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Low-Cost Laboratory Data Acquisition System Based on the Z8 ENCORE!™ Microcontroller for pH Measurement

Ian Mitchelle S. De Vera and Edward T. Chainani

Chemistry Department
School of Science and Engineering
Ateneo de Manila University
Loyola Heights, Quezon City 1108, Philippines

A pH measurement-auto-titration data acquisition system based on the Z8 Encore!™ Z8F6401 Flash microcontroller was devised with a glass electrode acting as a pH sensor. The data acquisition system allows buffer calibration, pH measurement of samples and the option to perform an automated strong acid-strong base titration via a solenoid pinch valve which actuates the flow of titrant. The results given by the pH measurement system were comparable to that of Sartorius® PB-20 pH meter using t -Test within the pH range 4.00 to 10.00. This can be attributed to the very linear response of the sigma-delta analog-to-digital converter (ADC) of the Z8F6401 to changes in potential. The auto-titration setup gave an accurate titrant volume delivery to the bromothymol blue endpoint (pH 6.2 to 7.6) for a strong acid-strong base titration.

Keywords: pH sensor, microcontroller, pinch valve, ADC, auto-titration, glass electrode

INTRODUCTION

The Z8 Encore!™ Z8F6401 is a Flash-capable microcontroller based on Zilog's advanced 20 MHz eZ8 8-bit microprocessor core [1]. This microcontroller has a built-in 8-channel, 10-bit analog to digital converter (ADC). Its rich peripheral set makes it versatile for different applications such as sensors and motor control—applications compatible to digital chemical instrumentation.

A platform based on Z8F6401 microcontroller can be created, which can serve as a laboratory data acquisition system for various chemical processes and experiments. In fact, a previous project known as "The Chem Buddy" developed a similar data acquisition system for temperature sensors and voltmeters using the Atmel AT90S8535 microcontroller [2].

Different kinds of sensors are readily available in the market—temperature, pH and pressure sensors. With a multi-channel data acquisition system we can change the sensor or add more sensors to the remaining ADC channels to suit the needs of chemistry experiments. This feature gives versatility to a microcontroller-based data acquisition system. Also, repair and upgrading of the system is easy since the design is not proprietary. Most importantly, it is relatively

*Author to whom correspondence should be addressed

cheaper compared to commercial digital instruments.

A typical commercial pH meter, Sartorius® model PB-20 costs $695.00, which is approximately equivalent to PhP36,835.00 in today's average exchange rate [3]. On the other hand, a glass electrode type pH sensor costs only around $74.00 or PhP3,922.00 [4]. Adding the needed electronic components, brings the total price for a "low-cost pH meter" to approximately PhP6,197.00, 83.2% cheaper compared to its commercial counterpart. A similar low-cost pH meter has also been developed using a carbon / quinhydrone electrode for a UNESCO-IUPAC Low Cost Equipment project, showing serious efforts in providing cheaper instrumentation [5].

In this project, we evaluated the performance of a Z8F6401 data acquisition system in an actual laboratory set-up, i.e., if a single data acquisition system is comparable to two expensive commercial laboratory equipments, a pH meter and a commercial auto-titrator in terms of accuracy and precision.

EXPERIMENTAL

The framework for the project can be presented as a block diagram in Figure 1.

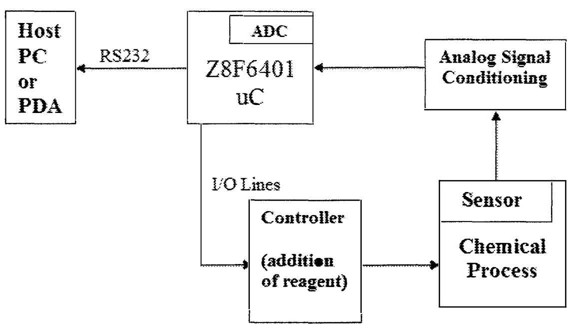

Fig. 1. *Block Diagram for the Project*

A glass electrode acting as a pH sensor was in close proximity to a chemical process. The analog signal-conditioning block can be subdivided into two parts: the amplifier and level-shifter sub-blocks. The analog signal was amplified by using op-amps (type LF353N), since the incoming voltage was too small [6]. The same signal-conditioning block was used to level shift the signal to positive voltage values, since the voltage input sensed by the glass electrode was negative above pH 7.00 and positive below this pH value. For instance, a standard buffer with pH 7.00 has typical voltage values within 0±30 mV. A pH 4.00 standard buffer has voltage values 169 to 186 mV more than pH 7.00. A pH 10.00 standard buffer has voltage values 159 to 185 mV less than pH 7.00 [7].

