Improving $pH$ Probe Measurement Accuracy for an Automatic Marine Alkalinity Measurement Device

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Problem Statement

The purpose of this project is to improve upon a device that automatically measures pH in order to calculate the alkalinity of seawater using the patented method of reverse gran titration [6] by Dr. Kenneth Hintz and Dr. Christopher Hintz. The current device (*Figure 1*), designed and implemented by Dr. K. Hintz, obtains an inaccurate reading from the pH electrodes. The task of improvement consists of obtaining an accurate reading of pH with a ±0.02 error margin. The final stage of our project will be incorporated into the current device prototype as shown in figure 1.

![Current Alkalinity measurement device prototype](image)

*Figure 1: Current Alkalinity measurement device prototype*

Introduction

Alkalinity is a measurement of the ability of a solution to neutralize acids. Alkalinity of water is due primarily to the presence of bicarbonate, carbonate, and hydroxide ions. Alkalinity is significant in the treatment process of water. Furthermore, if any changes are made to water that could raise or lower the pH value, alkalinity acts as a buffer, protecting the water and its life forms from sudden shifts in pH. Alkalinity should not be confused with pH. The pH of a solution is a measure of the concentration of acid, or H⁺ ions, in that solution. The mathematical formula is defined as follows:

\[ pH = -\log(H^+) \]
Alkalinity is a measurement of the water’s capacity to neutralize an acid, or H⁺ ions, thus keeping the $pH$ value at a fairly constant level. The term alkalinity is expressed as phenolphthalein alkalinity or total alkalinity. Both types can be determined by a titration method with a standard acid solution to an end point $pH$, evidenced by the color change of a standard indicator solution. The $pH$ level also can be determined using a $pH$ meter. [11]

In the usual method of gran titration, the process begins with a solution with an unknown $pH$ and an acid with known $pH$ is dropped into the solution until no more change in $pH$ is detected (equivalence point) which means that the concentrations of the sample and the acid are the same. In the process of our research, we have found different attempts to automate an alkalinity measuring system, however most attempts use the method of gran titration such as the one by J.C. Kim et al. [5]. In reverse gran titration (method proposed in Dr. Hintz’s, et al. patent [6]), the process is the same except that the solution begins with an acid of known $pH$ and a sample is constantly dropped until no more change in $pH$ is detected in the entire solution.

Using the Gran titration method, accurate measurement requirements possess downsides, such as large sample sizes, large amount of acid used to titrate, time consumption, etc. On the other hand, the patent by Dr. Hintz, et al. [6] offers more advantages such as smaller samples for the same accuracy to calculate concentrations, acid fluid needs not be calibrated, it also offers to utilize ordinary analytical equipment to achieve high-precision results, and time consumption is limited to less than 10 minutes as compared to the traditional 20 to 30 minute wait. Additionally, the most important aspect is that it enables the design of an in-situ measurement design that can be left on coral reefs for long periods of time in order to acquire longitudinal alkalinity data.

**Approach:**

The marine alkalinity measurement project is a process that enables to sample contents of any given body of water automatically. The mechanism which allows the user to conduct such a feat consists of key components such as the GUI software (code developed by Dr. K. Hintz) which enables the user to execute the process of extracting the sample of water, the hardware components (relay board and analog-to-digital converter (ADC)) connected to the computer via USB in where the relay board processes the water sample through a series of valves and pumps and the ADC processes the voltage coming from the amplifier after passing through the $pH$ electrodes.
In the existing prototype, the GUI software controls the microcontroller USB ERB08, which is what controls the solenoid valves and pumps in the relay board. It will have capabilities such as closing or opening specific valves, operating the pumps, determining the exact amount of salt water extracted (at least 50 milliliters), the amount of acid injected, and obviously executing the process. Once the software execution on the mechanism is complete, the user no longer has control over the process itself, unless stopped manually.

Since we already know the problem at hand (namely, a wrong pH measurement after reading, amplifying the voltage produced by the pH electrodes, and computing the actual pH value) we will identify the main source of the issue. All mechanical components (Figure 1) have been tested for proper behavior and the ones that did not succeed were the pH electrodes along with the precision instrumentation amplifier. Individually, each carries their own function. That is, the pH electrodes produce a voltage based on the fluids flowing through them and the amplifier amplifies the voltage at a predetermined gain in order to make the dynamic range of the pH measurements match the dynamic range of the input to the ADC. However, when operated collectively, the pH measurement from a solution with a known pH value does not yield the correct result.

**Requirements Specification**

In this project, we must replace or improve upon components of previous prototype to ensure an accurate pH reading from electrode to 2 decimal places (e.g., 8.32 ± 0.02). Errors of measurement must be minimized and analyzed in an oscilloscope for a more qualitative result. If the task is successfully completed prior to the end of senior design, we will assist in the implementation of a mixing chamber for proper intermingling of acid and seawater. The components to be reevaluated and/or replaced will be the pH electrodes and the instrumentation amplifier.

