

Project Report
on
**Auto Titrator: A Low Cost Automatic Titration
Machine using pH End-point Detection**

submitted in partial fulfillment of the requirement
for the award of the Degree of

Bachelor of Engineering

by

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Certificate

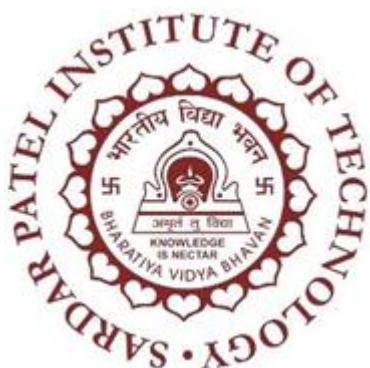
This is to certify that the Project entitled Auto Titrator: A Low Cost Automatic Titration Machine using pH End-point Detection has been completed successfully by Ms. Pallavi Avle , Mr. Tejas Badgujar and Mr. Brendon Faleiro under the guidance of Prof. Payal Shah for the award of Degree of Bachelor of Engineering in Electronics Engineering from University of Mumbai.

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Project approval Certificate

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Abstract

Our final year project relates to the field of Embedded Systems for a pH based low cost automatic titration systems. The objective of our project is to develop an automated system at a low cost, which carries out the authentic titration process with minimal human intervention. A miniaturized micro-volume auto-titrator with potentiometric end-point detection is proposed. The developed system has a compact and robust design with and uses a pH probe.

The method is based on on-line potentiometric titration of the acids with various bases. Various modules like flow control, end-point detection and display were prepared separately and then combined to acquire the required output.

Our project has been designed keeping in mind the basic requirements of small scale applications like a college chemistry laboratory, testing of pH and acidity of milk and other such fluids and hobby based titrators. Strict quality and test standards applied to our product throughout design stages ensure good accuracy and speed and low product failure rate and uniform part-to-part characteristics.

Chapter 1

Introduction

1.1 Autotitrator Definition

Titration is a common laboratory method of quantitative chemical analysis used to determine the unknown concentration of an identified analyte. Since volume measurements play a key role in titration, it is also known as volumetric analysis[1].

The auto-titrator is a commercial apparatus that carries out the titration operation automatically and provides the equivalence point data. Auto-titrators are often used in laboratories and they bring many benefits over performing titrations using manual methods.

1.2 Problem Statement

The process of manual titration, inspite of its various applications, is very tedious and has several drawbacks. Hence attempts have been made to automate the entire process. Commercially available autotitrators are highly specialized and as such they are expensive, bulky and need skilled experts for their operation. As a result, they are not used in small scale applications such as in college laboratories.

1.3 Solution

In order to create a technology that can be utilized at a low cost,we have implemented a potentiometric auto-titration system with a pH based end-point detector. The system automatically performs the titration with minimum human intervention and calculates the parameters of the reagent under test such as its concentration. To reduce the cost of the system, instead of high-end sampling mechanisms, a low cost solenoid valve is used to sample the solutions. Accessories and other functionalities not required for small scale applications such as data-loggers and printers have been removed.

1.4 Current Scenario

Currently a wide range of auto-titrators with various probes are available in the market. These auto-titrators cover a wide range of reactions including neutralizations, redox reactions, Karl-Fischer titrations, etc. Some companies manufacturing auto-titrator systems are Mettler Toledo, Hanna instruments, Metrohm, etc.

1.5 Objective

Titration has been used for several years to determine unknown concentrations of reagent.

The classical technique of titration is used extensively for this purpose.

In the present form, the classical manual methods of titration are said to have the following disadvantages:

1. Is a very slow process.
2. Determining end point may be difficult and it depends on the indicator being used.
3. Accuracy depends on the perception of the user.

In order to overcome these drawbacks, over the years attempts have been made to automate the process by using controllers and other mechanisms.

The commercially available automated titration systems are still known to have the following disadvantages:

1. Extremely high price.
2. Require skilled knowledge to operate.
3. Systems are bulky.

Due to these issues, it is difficult to purchase and use these systems on a small scale level.

Thus there is a need to address these above mentioned disadvantages. With an aim to build a low cost system that overcomes all these disadvantages considering the system to be used at a small scale level, we designed an "Auto-titrator with pH based End-point Detection". With this project, we sincerely believe that we will be able to produce a complete system that can be used in college laboratories and other small scale industries.

1.6 Organization of the Report

The report is organized into different sections.

1. Chapter 1 includes the introduction of our project.
2. Chapter 2 has been dedicated to the literature survey done related to the project. This chapter mainly includes the patent analysis of 3 patents similar to our topic.
3. Chapter 3 includes the description and brief explanation of the block diagram of the system. The detailed working of the system is discussed in this chapter.
4. Chapter 4 has been dedicated to describe the software implementation of the developed system. This mainly includes the process flow, algorithm used to detect endpoint and other software aspects of the project.
5. Chapter 5 deals with Experimentation and Result analysis section.
6. Chapter 6 includes conclusion and future scope of the project.
7. Lastly, PCB details of the components, Microcontroller board details and the C codes have been included in the Appendix section.

Chapter 2

Literature Review

Several auto-titrator systems have been developed using different technologies for implementing the various parts of the auto-titrator. Since the early 1970s extensive research has been done in the fields of speed up and improvement in the auto-titration working. Some of the more noteworthy research is covered below:

2.1 Automatic Process Titration System

An automatic titration system[3] in which the titrant is generated electrolytically and a two-position slider type ceramic sample valve that obtains a volumetric sample from a process loop and introduces it to a titration cell containing a generator or working compartment and an auxiliary compartment separated by a porous frit is developed. Titrant created at a generator electrode surface is dispersed into the bulk of the solution by a magnetically coupled impeller in the working compartment which mixes and also pumps the contents of the cell through the reagent and sample valves in a closed loop.