The built-in analog-to-digital converter (ADC) was responsible for the digitization of the conditioned analog signal. This data was transferred via RS232 or serial port to a host PC. For more portability a personal data assistant (PDA) can be used instead. In the current working prototype, the data were displayed by using Hyperterminal® (serial communications program) on a PC.

Signals were sent by the Z8F6401 microcontroller to an external controller by using one of its 31 I/O (input-output) lines (PB1) to control the addition of reagent. In this case, the controller is a pinch valve. This valve is a solenoid which opens when current is passed through it and closes or pinches if otherwise.

The Microcontroller Miniboard. This project used an Encore PLCC Mini Board acquired from the University of the Philippines Diliman, Electronics and Electrical Engineering Department (EEE) [8]. The Encore PLCC circuit board module was built around a Zilog Z8F6401 Flash Microcontroller. This microcontroller includes on-chip peripherals useful in instrumentation such as the eight-channel analog-to-digital converter (ADC) and the universal asynchronous receiver /transmitter (UART). A 9VDC adapter was employed to power the board. The I/O pins of the Z8F6401 can be conveniently accessed through pin headers.

ADC Calibration / Testing. In the calibration of the Z8F6401 ADC, the incoming analog signal was varied at desired voltage increments from 0.1V to voltage reference (3.31-V) and then back to 0.1 V via a Bourns potentiometer potential-divider circuit. The single-shot ADC output was sampled 10 times for each data point (the observed variation was only ± 1 in the last digit). The scanning was done in both directions to compare the response of the ADC towards increasing and decreasing voltage. The output was displayed using Hyperterminal® and simultaneously measured using a YEW® Model 2501A Precision Digital Multimeter and Hewlett-Packard® E2373A Multimeter.

The calibration was performed at two temperatures, 24.5°C and 28.5°C, to determine the effect of temperature to the ADC output, and consequently, to pH measurements.

Signal Conditioning Block. The signal conditioning block was composed of an LF353N monolithic dual FET input op-amps in a single dual-in-line package (DIP) [9]. The incoming analog signal from the glass electrode was amplified by an op-amp by a factor of 8.27, chosen to bring the 0-14 pH range into the ADC's input voltage range. The amplified analog input was level-shifted to positive voltage values by using an output shifting voltage equal to 3.30 volts. The level shifted signal was sent to one of the analog inputs of the Miniboard. Two stages of RC low pass filter with cut-off frequencies (f_c) at approximately 20 Hz and 26.5 Hz were used to reduce noise [10].

The pH program. The software was written in C and compiled into microcontroller opcode using Zilog Development Studio II (ZDS II) version 4.6.1 [11].

The program flow can be summarized in 4 stages (Figure 2): (1) buffer calibration (2) sample presentation, (3) pH range selection and (4) pH determination.

Standard buffers with pH 4.00 (±0.02 20°C, 9884 Titrisol® citrate-HCl buffer), 7.00 (±0.02 20°C, 1.09887 Titrisol® phosphate buffer) and 10.00 (±0.05 20°C, 9890 Puffer-Titrisol®) were employed for the calibration phase. Initially, the user was prompted to present the standard buffers to the glass electrode. The voltage sensed by the electrode was digitized by the ADC. Decimal equivalent of the ADC output (with a maximum value of 3FF in hexadecimal) was converted to volts using a normalization factor [voltage reference/(2^{10}-1)]. After obtaining the voltage equivalent of each of the standard buffer solutions, the user was asked to choose between a two-point and a three-point calibration. For a two point buffer calibration, the user had to decide what pH range to use: 4.00 to 7.00 or 7.00 to 10.00. The equation of the line, with pH and voltage in the x and y-axis respectively, was generated for each case. For a three-point calibration, the equation of the best-fit line for pH range 4.00 to 10.00 was determined.

