INNOVATIVE SCHOOL-LEVEL QUANTITATIVE CHEMISTRY EXPERIMENTAL TECHNIQUE (II)
AN AFFORDABLE, SENSITIVE, STABLE AND USER-FRIENDLY COLORIMETER

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ABSTRACT

The paper is a continuation of Part (I) of the article [1] published in the Special Issue of AJCE, Vol 9 No. 3, 2019. It introduces a home-made colorimeter sensor which when connected to a commercial digital multi-meter (DMM) can act as a conventional colorimeter. Rationale of the sensor design is based on affordability without sacrificing sensitivity, stability and availability. As such, it has the following features: (i) a professional cuvette is used, ensuring reading display reproducibility (Fig. 1), (ii) improved circuit design , (iii) a RGB tri-colour LED is used instead of optical filter for near-monochromatic light source (Fig. 2), (iv) the "DMM Display" technique is adopted in which the sensor output is limited to a full-scale reading of 2000 mV DC with the DMM's voltage readings acting as transmittance parameter, (v) do away with the concept of absorbance and Beer's law which are not recommended for most school level chemistry syllabuses. When using the sensor, output voltage readings are treated as quantified transmittance and that a blank sample transmittance is adjusted to have a voltage reading of 100 mV which is regarded as a full-scale reading of 100 with no unit, (vi) portable with no location limitation and (vii) battery operated capable of long period of continuous operation. *[African Journal of Chemical Education—AJCE 10(2), July 2020]*

INTRODUCTION

The paper advocates the use of "DMM Display" technique in which a single piece of instrument, digital multi-meter (DMM), is used as a terminal display for more than one type of experiment. The sensor circuit design aims at providing a "user-friendly" environment for school-level experimentation.

Features of the design

(i) Commercial colorimeters use "absorbance" as reading unit. The term incorporates quantitative calculation of optical intensity which is usually not required for most school-level chemistry lessons. Hence the design aims at doing away with reading units. When the sensor is connected to a DMM, set at the FS 2000 mV DC range, blank sample transmittance results in a display of 100 and complete blockage of light source a display of near 0 (Fig. 3 and 4). This offers a "user-friendly" and less threatening situation for dexterity less competent school students.

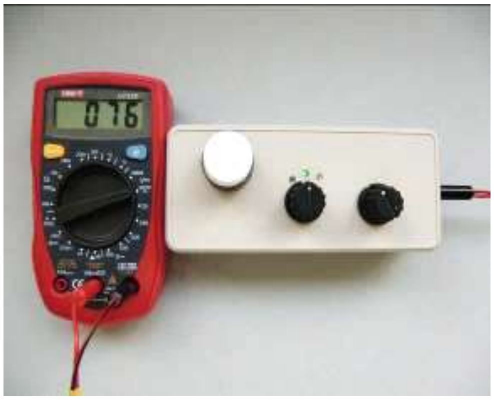
(ii) Traditional school colorimeters use monochromatic RGB color filters. Today's technology enables tri-color LEDs to emit near monochromatic red, green and blue lights. The trend tends to be that these LEDs are becoming more and more popular. Hence the design uses LED instead of color filters.