Generator and auxiliary electrodes are connected to a current source which provides the electrolysis current. The progress of the titration is monitored by indicating and reference electrodes in the titration cell connected to an appropriate endpoint indicator, output of which is compared to a known set point corresponding to the titration endpoint. The total charge delivered to the generator and auxiliary electrodes during titration is measured by a timer or integrator and read out as a trend output signal. The automatic titration system and method of this invention advantageously lends itself to microprocessor control over the titration reaction and titrator sequencing.

2.2 Automatic Titration Analysis Apparatus

Automatic titration analysis apparatus includes a sampling mechanism, a titration mechanism, an analysis mechanism and a control mechanism. The sampling mechanism takes a prescribed quantity of a sample for analysis in accordance with a first signal[4]. The titration mechanism titrates a prescribed quantity of a reagent for analysis of the sample and provides a titer at an end point of the titration according to second signals. The analysis mechanism receives the sample from the sampling mechanism, analyzes the sample and converts a change in the physical properties of the sample caused by the titration into an electrical quantity.

The control mechanism provides and applies the first signal to the sampling mechanism, provides and applies the second signals to the titration mechanism, receives the titer from the titration mechanism, receives the electric quantity from the analysis mechanism, sets the quantity of the sample converted and the titer of the reagent to prescribed values, reads the titer at the end point of the titration, outputs the measured density of the sample calculated there from, and controls in sequence the operations of the sampling, titration and analysis mechanisms.

2.3 Speed-up of the auto-titrator operation

The acid-base titration is used wide in the fields of chemical engineering, environmental engineering, agriculture, and medical science. The auto-titrator is a commercial apparatus that carries out the titration operation automatically and provides the equivalence point data. For some test samples and operating conditions, titration operations require up to around 5 minutes. Here a method to reduce this operation time by one-fifth is proposed[6]. For this, systems technologies such as reducing sensor time-constant with a lead-lag filter, parameter identification and alternative dosing of titrating and sample solutions have been applied. Test equipment that simulates commercial auto-titrators is introduced.

2.4 Design and fabrication of a micro-volume autotitrator with potentiometric end-point detection for the determination of acidity of some fruit juices

A miniaturised micro-volume autotitrator with potentiometric end-point detection was designed and fabricated for the determination of acidity of some Thai fruit juices[5]. The method was based on on-line potentiometric titration of the organic acids with sodium hydroxide. The conditions such as volume of fruit juice sample, volume and concentration of potassium chloride used as supporting electrolyte, and flow rate of the titrant were optimised by using univariate optimisation. A sample throughput of 83 samples/hr at the titrant flow rate of 0.28 mL/min was achieved with satisfactory results. The results obtained by the proposed method agreed with those obtained by the classical tiCitric acid (2-hydroxy-1,2,3-propanetricarboxylic acid), unlike other hydroxy acids, is tribasic with a major advantage of high solubility in water. Several fresh fruits such as lemon and lime owe their tangy taste to the presence of citrate ions.

Acidity can be determined by a large number of methods such as ion chromatography, gas chromatography, high performance liquid chromatography, capillary electrophoresis, and flow injection analysis. Although some methods can selectively determine different acids, the acidity is usually reported in terms of the citric acid content. Titration is used as the classical method for the determination of citric acid in fruit juices. The disadvantage of titration is that it is time and reagent consuming. Potentiometry is also alternatively used to determine the total acid content in fruit juices in comparison with classical titration. In this present work, we have designed and fabricated a micro-volume autotitrator with potentiometric end-point detection for the determination of acidity of the juices of eight Thai fruits collected in the northern area of Thailand. The method is based on an on-line potentiometric titration. Variables affecting the proposed method, viz. volume of fruit juice sample, volume and concentration of potassium chloride used as supporting electrolyte, and flow rate of titrant were evaluated and optimised.

2.5 An automatic determination method based on color sensor at the end point of the titration

An automatic determination method at the end of the titration is introduced, in which using the Large Power White-Light LED as a light source, with TCS3200 converting color light to frequency and 89C51 collecting the color information of the solution[7].

Chapter 3

Theory

Titration as a process to detect concentration of substances has been used for several years. However manual performance of the experiment has often been inefficient and tedious. The basic idea is to cause two reagents to react, one of whose concentration and volume is known. The concentration of the second reagent can be calculated if its volume is known at the end of the reaction.

3.1 The Titration Process

3.1.1 Elements of Titration:

- (a) The standard solution is the solution of known concentration. An accurately measured amount of standard solution is added during titration to the solution of unknown concentration until the equivalence or endpoint is reached. The equivalence point is when the reactants are done reacting.
- (b) The solution of unknown concentration is otherwise known as the analyte. During titration the titrant is added to the analyte in order to achieve the equivalence point and determine the concentration of the analyte.
- (c) The equivalence point is the ideal point for the completion of titration. In order to obtain accurate results the equivalence point must be attained precisely and accurately. The solution of known concentration, or titrant, must be added to the solution of unknown concentration, or analyte, very slowly in order to obtain a good result. At the equivalence point the correct amount of standard solution must be added to fully react with the unknown concentration.
- (d) The end point of a titration indicates once the equivalence point has been reached. It is indicated by some form of indicator which varies depending on what type of titration being done. For example, if a color indicator is used, the solution will change color when the titration is at its end point.