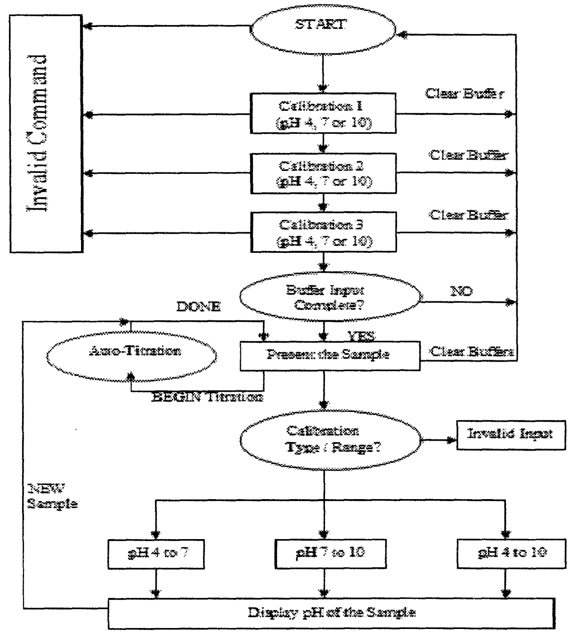

Fig. 2. *Program flow chart*

Once buffer calibration was complete, the user was prompted to present the sample and determine which calibration type and pH range to employ. The voltage sensed by the electrode for this sample was converted to pH using a suitable calibration curve for the pH range and calibration type selected.

For the automated titration feature, the pH of the solution was checked and compared to a predetermined set-point pH via a feedback control loop. The chosen set-point pH was 7.00—the equivalence point for this type of titration—which can be signaled by the endpoint of bromothymol blue indicator. The color of this indicator changes from yellow to blue for the pH transition range 6.2 to 7.6 (pKa = 7.10) [12].

Free flow of titrant was allowed by the pinch valve up to pH 3.00. Between pH 3.00 and 7.00, a 16-bit hardware timer of the Z8F6401 was programmed to synchronize the opening and closing of the pinch valve for 455 milliseconds intervals. The open-close action of the valve resulted to a more controlled titrant delivery which avoided overshooting. At pH 7.00 and above, the pinch valve was permanently closed and titrant delivery was terminated.

The Auto-Titration Setup. In the auto-titration setup (Figure 3), the titrant (ca 0.1 M standardized NaOH) was delivered using a buret. A solenoid valve (ASCO Scientific Series 388) was used to pinch a piece of silicone tubing attached to the buret [13]. In the default closed position, no reagent was delivered. After invoking the command for titration, the valve was opened and NaOH was delivered to 25.0 mL of the acid sample (ca 0.1 M HCl) in a 250-mL beaker.

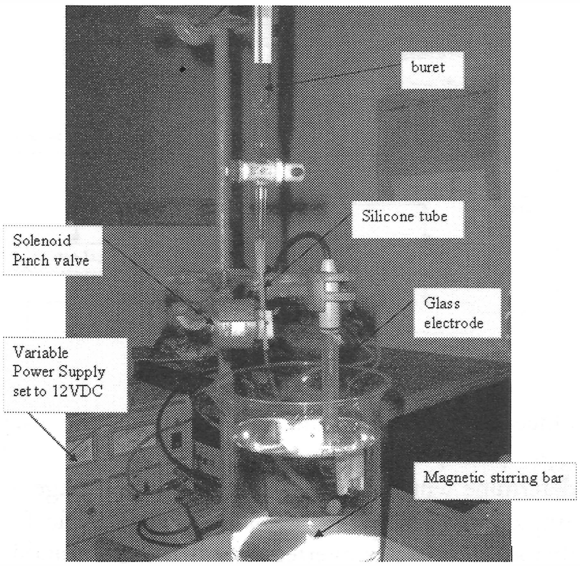

Fig. 3. *The auto-titration setup for the Z8F6401 system*

To make sure that the titrant was evenly distributed in the solution, a magnetic stirrer was used. The glass electrode was immersed into the acid sample.

