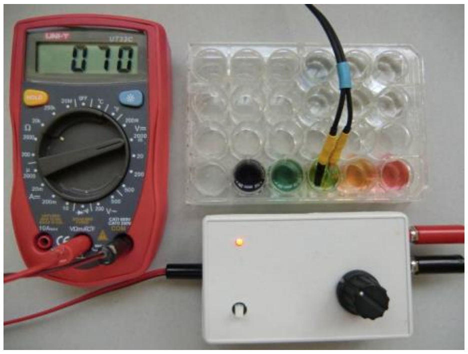


Fig. 16 pH 7.0 "One-point calibration"

EXPERIMENTAL RESULTS

Traditional pH titration curves can be performed with the design in a micro-scale setting. Materials required are: 24 well plate, micropipette, 0.1 M solution of HCl, CH_3COOH and NaOH, phenolphthalein indicator, Sb/Cu combination electrode, sensor and a DMM.

Plots of (i) 0.1M NaOH vs 0.1M HCl and (ii) 0.1M NaOH vs 0.1M CH_3COOH are illustrated as follows:

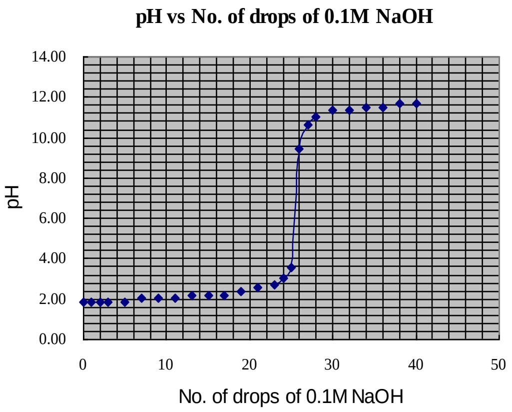


Fig.17 Titration curve of 0.1M NaOH vs 0.1M HCl

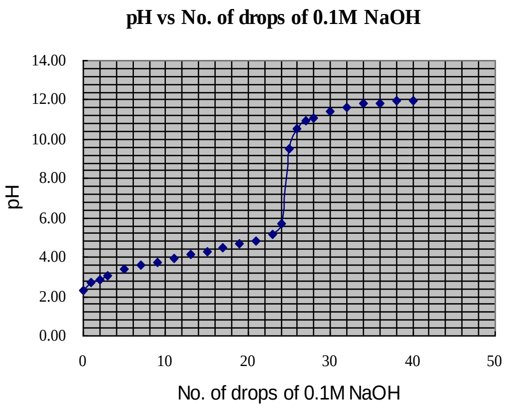


Fig.18 Titration curve of 0.1M NaOH vs 0.1MCH_3COOH

CONCLUSION

Antimony metal in aqueous solution forms a half-cell whose e.m.f. varies linearly with pH over a commonly used pH range. A Cu/Cu(II) reference half-cell is used for pH measurement. The reference half-cell is fabricated by incorporating an innovative "salt-plug". A commercial low-cost digital multimeter is used for cell e.m.f. measurement. Display of pH is achieved by using a self-devised electronic sensor which limits an analogue voltage output of 10 mV per pH.

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