3.1.2 Titration Curves

- (a) A titration curve is a curve in the plane whose x-coordinate is the volume of titrant added since the beginning of the titration, and whose y-coordinate is the concentration of the analyte at the corresponding stage of the titration (in an acid-base titration, the y-coordinate is usually the pH of the solution).
- (b) In an acid-base titration, the titration curve reflects the strength of the corresponding acid and base. For a strong acid and a strong base, the curve will be relatively smooth and very steep near the equivalence point. Because of this, a small change in titrant volume near the equivalence point results in a large pH change and many indicators would be appropriate (for instance litmus, phenolphthalein or bromothymol blue).
- (c) If one reagent is a weak acid or base and the other is a strong acid or base, the titration curve is irregular and the pH shifts less with small additions of titrant near the equivalence point. For example, the titration curve for the titration between oxalic acid (a weak acid) and sodium hydroxide (a strong base) is pictured. The equivalence point occurs between pH 8-10, indicating the solution is basic at the equivalence point and an indicator such as phenolphthalein would be appropriate. Titration curves corresponding to weak bases and strong acids are similarly behaved, with the solution being acidic at the equivalence point and indicators such as methyl orange and bromothymol blue being most appropriate.
- (d) Titrations between a weak acid and a weak base have titration curves which are highly irregular. Because of this, no definite indicator may be appropriate and a pH meter is often used to monitor the reaction.
- (e) The type of function that can be used to describe the curve is called a sigmoid function.

3.2 Developments in the field of Titration

- (a) Classical Technique : Titration is a classical analytical technique widely used. Originally, it was performed by adding the titrant using a graduated glass cylinder (burette). With a tap the titrant addition was regulated manually. A change in colour indicated the end of the titration reaction (endpoint). At first, only those titrations showing a significant colour change upon reaching the endpoint were performed. Later titrations were coloured artificially with an indicator dye. The precision achieved depended mainly on the chemist's skills and, in particular, on his different colour perception.
- (b) Modernization and use of Technology : Titration has experienced a strong development; manual and motorized piston burettes allow reproducible and accurate titrant addition. Electrodes for potential measurement replace the colour indicators, achieving higher precision and accuracy of the results. Graphical plot of potential versus titrant volume allows a more exact statement about the reaction than the colour change at the endpoint. With microprocessors the titration can be controlled and evaluated automatically. This represents a relevant step towards

complete automation

- (c) Automation and Autotitrators : Modern autotitrators allow the definition of complete analysis sequences achieving maximum flexibility in method development. For each application the specific method can be defined by combining simple operation functions like "Dose", "Stir", "Titrate", and Calculate" in a defined sequence. Auxiliary instruments (sample changers, pumps) help in reducing and simplifying the work load in laboratories. A further trend is the connection to computers and Laboratory Information Management Systems (LIMS)

3.3 Commercial systems

An automatic titrator is an instrument with at least one burette controlled by a signal from a probe which provides a defined amount of titrant. The determination of the equivalence point is to be done automatically after processing the data obtained, in order to report a final calculated result in the appropriate unit.

A typical auto-titrator [2] consists of the syringe pump, pH sensor, titrating reactor with a magnetic stirrer and a control computer(Refer Fig. 3.1). The syringe pump can dose the titrating reagent to the titrating reactor at micro litre accuracy. For each dosing of the titrating reagent, the pH value in the titrating reactor is measured.

The titrant can be added

- (a) volumetrically,with a burette or a low flow rate pump
- (b) coulometrically, with an electrochemical generation from a proper electrolyte.