Two drops of bromothymol blue indicator was added prior to the titration. The flow of titrant was actuated by a pinch valve circuit. The pinch valve was controlled by logic output port PB1 of the Miniboard via a transistor. If PB1 of the Miniboard was logic high, current flow through the solenoid can occur and the valve was opened, allowing reagent delivery. If PB1 was logic low, there was no current flow and reagent delivery was stopped. The closing of the valve was expected to coincide with the yellow to blue color change of the indicator since the set-point pH was assigned a value within the pH transition range of the indicator.

RESULTS AND DISCUSSION

Calibration of the Z8F6401 ADC. The output of the ADC was compared to the output of YEW® Model 2501A Precision Digital Multimeter and Hewlett-Packard® E2373A Multimeter as described in detail in the Experimental part of this paper.

Results show that there was an offset of +0.04 to +0.05 V in the output of the ADC relative to the output of the two multimeters. The lower limit by which the ADC output was valid and nonzero was above 0.045-V analog input. Between 0.040 and 0.045 V, nonzero values were observed, but these were mostly noise, because such inputs were possibly right below the minimum threshold input for a sigma-delta ADC, the type of ADC employed by the Z8F6401. The output was clearly zero below 0.040 V.

For simplicity in presentation, all hexadecimal numbers are represented as decimal equivalents. The calibration curves for both increasing and decreasing voltage scans from 0.03-V to V_{ref} at 24.5°C are superimposed (Figure 4). The calibration curves represent a plot of the decimal equivalent of ADC output vs. analog input in volts. The YEW® multimeter was chosen because it has inherently more significant digits (4½ digits) compared to the Hewlett-Packard® multimeter (3½ digits).

The response of the ADC from 0.1 V to voltage reference was very linear (Figure 4). The calibration curves for the increasing and decreasing voltage scans overlapped. This implies that the ADC output for a given analog input was not affected significantly by the voltage scan direction.

This same procedure was performed at 28.5°C. Results show that a 4-degree temperature change had no significant effect on the ADC calibration curve.

The calibration curve in the 0.04 to 0.12 V range was constructed by obtaining ADC output at 1 to 3 mV increments in the analog input (Figure 5). A significant decrease in the linearity coefficient (R^2) was noted.

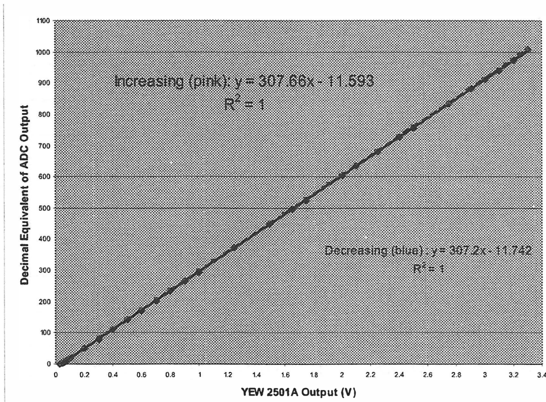

Fig. 4. *Calibration of Z8F6401 ADC at 24.5 °C using YEW' 2501A Precision Multimeter for both increasing and decreasing voltage*

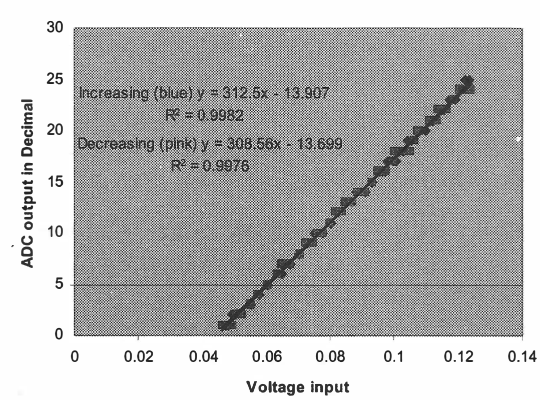

Fig. 5. *Calibration of Z8F6401 ADC from 0.04 to 0.12 V using Yew 2501A Precision Multimeter at 24.5°C (increasing and decreasing voltage)*

The hexadecimal output changed by a unit only after a 3 to 4 mV change was applied at the input. The "step size" correlated well with the calculated 3.2 mV (3.31 V ÷ 1024) ADC resolution.