(Fig. 1) Full set of colorimeter sensor

(Fig. 2) RGB tri-colour light source and cuvette compartment

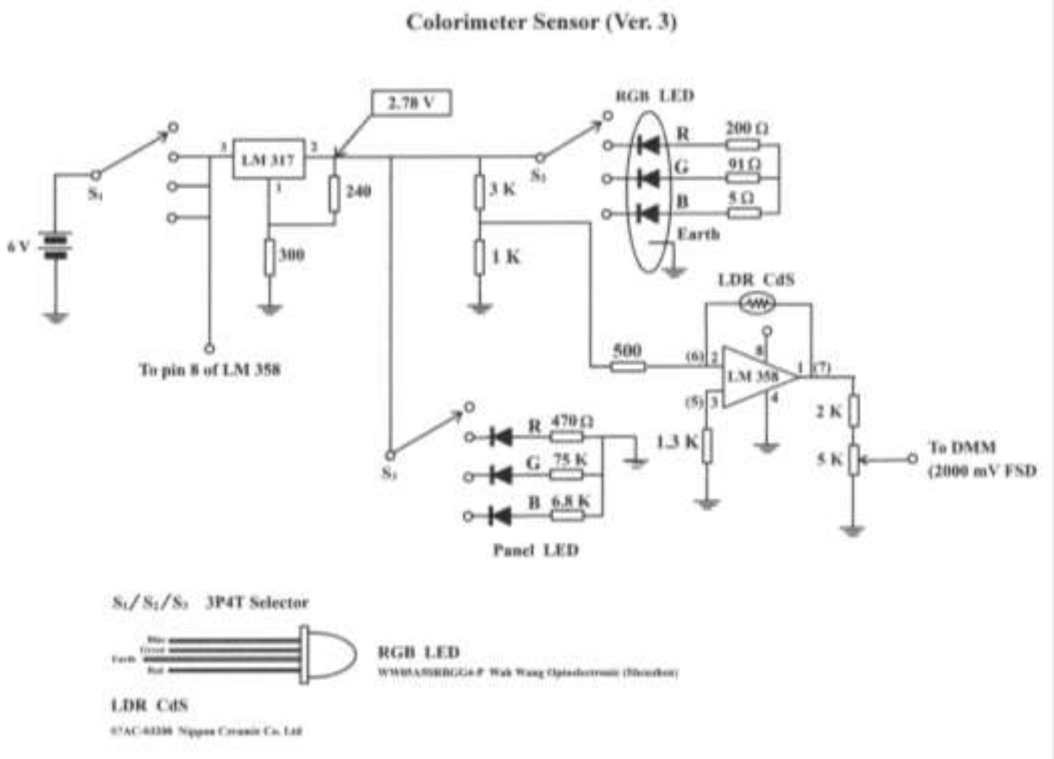
(Fig. 3) Blank sample transmittance

(Fig. 4) Complete blockage of light



(Fig. 5) Colorimeter in operation

SENSOR CIRCUIT AND DESCRIPTION



(Fig. 6) Sensor circuit

(i) Power supply

The sensor circuit (Fig. 6) employs an adjustable voltage regulator LM 317[2] to generate a regulated output of 2.78 V, i.e. ± 15% of [1.25 x (1+ 300/240)] V (total resistor color coding error assumed to be ± 15%), for powering the tri-color LED and the whole circuit. A stable and regulated light source is the vital part of colorimeter design. V_{cc} of Op Amp LM 358[3] does not need a regulated voltage supply since the chip itself is designed for a span of supply voltage variation and specially for a single supply low-voltage power source, i.e. it does not need V_{ee} or a negative voltage supply.

(ii) Circuit description

1. *Selection of wavelength of light source*

A 3P4T selector is used as a switching device for power source and for selecting red (mainly 625 nm), green (mainly 520 nm) and blue (mainly 470 nm) lights (Fig. 2).

2. *Op Amp input*

A portion of the regulated voltage at output pin 2 of LM 317 is tapped by the resistor ladder 3K/1K to act as input signal source for the inverting input of LM 358 (pin 2). This pre-set source voltage is [2.78 x ($\frac{1}{4}$)] V or 0.7 V.

3. *Voltage amplification*

LDR CdS photoresistor used has an approximate resistance of 3K under normal blank monochromatic light (400 Lux) and a resistance around 500K in total darkness. The resistor network used for amplification (inverting amplifier) has a negative voltage gain of (R/500) [4] or an approximate range of (- 3000/500) or - 6 to (- 500000/500) or -1000.