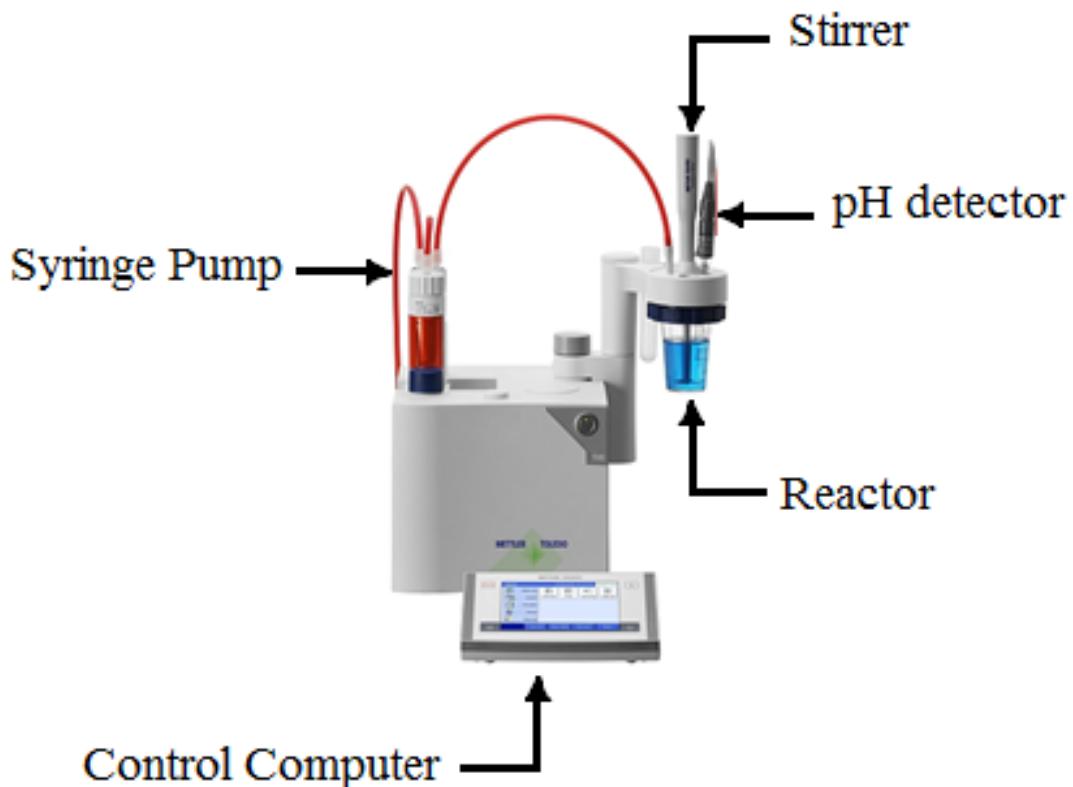


Figure 3.1: Typical Commercial Auto-titrator

3.4 Autotitrator Process Flow

Automated titrators follow a defined sequence of operations. It is performed and repeated several times until the endpoint or the equivalence point of the titration reaction is reached (titration cycle). The titration cycle consists mainly of 4 steps:

- (a) Titrant addition
- (b) Titration reaction
- (c) Signal acquisition or end-point detection
- (d) Evaluation

Each step has different specific parameters (e.g. increment size) which have to be defined in according to the specific titration application. More complex applications require more steps, e.g. dispensing of an additional reagent for back titrations, dilution, adjusting of pH value, etc. These steps and the corresponding parameters are resumed in a titration method.

3.5 Methods of Implementation

Automated titrators are microprocessor-controlled instruments which allow the automation of all operations involved in titration:

1. Titrant addition
2. Monitoring of the reaction (Signal acquisition) and recognition of the endpoint
3. Data storage and Calculation
4. Transfer of data to printer or computer/external system

1. Titrant addition : Several methods of titrant addition were studied. These include an automatic titration system in which the titrant is generated electrolytically and a two-position slider type ceramic sample valve that obtains a volumetric sample from a process loop and introduces it to a titration cell containing a generator or working compartment and an auxiliary compartment separated by a porous frit is developed. Titrant created at a generator electrode surface is dispersed into the bulk of the solution by a magnetically coupled impeller in the working compartment which mixes and also pumps the contents of the cell through the reagent and sample valves in a closed loop[3]. Other implementations include a sampling mechanism that takes a prescribed quantity of a sample for analysis in accordance with a first signal using peristaltic motors or servo motors[4]. However, in our implementation, we have used solenoid valves[6] as the suction of fixed quantities of titrant with the use of servo motors is a tedious affair while peristaltic motors are extremely expensive.

Solenoid valves can be used to bring about flow control. The media controlled by the solenoid valve enters the valve through the inlet port. The fluid media flows through the orifice before continuing into the outlet port. The orifice is closed and opened by the plunger.

Normally closed valves use a spring which presses the plunger tip against the opening of the orifice. The sealing material at the tip of the plunger keeps the media from entering the orifice, until the plunger is lifted up by an electromagnetic field created by the coil.

2. Monitoring of the reaction (Signal acquisition) and recognition of the endpoint : Titrations can be classified according to the indication principles and the chemical reaction occurring. These indication principles are classified as follows:

Potentiometry:

The concentration-dependent potential (mV) of a solution is measured against a reference potential.

Examples: Acid/Base (aqueous/non-aqueous), redox, precipitation reactions.

Voltammetry:

The concentration-dependent potential of a solution (mV) is measured at a constant polarizing electric current.

Examples: Karl Fischer water determination.

Amperometry:

The current flowing in a sample solution (A) is measured at a constant polarizing potential.

Examples: Iron(II) and Vitamin C determination.

Photometry:

The light transmission (mV or % transmission) of a coloured or turbid solution is measured with a photometric sensor.

Examples: Complexometric and turbidimetric reactions.

Conductivity:

The conductivity of a solution (S/cm) is measured by a conductivity meter.

Example: Alpha acids in beer.

Thermometry:

The temperature of a sample is measured by a temperature sensor.

Example: Boric acid content.

The selection end-point detection mechanism and signal acquisition depends heavily on the indication principle adopted. Some mechanisms are as follows:

- (a) **pH detectors:** pH detectors are used in the testing of acids such as Hydrochloric acid and bases such as Sodium Hydroxide (pH is low for acids and high for bases). They are used mainly to detect the end-point of neutralization type titrations.
- (b) **Colorimetric detectors:** Used for end point detection in color reactions such as Sodium Thiosulphate. These detectors generally make use of CCD arrays to detect the color of the titre and detect the end-point(the point at which the color changes). Another automatic determination method at the end of the titration, uses the Large Power White-Light LED as a light source, with TCS3200 converting color light to frequency and 89C51 collecting the color information of the solution[7].

In our mechanism we use the dual electrode pH detector which uses a Glass Electrode and a reference electrode due to its efficiency, small size and low cost.

3.6 Advantages of Autotitration

Autotitration have applications across sectors ranging from pharmaceutical, food processing and chemical industries as well as in educational institutes. Here are some of the most significant benefits of using an Autotitrator:

1. An Autotitrator can give a more accurate reading than a human.
2. There isn't any discrepancy for human error (what one person sees as 1.5ml another person may see as 1.6ml). With an Autotitrator there is no confusion.
3. The end-point detection does not rely on human colour perception and as such results are not as prone to operator error.
4. An Autotitrator performs tests much faster than a human could.
5. In light of the above, when using an Autotitrator chemists will often perform tests on more samples than they would if they had to perform a test manually

6. A more representative sample is a further benefit of using an Autotitrator

The proposed design for the Autotitrator, provides all the above benifits at a much lower cost than other commercially available systems.