The linearity of the microcontroller's ADC was very high (R^2 approaching unity) within the range of 0.1 V to reference voltage. The ADC can be used only above the minimum ADC threshold input of 0.045 V.

Calibration and Testing of the pH sensor. When the ADC was determined to be operational, the signal conditioning block was constructed and used to interface the pH sensor to the ADC input. In the calibration phase, the buffers with pH 4.00, 7.00 and 10.00 were presented to the electrode. The decimal equivalent of the ADC output and the amplified and level-shifted voltage equivalent for these buffers were determined (Table 1). If a plot of voltage (V) vs. pH is constructed, R^2 is equal to 0.998, which translates to a satisfactory response of the electrode towards pH change. This result was based on one calibration. *All* calibrations performed have R^2 value greater than 0.985.

Table 1. Calibration of the glass electrode.

pH of standard buffer	Decimal Equivalent of ADC output	Voltage equivalent (V)
4.00	705	2.294
7.00	498	1.619
10.00	324	1.042

Comparison between pH measurements of "low-cost" and commercial pH meter. After the calibration phase, the electrode was used on buffer samples with different pH values. Values for pH derived using the Z8F6401 system were compared to that of Sartorius® PB-20 pH meter. This was done by attaching the same glass electrode employed for the Z8F6401 pH measurement system to the PB-20 pH meter, but with the Temperature Compensation probe disconnected, since this feature is not available in the Z8F6401 pH measurement system.

The average pH measurement for different buffer samples using the Z8F6401 based pH measurement system and the Sartorius® PB-20 pH meter were calculated (Table 2). The Z8F6401 based pH meter consistently gave pH values 0.03 to 0.05 pH units lower than the result of the Sartorius PB-20 within the pH range 4 to 10. However, the difference was significant below and above this pH range. As we deviated farther from this range, the difference became greater. The result for Z8F6401-based pH meter was higher than that of Sartorius® below pH 4 and significantly lower relative to Sartorius® above pH 10.

Table 2. Average pH values of triplicate runs for Z8F6401-based pH measurement system and Sartorius PB-20 pH meter and comparison between these two methods by applying t-Test at 99% confidence level and 4 degrees of freedom (t = 4.60).

Sample Code	Sartorius		Z8F6401		Difference	S_{pooled}	Inference*
	Average pH (pH_s)	Std. Dev.	Average pH (pH_z)	Std. Dev.	$\lvert pH_s-pH_z \rvert$		
1	7.10	0.02	7.07	0.02	0.03	0.02	NS
2	9.16	0.01	9.10	0.02	0.06	0.02	NS
3	9.60	0.02	9.55	0.02	0.05	0.02	NS
4	3.22	0.02	3.34	0.02	0.12	0.02	S
5	10.38	0.02	10.30	0.01	0.08	0.01	S
6	5.80	0.02	5.75	0.01	0.05	0.01	NS
7	6.15	0.03	6.10	0.01	0.05	0.02	NS
8	8.19	0.01	8.14	0.02	0.05	0.02	NS
9	4.15	0.01	4.12	0.02	0.03	0.02	NS
10	2.24	0.03	2.39	0.02	0.15	0.02	S
11	10.95	0.01	10.80	0.01	0.15	0.01	S

*NS = not significantly different, S = significantly different

Statistical analysis, particularly the t-test, was used to determine if the two methods are comparable at 99% confidence level using four degrees of freedom. The degrees of freedom is equal to the sum of the number of pH measurements made on the sample for each method, diminished by the number of methods (3 runs + 3 runs – 2). [14]

Applying t-test to the data showed that the pH measurements of the Z8F6401-based system was comparable to that of Sartorius® PB-20 for samples 1, 2, 3, 6, 7, 8 and 9 but not for samples 4, 5, 10 and 11. If the difference between the means of the results for the two methods was less than $ts_{pooled}\ (2/3)^{1/2}$, then the results for the two methods were not significantly different; if not, then otherwise. Here, s_{pooled} is the pooled standard deviation and t is equal to 4.60.