As the input to pin 2 of LM 358 is not a negative voltage, output voltage at pin 1 has to be calculated as follows:

The pre-set source signal of 0.7V provided by a voltage divider and tapped from a 1KΩ resistor, would not warrant a "virtual ground" of 0 voltage at pin 2, the same as the main ground of the 6V power voltage. Hence a bias resistor is required at the non-inverting input pin 3 to rectify the offset. Value of this resistor is calculated as:

$$[\frac{(1K+500)\ x\ (\text{avg resistance of LDR Cds})}{(1K+500+\text{avg resistance of LDR Cds})}]\ \Omega$$ [5]

$$= [\frac{(1K+500)\ x\ (10K)}{(1K+500+10K)}]\ \Omega = [\frac{(1000+500)\ x\ (10000)}{(1000+500+10000)}] = 1304\ \Omega$$

Upon normal irradiation by green light, the LDR CdS has a resistance about 3 KΩ and the p.d. developed across the 500 Ω resistor is 0.078V. This input is amplified to [(0.078) x (- 6)] V or - 0.468 V. Thus the voltage measured at pin 1, w.r.t. the ground of the 6V main voltage is about [0.7 + (0.078) – (0.468)] V = 0.310 V, i.e. 310 mV

In total darkness, the LDR CdS will have an approximate resistance of 500K Ω and the p.d. developed across the 500 Ω resistor is 0.00069V. This input is amplified to [(0.00069) x (- 1000)] V or - 0.69V. Thus the voltage measured at pin 1, w.r.t. the ground of the 6V main voltage is about [0.7 + (0.00069) – (0.69)] V = 0.011V, i.e. 11 mV

This range of voltage output is ideal for tapping, using a resistor ladder (2K + 5K) at output pin 1 of LM 358, to give a FSD of 100 mV set at a 2000 mV DC range by adjusting the 5 KΩ variable resistor.

4. *Circuit performance*

As all inputs are regulated by LM 317, final output stability depends only on the quality of the LDR CdS photoresistor used. The design used S7AC-03208, manufactured by Nippon Ceramic Co. Ltd.[6] On the whole, the instrument has high display reproducibility and almost no reading drift.

Op Amp LM 358 is designed to operate at a single supply voltage as low as 3V. As long as the battery supply voltage is not less than 4V, the whole circuit, including regulated voltage for powering the RGB LED and V_{cc} for the Op Amp, remains very stable. Newly replaced 4 dry cells (1.5V @) can maintain a substantial period of continuous operation.

DETAILS OF PROTOTYPE CONSTRUCTION

The design aims at home construction with local resources. Essential electronic skill is assumed. Consumer parts can be changed according to availability. World-wide marked prices of electronic components do not vary much and it seems that they do not increase as the ever-rising inflation rate does. In Hong Kong, whole assembly of the sensor, excluding the DMM, costs around HK$100.

(i) Plastic case

A plastic utility box measuring (62 x 145 x 40) mm is used to house the entire assembly. Holes are drilled on the cover to accommodate the 3P4T selector, the panel LEDs, the cuvette adapter, the output socket and the 5K □□variable resistor (Fig. 7).

(ii) Power source and battery holder

Four AAA batteries (6V) are accommodated in a plastic holder and fixed at the base of the case by hot glue (Fig. 7).

(Fig. 7) Upper (with holes) and lower (with battery holder) parts of plastic case

(Fig. 8) Medicine bottle, cap and cuvette adapter

(Fig. 9) PVC strips combination and cuvette adapter

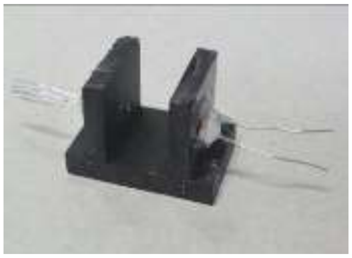
(iii) Monochromatic light source

Unlike ten years ago, nowadays RGB tri-colour LED is becoming more and more popular. They are compact, inexpensive and can emit near monochromatic visible light. A brand from Shenzhen, China[7] (WW05A5SRBGG4-P Wah Wang Optoelectronic (Shenzhen) CO. Ltd.), emits strong red (625 nm), green (520 nm) and blue (470 nm) lights upon applying a DC voltage of 3V. The method is superior than using RGB color filters.