Chapter 4

System Design

4.1 Block Diagram

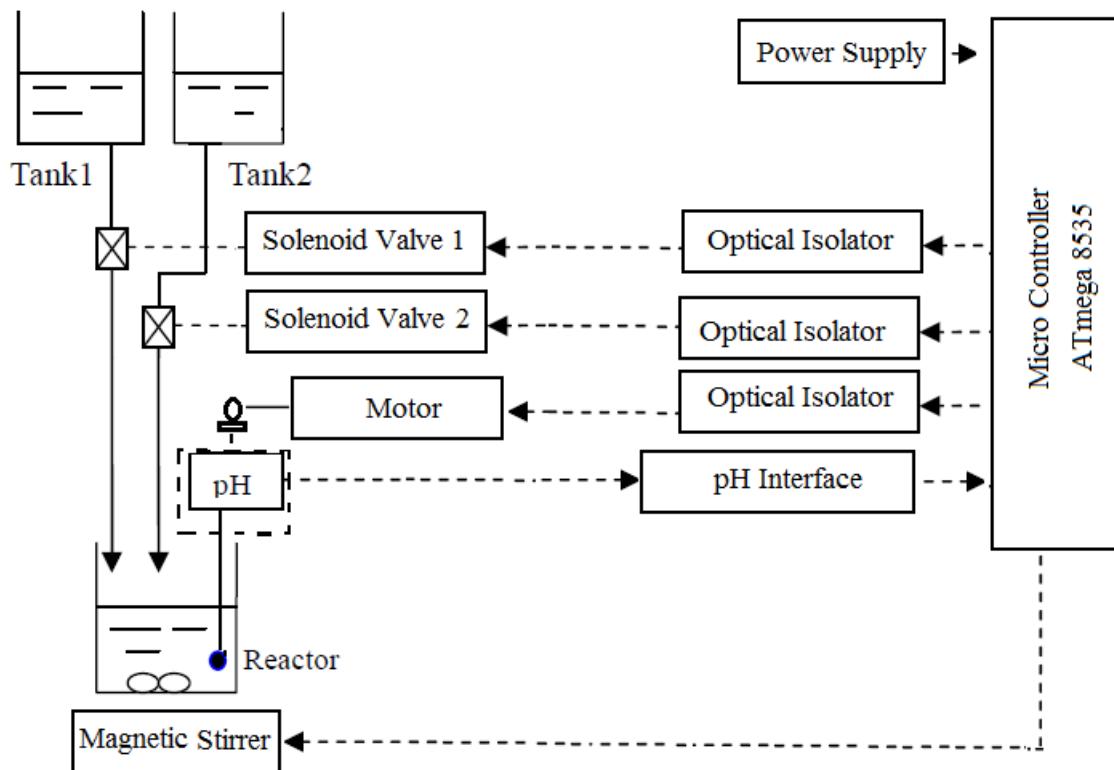


Figure 4.1: Block Diagram: Automatic Titration Machine

The Block Diagram shown in Fig. 4.1 consists of major sections mentioned as follows:

1. Optical Isolator: To provide electric isolation between the controlling signals from the microcontroller and the output driving signals to the solenoid valves and motors. IC

used is PC817.

2. ATmega 8535: This block is used to control the working of the complete system and perform calculations once the end-point is detected.[8].
3. Solenoid Valves: The normally closed solenoid valves were used to implement a flow control mechanism while sampling the solutions.
4. pH Electrode: The combination pH electrode is used as a sensor to detect the pH of the solution under test and thus detect the end-point of the titration. The probe used is a combination probe that comes along with the Systronics 335 pH meter.[9].
5. pH Interface: The pH interface block consists of a JFET Operational Amplifier that is used to amplify the signal received from the pH meter before it is fed to the ADC of the ATmega 8535. The operational amplifier used is TL082.
6. Stirrer: The stirrer block is a magnetic stirrer used to stir the contents of the solution to ensure even distribution of the solution. It has been implemented using a computer fan, a pair of simple magnets and a Teflon coated magnet.[10]

Each of these blocks have been explained in detail in the following sections:

4.2 Flow control mechanism

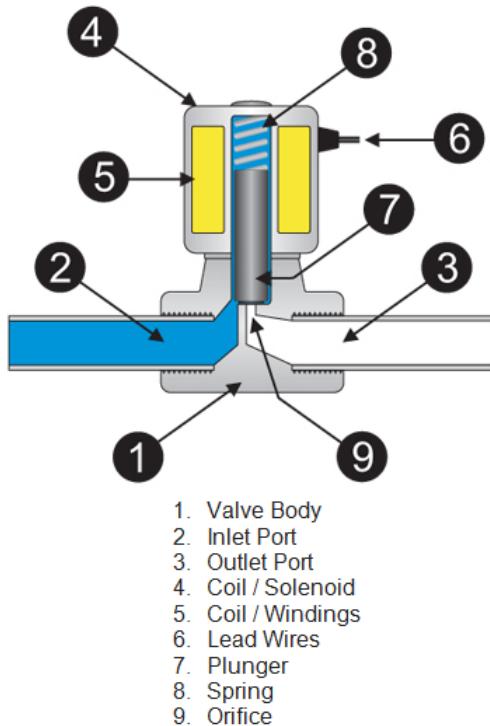


Figure 4.2: The Normally Closed Solenoid valve

Flow control is implemented with the use of solenoid valves. The solenoid valves used are of the normally closed type. The media controlled by the solenoid valve enters the valve

through the inlet port. The fluid media flows through the orifice before continuing into the outlet port. The orifice is closed and opened by the plunger.