Our project is specifically focused on obtaining a pH reading. Figure 2 shows our black box design where we have a sample fluid and power as the primary inputs and de-ionized water as a secondary input to flush out the system. The resulting voltage from the pH measurement will be read into the A/D converter which in turn, will be read to the GUI.
Figure 2: Our black box design

Figure 3: Our white box design

Figure 4: Our Level 2 design
Background Knowledge

One of the key components in the entire mechanism is the pH probe which has two electrodes; the reference electrode and the pH electrode (also known as measurement electrode.) The reference electrode has a specific concentration of hydrogen ions and the pH electrode obtains the fluid of which the pH is to be measured. As a result, the difference of hydrogen ions between the reference and pH electrodes generates a voltage that is directly proportional to the pH value.

In figure 5, we have a more detailed diagram that explains how a pH measurement electrode operates. The fundamental design of the pH electrode is that the glass body essentially separates the hydrogen ions from all other ions. The glass is doped with lithium ions and this makes it electrochemically reactive to hydrogen ions. The glass acts as a strong insulator which means that if we wish to establish a circuit connection between the measurement and reference electrode, there is a tremendously high resistance. This high resistance makes it difficult to measure the voltage across the two electrodes. [1] [11]

![Figure 5: Measurement electrode](image-url)
In figure 6, we have the reference electrode which is made from a neutral $pH$ chemical buffer solution (usually potassium chloride) allowed to interchange ions with the process solution through the porous separator, thus forming a relatively low resistance connection to the test fluid [1].

![Reference Electrode Diagram](image)

**Figure 6: Reference electrode**

Ideally, the $pH$ electrodes produce a voltage of approximately 59.16 mV per level of $pH$, thus demonstrating a linear relationship between voltage and $pH$. More simply,

$$V = (0.05916 \times pH) \text{ Volts, where } pH = 1 \text{ to } 14.$$

Therefore, the range of voltages corresponding to the range of possible $pH$ values is 59.16 mV to 828.24 mV [1].
Voltage Buffer (unity gain buffer) Amplifier

A voltage buffer amplifier is used to transfer a voltage from a first circuit with a high output impedance level to a second circuit with a low input impedance level. The interpolated buffer amplifier prevents the second circuit from loading the first circuit inadmissibly and interfering with its desired operation. In the ideal voltage buffer in the diagram, the input resistance is infinite, the output resistance zero (impedance of an ideal voltage source is zero). Other properties of the ideal buffer are: perfect linearity regardless of signal amplitude and an instant output response regardless of the rise time or bandwidth of the input signal.

If the voltage is transferred unchanged (the voltage gain $A_v$ is 1), the amplifier is a unity gain buffer; also known as a voltage follower because the output voltage follows the input voltage. Although the voltage gain of a voltage buffer amplifier may be (approximately) unity, it usually provides considerable current gain. However, it is commonplace to say that it has a gain of 1 (or the equivalent 0 dB), referring to the voltage gain. [12]
Use of Voltage follower as an input to instrumentation amplifier will be used to bring down the high input impedance as well as the high input bias current.

In our design, we propose to use voltage follower circuit for the following reasons:

- High gain accuracy
- High Common Mode Rejection Ratio (CMRR)
- High gain stability with low temperature coefficient
- Low DC offset
- Low output impedance
- High input impedance

**Instrumentation Amplifier (Gain)**

The differential configuration of the AD8222 has the same excellent dc precision specifications as the single-ended output configuration and is recommended for applications in the frequency range of dc to 100 kHz. The circuit configuration is shown in Figure 9. The circuit includes an RC filter that maintains the stability of the loop. [2]

The transfer function for the differential output is:

\[ V_{DIFF\_OUT} = V_{+\_OUT} - V_{-\_OUT} = (V_{+\_IN} - V_{-\_IN}) \times G \]
Where

\[ G = 1 + \frac{49.4k\Omega}{R_G} \Rightarrow R_G = \frac{4.94k\Omega}{G-1} \]  

[9]

**Figure 9**: AD8222 Differential mode configuration

**Prototyping**

In order to determine a conclusive plan, we conducted a series of tests on the precision instrumentation amplifier AD8222 with a test input source of 9V in a voltage divider circuit. Table 2 shows the unsatisfactory results.