(iv) Cuvette cavity and compartment

Select a plastic medicine bottle the mouth of which can just accommodate a disposable cuvette with a dimension of (12.5 x 12.5 x 45) mm. Chop off the top part, cement it to a section of PVC tubing with PVC glue to form a cuvette adapter (Fig. 8). Fix it to the cavity hole with the same kind of glue. Arrange and fix with PVC glue four pieces of small strips of PVC so that it forms a shape of (井, Chinese meaning a well) (Fig. 9). Size of the central part of this strip combination should just allow a cuvette to pass through. Glue it to the bottom part of the cavity hole of the case cover (Fig. 10).

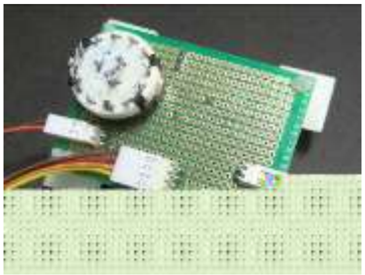
(Fig. 10) Cuvette adapter and PVC strips combination



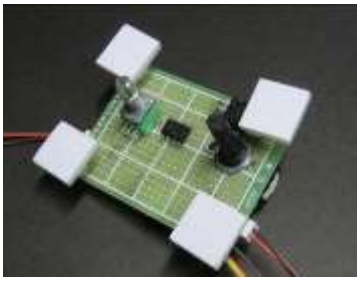
(Fig. 11) U-shaped acrylate stand with RGB LED and LDR Cds photoresistor

(Fig. 12) Cavity compartment allowing cuvette to go through

With the help of trichloromethane, cement 3 pieces of dark brown (or black, if available) thick acrylate sheets together to form a U-shaped stand. Drill opposite holes to hold the tri-colour LED and LDR respectively. Fix them into position with hot glue or epoxy glue (Fig. 11). Glue the whole assembly to the bottom part of the case to form a complete cuvette compartment (Fig. 12). There should be no room for movement once the cuvette has been inserted into the cavity, otherwise it may result in unstable DMM display



(Fig. 13) Universal PC board, 3P4T selector, 5K pot, LM 358, LM 317 and connectors (back view)



(Fig.14) Universal PC board, 3P4T selector, 5K pot, LM 358, LM 317 and connectors (front view)

(Fig.15) Wired PC board, detached upper and lower parts of the plastic case

(v) Component layout and circuit soldering

The whole circuit (Fig. 6) is soldered onto a universal PC board as shown in Figure 13 and 14. Layout design should consider the need for easy maintenance. As such, the completed PC board is made detachable and the upper and lower parts of the case can be separated (Fig. 13, 14 and 15). Style of design is up to one's favour, but convenience is the major factor to be considered.

Lastly, all parts liable to movement and hence loss of contact should be permanently sealed by hot glue. This includes soldered joints involving wires on the PC board and junctions of other wired-joints of components.

SETUP FOR EXPERIMENT

(i) Calibration for a particular experiment

Calibration of the colorimeter has to be done with each experiment, as colour displayed by the chemical reaction varies.

Selection of light source

Switch on the sensor and DMM, select the 2000 mV FS range and connect the sensor output to the DMM. Fill a clean cuvette (smooth opposite sides facing the light source and the LDR) with 3/4 full of deionized water. Place back the cuvette cap, select the red light source by turning the 3P4T selector and adjust the 5K Ω variable resistor until a display of 100 mV is observed.

Remove the blank sample, fill the ***same*** clean cuvette 3/4 full with the colour sample. Observe the DMM reading, say 85 mV is displayed. Select the next light source, say the green light and again observe the DMM reading. Repeat the procedure for the blue light source. Determine the light source which give the lowest reading less than or equal to 85 mV. This is the chosen wavelength for the experiment. For a purple or brown solution, green light source should be used.

Set for full-scale

Select the pre-determined light source suitable for the experiment. Place a clean cuvette filled with 3/4 full of deionized water. Adjust the 5K Ω variable resistor until a display of 100 mV is observed.