The normally closed solenoid valve(Ref. Fig. 4.2) uses a spring which presses the plunger tip against the opening of the orifice. The sealing material at the tip of the plunger keeps the media from entering the orifice, until the plunger is lifted up by an electromagnetic field created by the coil.

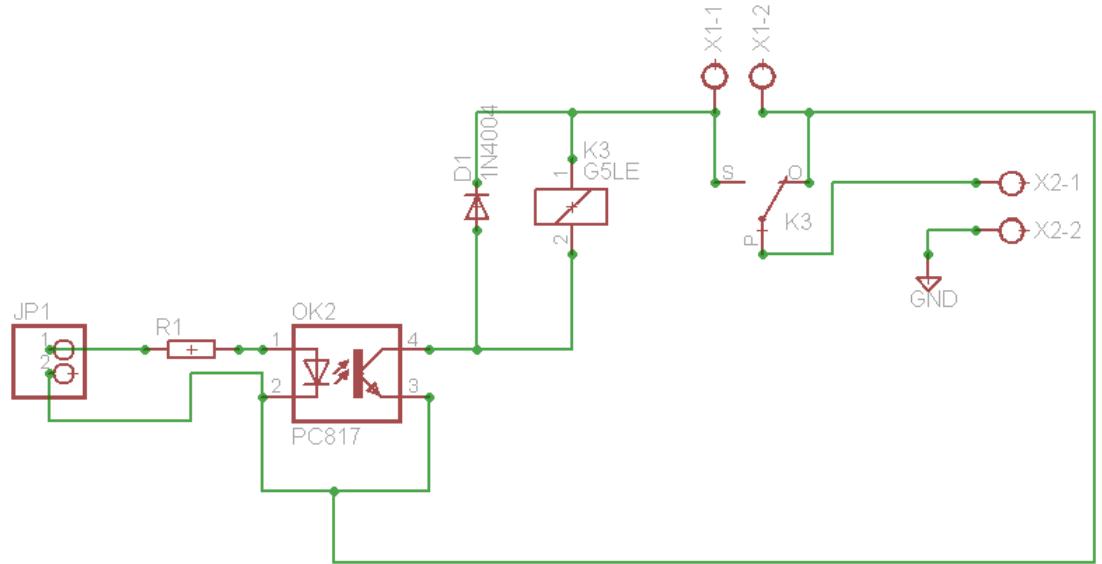


Figure 4.3: Schematic for the solenoid driver

The solenoid valves needs a +12V supply to open up. The output of the controller is +5V. The circuit in Fig. 4.3 is used to drive the solenoid valves. The board receives +5V supply from the ATmega 8535 development board. This voltage is then supplied to the PC 817 which is an opto-coupler. The opto-coupler, or opto-isolator, prevents high voltages from affecting the system receiving the signal and thus provides electrical isolation. The opto-coupler consists of an LED and a phototransistor in the same opaque package. When PC 817 receives the signal from the controller, internally, the LED turns on and the detector detects the signal and passes it to the output thus providing +5V to the relay. Due to this, the relay turns on connecting its pole to Normally Open and thus to the +12V supply which is the transferred to the input of the solenoid valve. On receiving this +12V supply, the solenoid valves are opened.

4.3 Stirrer Mechanism

Each time a drop of titre is added to the solution, it must be stirred so that it is evenly distributed. This function is performed by the stirrer mechanism. The stirrer mechanism is implemented in our project by developing a Magnetic Stirrer.

To implement a magnetic stirrer, we used an old computer fan, a pair of small permanent magnets and a teflon coated magnet. The pair of permanent magnets are stuck to the old computer fan.

The stirrer is powered by a +12V supply driven by an optical-isolator system which is similar to the driver used with the solenoid valve.

4.4 End-point detection

The process of titration continues until the end-point is detected. The method of pH based potentiometric end-point detection is implemented in our system.

To implement the system, a pH electrode probe is used. The probe Ref. Fig. 4.4 is a rod like structure made up of glass. At the bottom of the probe there is a bulb, the bulb is a sensitive part of a probe that contains the sensor. To measure the pH of a solution, the probe is dipped into the solution[11].

The pH probe consists of two electrodes, namely a reference electrode and a measuring

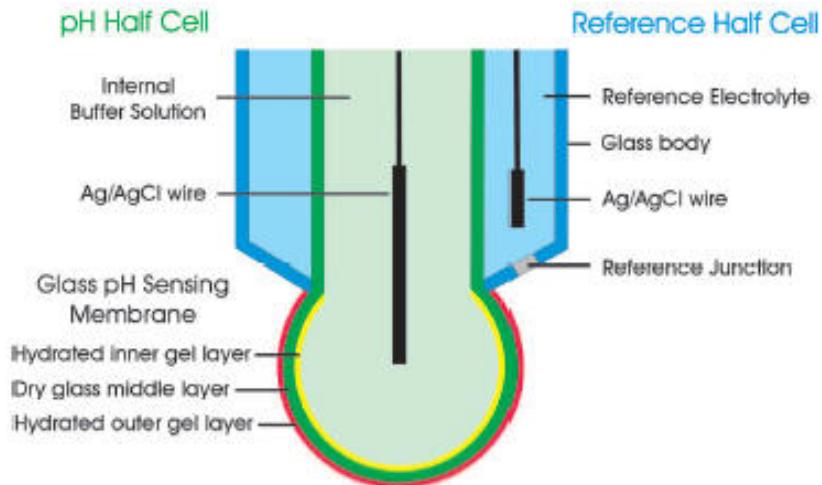


Figure 4.4: The combination pH electrode

glass electrode. The measuring electrode, which is sensitive to the hydrogen ion, develops a potential (voltage) directly related to the hydrogen ion concentration of the solution. The reference electrode provides a stable potential against which the measuring electrode can be compared. When immersed in the solution, the two electrodes generate e.m.f. which is proportional to the pH of the solution. The magnitude of the e.m.f. is dependent on the magnitude of the pH of the solution. The reference electrode potential does not change with the changing hydrogen ion concentration. A solution in the reference electrode also makes contact with the sample solution and the measuring electrode through a junction, completing

the circuit.