<table>
<thead>
<tr>
<th>Amplifier Input via 9V battery (Vin)</th>
<th>Amplifier output w/ 11.51 gain (Vout)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0378</td>
<td>0.511</td>
</tr>
<tr>
<td>0.102</td>
<td>1.26</td>
</tr>
<tr>
<td>0.2</td>
<td>2.36</td>
</tr>
<tr>
<td>0.313</td>
<td>3.69</td>
</tr>
<tr>
<td>0.422</td>
<td>4.96</td>
</tr>
</tbody>
</table>

*Table 1: DC Input source with a 9V battery constructed in a voltage divider circuit using a potentiometer in order to get different output voltages*
We injected a set of buffer fluids, each with their own specific pH values, through the previous prototype. Each buffer fluid was pumped into the pH electrodes and the values were read into the GUI as shown in figure 10. We tabulated our results obtained from the pH buffer fluids from trials in table 2 with the properties displayed by the GUI as in the case for tap water in figure 10. The results are obviously incorrect and the reasons for this are most likely due to the AD8222’s high input impedance (1 GΩ). To fix the issue we will implement a MAX406 differential voltage buffer between the pH electrodes and the AD8222. The MAX406 has high input impedance which makes a good voltage buffer and is known for its pH probe applications. [12]

**Table 2:** Blatantly incorrect results from existing prototype when reading solutions with a certain pH level.

<table>
<thead>
<tr>
<th>pH Level</th>
<th>Electrode Voltage</th>
<th>Standard Deviation</th>
<th>pH Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>-8.8*10^-9 mV</td>
<td>3.23*10^-5 mV</td>
<td>21.17</td>
</tr>
<tr>
<td>7.0</td>
<td>-8.51*10^-5 mV</td>
<td>3.49*10^-5 mV</td>
<td>21.17</td>
</tr>
<tr>
<td>10.0</td>
<td>-7.026*10^-9 mV</td>
<td>3.58*10^-5 mV</td>
<td>None</td>
</tr>
</tbody>
</table>

**Figure 10:** A sample run of pH test on GUI

Below is the result of MAX406 amplifier. Our main purpose is to use MAX406 amplifier as a voltage buffer and we have checked its performance. Figure 11 shows the input voltage using 9V
battery with potentiometer connected in a voltage divider manner. We set our input at 399mV and as shown in figure 12 had obtained an output of 399mV as we expected.

*Figure 11: MAX406 input voltage*

*Figure 12: MAX406 output voltage*
Figure 13: MAX406 unity-gain circuit setup

The following oscilloscope images shows a noisy signal when the lights turned on.

Figure 14: Data capture when environmental noise was introduced (fluorescent lights)

An interesting was observation was made with this data; we were able to conclude that fluorescent lights will also impact the reading of our data due to their electric fields. We meant to use coaxial cable in lieu of un-shielded cable during our prototype testing. In future testing, we will use stranded 22-Guage shielded wire in our future prototyping testing.
Implementation Plan

In our design, we will use one of the two different amplifiers in order to meet our specifications: MAX406 or INA116. Because our project requires a precision $pH$ reading of ±0.02 as well as overcoming the high output impedance generated by the $pH$ probes, one of these two high input impedance amplifiers will suffice our needs.

According to the datasheet from the MAX406 amplifier (manufactured by MAXIM), one of its various typical applications is to incorporate it as a buffer for $pH$ probes. *The MAX406 has less than 20pA input leakage current over the commercial temperature range, and is typically less than 100fA at +25°C. These characteristics are ideal for buffering $pH$ probes and a variety of other high output impedance chemical sensors.* [12]
The circuit in figure 16 eliminates expensive low-leakage cables that often connect pH probes to meters. This schematic also proposes the use of a low-cost coaxial cable (a stranded coaxial cable will be more optimal to block environmental noise) to carry the voltage directly to the A/D converter to then be read in the software. However, there are two things to consider, A/D range and proper measurement. As mentioned earlier, these voltages will be measured using an oscilloscope. Also, if the output voltage from the buffer does not meet the A/D converter range (up to ±20V on a differential configuration and ±10V for single-ended mode), it will have to be amplified to meet that criteria. In theory, if the voltage needs to be amplified, any amplifier would work fine, however by using the MAX406 we would be eliminating the high input impedance. Furthermore, the proposed power supply for this circuit calls for a 3 volt battery to power up the probe and MAX406 which can be accommodated to a maximum of 10 volts because that is in the range of the MAX406 power supply.