(ii) Optical intensity measurement

After calibration, ***fix*** the position of the set full scale knob (5K Ω variable resistor). Fill the clean cuvette 3/4 full with the sample solution and place back the cuvette. Wait till the display becomes steady and record the reading. If a value of 76 mV is observed, then the optical intensity of the solution can be interpreted as 76% transmittance w.r.t. the selected light source (Fig. 5).

SUGGESTED EXPERIMENT

Kinetic order of oxidation of iodide by hydrogen peroxide

The kinetic order of the oxidation of iodide ion by hydrogen peroxide can be conveniently determined by colorimetry.

Equation for the reaction between acidified hydrogen peroxide and iodide is:

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l)$$

It is usually expressed as

$$\boxed{H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)}$$

The measured species is actually I_3^-(aq) which is intensely brown. Color imparted by I_3^-(aq) facilitates colorimetric measurement. The concentration of I_3^-(aq) increases as the reaction proceeds. Color of the solution mixture turns from colorless to slight brown, brown and finally deep brown. At the same time concentration of I^-(aq) decreases. The colorimeter registers optical intensity of the selected light through the solution. Use of colorimeter can follow the rate of the reaction by observing the change of color intensity of the reacting mixture with time.

Scheme of mixing for the reaction is summarized as below. A plastic micro-tip pipette is used for volume measurement in terms of number of drops.

Reagent	**Number of drops**	**Remarks**
0.6 M KI	4	Decent number of drops such that the half-life of the reaction is neither too long nor too short. An optimum $t_{1/2}$ about 200s is desirable. Amount used is assumed to be in excess since the pre-requisite is obtaining a brown solution with no I_2 ppt.
1 M H_2SO_4	5	
3% H_2O_2	1	Limited number of drops as excess may result in formation of iodine ppt which affects light transmission. Thus, H_2O_2 acts as the limiting reactant.
Deionized water	35	Adjust the number for a decent rate,

Experimental data

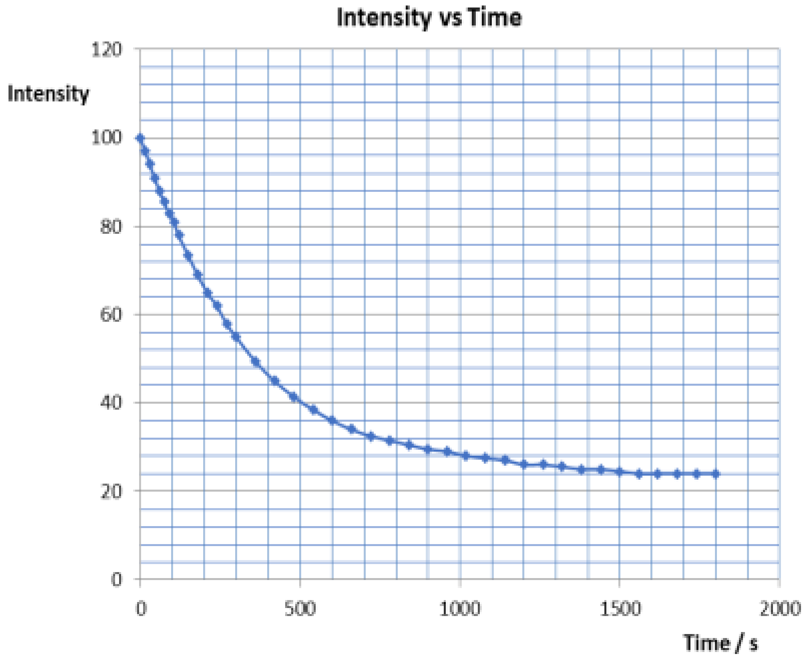
Time / s	**DMM reading / 2000 mV**	**Time / s**	**DMM reading / 2000 mV**
0	*100*	660	*34*
15	*97*	720	*32.5*
30	*94*	780	*31.5*
45	*91*	840	*30.5*
60	*88*	900	*29.5*
75	*85.5*	960	*29*
90	*83*	1020	*28*
105	*81*	1080	*27.5*
120	*78*	1140	*27*
150	*73.5*	1200	*26*
180	*69*	1260	*26*