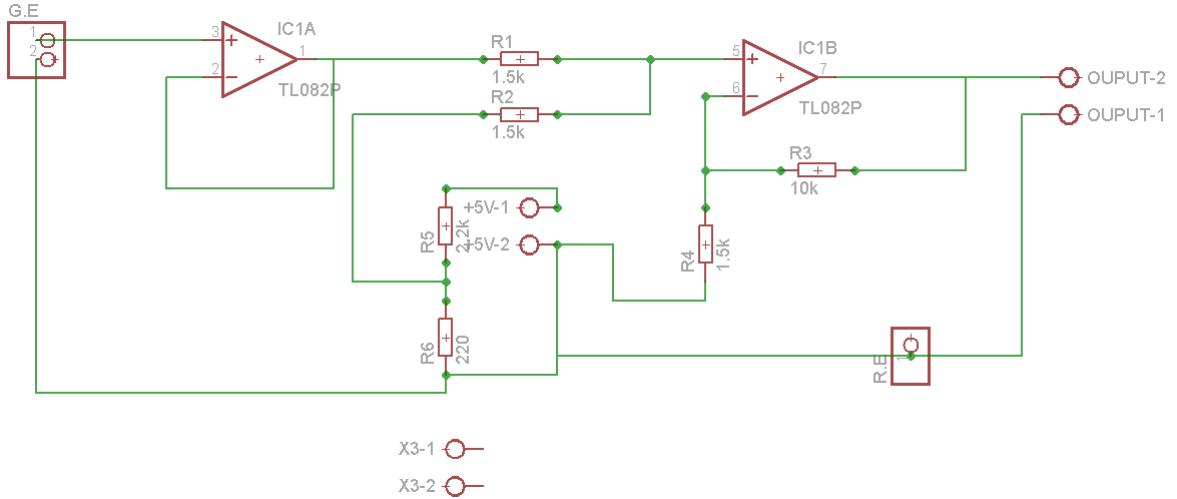


Figure 4.5: Schematic for pH electrode output conditioning circuit

Since the pH sensitive surface is glass, the internal resistance of the e.m.f. generating combination of electrodes and solution is very high, typically 500 Mega Ohms. Hence a low bias current and low drift JFET input operational amplifier has been used in this system. The output potential of the combinational probe is of the millivolt range. Hence it must be amplified before it is given to the ADC of the controller to achieve sufficient resolution.

The circuit shown in Fig.4.5 uses the TL082 which is a JFET input operational amplifier. There are basically two stages of operation. The first stage is used for impedance matching used as a single gain buffer amplifier. The glass electrode is used input to the amplifier, while the reference electrode is connected to the common ground. The output of the first stage is in millivolts and maybe positive or negative based on whether the solution is acidic, basic or neutral. This signal is then amplified by using an adder circuit again by using TL082. A DC voltage bias is added to ensure a positive voltage. This dc voltage is added to the first stage output and the sum is amplified. This output voltage is then passed to the ADC pins of the microcontroller which further processes this signal and converts it to the corresponding pH value.

4.5 Controller Module:

To control the complete working of the auto-titrator system, an ATmega 8535 microcontroller has been used. The ATmega 8535 controls the working of the various modules and then performs calculations on the outputs received from the pH electrode stage. The ATmega8535 is a low-power CMOS 8-bit microcontroller based on the AVR enhanced RISC architecture. By executing instructions in a single clock cycle, the ATmega8535 achieves throughputs approaching 1 MIPS per MHz allowing the system designer to optimize power consumption versus processing speed.