The other option is to use the instrumentation amplifier INA116 manufactured by Burr-Brown. Once again, the reason why we are choosing this component is because one of its few typical applications is pH measurement. Additionally, the extremely high input impedance of INA116 ($10^{15} \Omega$) will make it a great candidate to implement in our project. Figure 17 shows the complete schematic of this chip.
Figure 17: Instrumentation Amplifier INA116 schematics

The advantage of choosing this amplifier (Figure 17) over the MAX406 is that the INA116 has the ability to set the gain in order to meet analog-to-digital converter range. The gain (G) can be derived by choosing an appropriate value for $R_G$. It is defined as follows:

$$G = 1 + \frac{50k\Omega}{R_G}$$

Figure 18: shows the actual connection of the pH electrodes to the instrumentation-Amplifier INA116; however, in our project, we’re using the flow-through electrodes.
**Testing Plan**

Since our project will be based mostly on the accurate reading of the $pH$ electrode from an electronics perspective, we will have to perform several tests on the components obtained in order to succeed the task. Our experimenting and testing will consist of:

1. Setting up the circuit on a breadboard for the MAX406 unity-gain amplifier.
2. Using a $pH$ meter (figure 19) which will serve as a monitoring device for the accurate $pH$ reading of the solution we want to measure.
3. Running tests with different $pH$ solutions using the bread boarded prototypes of the amplifiers and checking to see if we obtain a correct reading in respect to the $pH$ values (59.16mV/pH.)
4. After getting the appropriate results using such amplifiers, we will work on a vector board so that the prototype of that specific circuit can be incorporated into the current prototype device implemented by Dr. Hintz (figure 20)
5. Running a series of tests on the current prototype device using buffers fluids with a known $pH$ so that the output we obtain is the same.
6. If we detect a repetitive inaccuracy and/or error during this procedure that cannot be fixed, we’ll change the amplifier to the instrumentation amplifier INA116

*Figure 19: pH meter to determine the exact pH value of the solution to be measured*
Figure 20: pH electrodes in current prototype, covered by shielded box, will host our project prototype.

Schedule

The following tentative schedule provides a time frame for the different tasks to be accomplished during the 493 semester. The allocated tasks are to be separated into:

1. Bread board implementation for the different amplifiers (Akash, Ambar)
   1.1. Implementation of unity-gain buffer MAX406
   1.2. Implementation of instrumentation amplifier INA116
2. Testing #1 (Akash, Ambar, Erick)
   2.1. Compare voltage readings to actual pH reading (59.16mV/pH) with the pH meter, using different pH solutions (4, 7, 10, etc.)
3. Progress Report #1 (Akash, Ambar, Erick)
4. Vector board implementation (Akash, Ambar)
   4.1. Implementation of MAX406
   4.2. Implementation of INA116
5. Testing #2 (Akash, Ambar, Erick)
   5.1. Compare voltage readings to actual pH reading (59.16mV/pH) with the pH meter, using different pH solutions (4, 7, 10, etc.)
6. Incorporation of sub-system into device
   6.1. Prepare PCB file (Erick)
6.2 Implement design into current prototype (Akash, Ambar)

7. Progress Report # 2 (Akash, Ambar, Erick)

8. System Testing (Akash, Ambar, Erick)

9. Mixing Chamber (extra credit) (Akash, Ambar, Erick)
Appendix

The following appendix shows the different components of the existing prototype as well as an overview of the whole system.

Relay Board

USB-ERB08 block diagram

USB-ERB08 functions are illustrated in the block diagram shown here.

The above diagram is for the relay board USB-ERB08 which acts as a series of switches in order to perform functions such as closing or opening the solenoid valves or for operation of pumps. The switches have two modes to set the relay control logic polarity for each relay bank for invert or non-invert. By default, the switches are shipped with all banks configured for non-inverted logic. There are two modes associated the switches; non-invert and invert. In non-invert mode, when “0” is written or read back via the USB bus, the relays are not energized. In invert mode, when “0” is written or read back via the USB bus, the relays are energized. The USB bus reads back the switch settings for polarity. [8]
Analog-to-Digital Converter

**USB-1408FS block diagram**

USB-1408FS functions are illustrated in the block diagram shown here.

![USB-1408FS block diagram](image)

**Figure 22: A/D converter block diagram**

The USB-1408FS is a USB 2.0 full-speed analog input and digital I/O data acquisition device supported under popular Microsoft Windows operating systems. It is designed for USB 1.1 ports, and was tested for full compatibility with both USB 1.1 and USB 2.0 ports. The USB 1408-FS features eight analog inputs, two 12-bit analog outputs, 16 digital I/O connections, and one 32-bit external event counter. The analog inputs are software configurable for either eight 13-bit single-ended inputs or four 14-bit differential inputs. The digital I/O lines are independently selectable as input or output in two 8-bit ports. The 32-bit counter can count TTL pulses. A SYNC (synchronization) I/O line allows one to pace the analog input acquisition of one USB module from the clock output of another. No external power is required for operation other than the USB port to a computer. The purpose of the above A/D converter is to ensure a reading from the pH
probe to the GUI and this required a higher voltage which is provided by the AD8222 instrumentational amplifier. [9]

**Level 0 design of current device**

![Diagram](image)

**Figure 23: level 0 design of overall long term device**
**Level 1 design of current device**

![Diagram](image)

*Figure 24: level 1 design of overall long term device*
Level 2 design of current prototype

Figure 25: level 2 design of overall long term device
References