The results of the t-Test for samples 4, 5, 10 and 11 for the two methods were expected to be "significantly different" since there was error inherent to extrapolation. The glass electrode became somewhat sensitive to alkali metal ions and gave low pH readings at pH values greater than 9. This is known as *alkaline error* [14].

Prior to performing t-test, it is a pre-requisite to do F-test to compare the precision of the two pH meters. The critical value for F is 19.00 for 2 degrees of freedom in each method. All of the results passed the F-test.

Accuracy, Precision and Limitations of Z8F6401 pH Measurement System. The system fluctuated by as much as ±0.04 pH unit in the pH determination of the same sample (for three trials). This fluctuation was calculated to be within the same magnitude of the ADC resolution, and was an inherent limitation of the system.

A Laboratory Experiment: An Automated Strong Acid- Strong Base Titration. Several strong acid-strong base titrations were performed. Sample titration curves are shown in Figure 6. The voltage of the solution was sampled by the ADC throughout the course of the titration at 0.5-s intervals, converted to pH, then displayed using Hyperterminal®.

After the pinch valve tightened, enough titrant was delivered to reach the bromothymol blue endpoint. Underestimating or overshooting the endpoint by 1 to 2 drops was typical. This can be improved by using proportional control in the program algorithm. As the pH change of the solution increases, logic output port PB1 of the Z8F6401 instructs the solenoid valve to decrease reagent delivery. This can be easily implemented by controlling the hardware timers such that the solenoid valve is in closed position for longer periods.

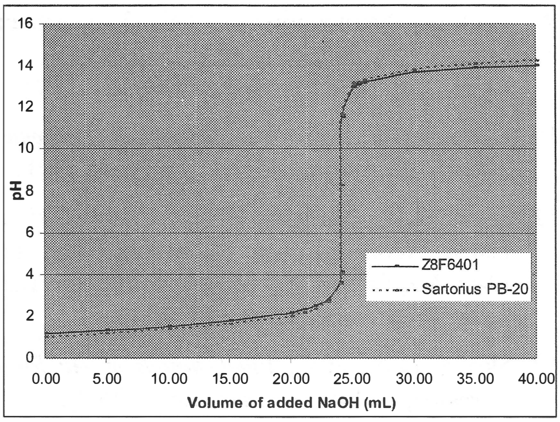

Fig. 6. *Titration curves for ca 0.1 M HCl titrated with 0.1035 M NaOH. Volume is read from a buret and pH is the average of triplicate runs. Results for Z8F6401 are superimposed to that of Sartorius PB-20 (broken lines).*

Limitations of the Auto-Titration System. After performing the titration, the user has to manually obtain the volume reading using the graduations of the buret. The system has no means of displaying the volume of titrant delivered because the flow rate of the titrant is not constant—decreasing as the volume delivered is increased. Consequently, it was very difficult to establish a straightforward relationship between time and volume delivered.

The pH, voltage equivalent of the solution, slope, and y-intercept of the calibration curve could be displayed only using Hyperterminal®. There was no means of saving these data yet.

Finally, only strong acid-strong base titration was tested. Other titrations (i.e., weak acid-strong base, strong acid-weak base, and weak acid-weak base) had not been tried.

CONCLUSIONS AND RECOMMENDATIONS

A low-cost and reliable pH measurement system was devised using a data acquisition system based on the Zilog Encore!™ Z8F6401 microcontroller. The system was comparable to that of Sartorius® PB-20 pH meter for pH measurements within the 4.00 to 10.00 range using a glass electrode. The difference in the results between the two methods was not comparable outside pH 4.00 to 10.00 and became more marked as deviation from the said range was increased. This was verified using t-test at 99% confidence level.

An automated strong acid- strong base titration system can also be coupled to the pH measurement system at a minimal cost. The user, however, has to read the volume of titrant manually using the graduations of the buret. Other sensors (i.e., temperature, conductivity) can be fitted to the system to perform a variety of tasks, which will suit the needs of other common chemistry laboratory experiments.

The system can be interfaced to a PDA or LCD readout and keypad for portable chemical instrumentation. Other features can also be added to the system, such as saving of calibration data and graphing of the titration curve.

It is recommended that proportional control be implemented in the titration algorithm. Also, temperature compensation can be added for more accurate pH measurements.

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