210	*65*	1320	*25.5*
240	*62*	1380	*25*
270	*58*	1440	*25*
300	*55*	1500	*24.5*
360	*49.5*	1560	*24*
420	*45*	1620	*24*
480	*41.5*	1680	*24*
540	*38.5*	1740	*24*
600	*36*	1800	*24*

Treatment of data

Activate the Microsoft "Excel" spreadsheet software. Input the time and DMM reading data. Plot the scatter diagram. Estimate the first, second, third, fourth and fifth half-lives of the reaction.

RESULTS



(Fig. 16) Graph of intensity vs time

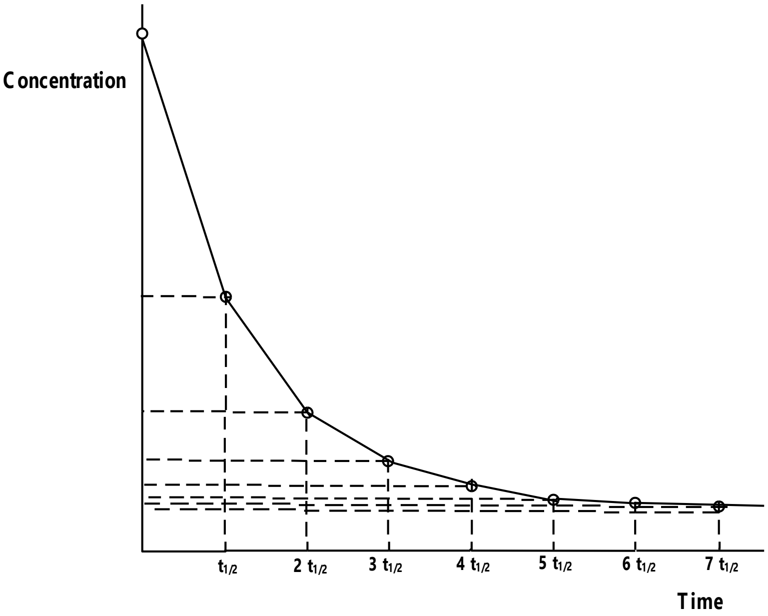
For a first order reaction,

$$[A] = [A]_o\, e^{-kt}$$

When the half-life period is attained, $[A] = \frac{1}{2}[A]_o$

Half-life of the reaction, $t_{1/2}$, is deduced as $\frac{\ln 2}{k}$ or a constant for a particular reaction.

Hence, differences between successive half-lives should also be a constant.



(Fig. 17) Decay curve of a first order reaction, showing successive half-lives

Half-life	Time/s	Difference between successive half-lives /s
First	*240*	*240*
Second	*470*	*230*
Third	*700*	*230*
Fourth	*950*	*250*
Fifth	*1200*	*250*

(Fig. 18) Experimental successive half-lives

Experimental differences between successive half-lives is a constant. Thus, the reaction is a first order reaction. Hence, using the method of trial-and-error by inspecting the decay curve, if the half-lives of a reaction are the same, then the reaction is a first order reaction.

Since I_2 (aq) and H^+(aq) are both in excess, the kinetic order determined is one w.r.t. H_2O_2 (aq). In other words, the oxidation reaction is a pseudo first order reaction w.r.t. H_2O_2 (aq).

In addition, order w.r.t. I^-(aq) cannot use this method as excess of H_2O_2 (aq) will result in ppt of solid iodine. The “iodine clock reaction”, a derived reaction of the experimental oxidation reaction, is a suitable method of finding the three kinetic order w.r.t. I^-(aq), H_2O_2 (aq) and H^+(aq) of the reaction.

CONCLUSION

A colorimeter designed for school student handling. Both visual and psychomotor needs are met by considering operators’ competence level. In addition, affordability is catered for without sacrificing sensitivity, stability and availability.

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