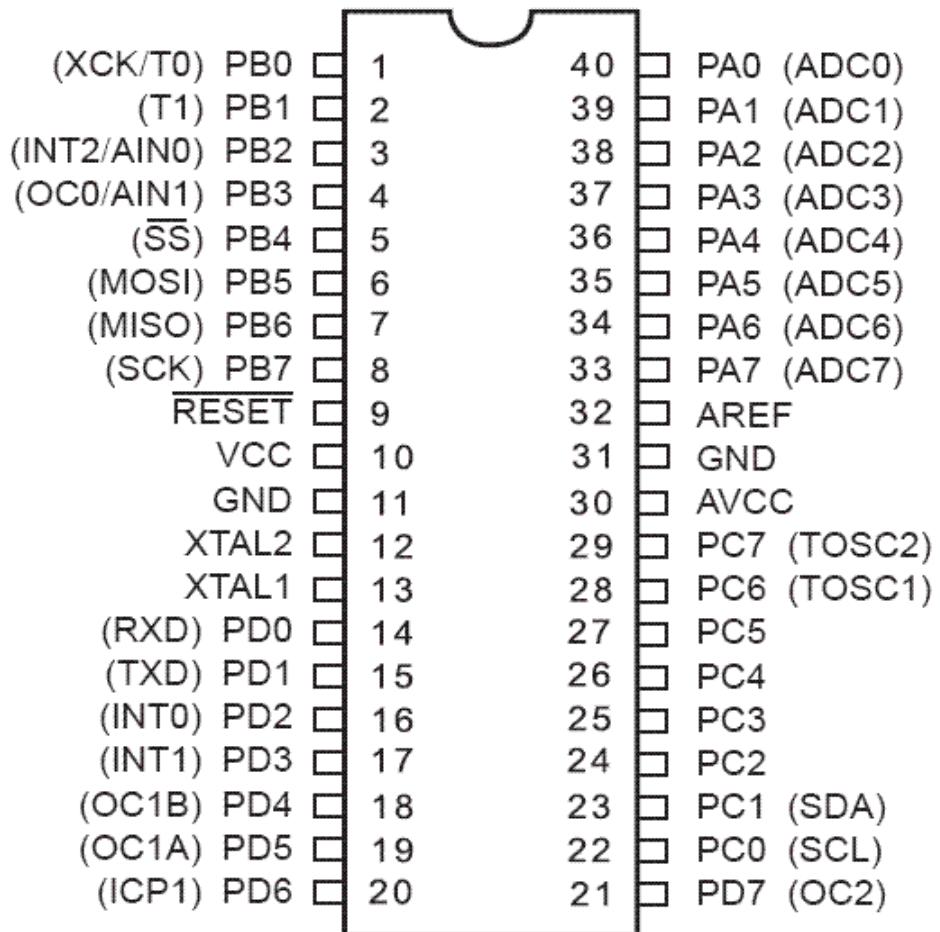


Figure 4.6: ATmega8535 Pinout

The AVR core combines a rich instruction set with 32 general purpose working registers. All 32 registers are directly connected to the Arithmetic Logic Unit (ALU), allowing two independent registers to be accessed in one single instruction executed in one clock cycle. The resulting architecture is more code efficient while achieving throughputs up to ten times faster than conventional CISC microcontrollers.

In order to maximize performance and parallelism, the AVR uses Harvard architecture - with separate memories and buses for program and data. Instructions in the program memory are executed with a single level pipelining. While one instruction is being executed, the next instruction is being executed in every clock cycle. The program memory is In-System

Reprogrammable Flash memory. The ALU supports arithmetic and logic operators between registers or between a constant and register. Single register operations can also be executed in the ALU. After an arithmetic operation, the Status Register is updated to reflect information about the result of the operation. Program flow is provided by conditional and unconditional jump and call instructions, able to directly address the whole address space. Most AVR instructions have a single 16-bit word format. Every program memory address contains a 16-bit or 32-bit instruction. Program Flash memory space is divided in two sections, the Boot program section and the Applications Program section. Both sections have dedicated Lock bits for write and read/write protection. The SPM instruction that writes into the Application Flash memory section must reside in the Boot Program section.

During interrupts and subroutine calls, the return address Program Counter (PC) is stored on the Stack. The Stack is effectively allocated in the general data SRAM, and consequently the Stack size is only limited by the SRAM size and the usage of the SRAM. All user programs must initialize the SP in the reset routine (before subroutines or interrupts are executed). The Stack Pointer (SP) is read/write accessible in the I/O space. The Data SRAM can easily be accessed through the five different addressing modes supported in the AVR architecture. The memory spaces in the AVR architecture are all linear and regular memory maps. A flexible interrupt module has its control registers in the I/O space with an additional global interrupt enable bit in the Status Register. All interrupts have a separate interrupt vector in the Interrupt Vector Table. The interrupts have priority in accordance with their interrupt vector position. The lower the interrupt vector address, the higher is the priority[8].

Details of ADC:

- The ATmega64 features a 10-bit successive approximation ADC. The ADC is connected to an 8-channel Analog Multiplexer which allows eight single-ended voltage inputs constructed from the pins of Port A. The single-ended voltage inputs refer to 0V (GND). The ADC contains a Sample and Hold circuit which ensures that the input voltage to the ADC is held at a constant level during conversion.
- In our developed system, the reference voltage to the ADC is equal to 5 V DC.

The microprocessor is also connected to the LCD which is used to display the current state of the system and the final results at the end of the complete process.

Chapter 5

Algorithm and Process Flow Model

We used CodeVision AVR and SinaProg to build and debug our code. The complete process flow and algorithms used in the system have been explained in the following sections:

5.1 Process Flow

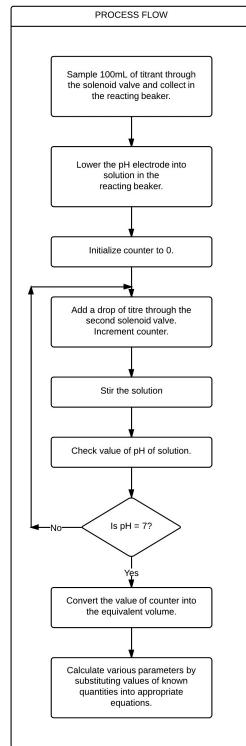


Figure 5.1: The Process Flow of complete Autotitrator System

5.2 Algorithm for the complete process

1. Sample 100mL of titrant through the solenoid valve and collect in the reacting beaker.
2. Lower the pH electrode into solution in the reacting beaker.
3. Initialize counter to 0.
4. Add a drop of titre through the second solenoid valve. Increment counter.
5. Stir the solution.
6. Check value of pH of solution. The end point is when the pH of the solution approaches 7.
7. If end-point is not detected repeat steps 4 to 7.
8. Convert the value of counter into the equivalent volume.
9. Calculate various parameters by substituting values of known quantities into appropriate equations.

The titrant is first sampled and sent to the glass beaker where the titration reaction occurs. This is done by turning on the solenoid valve for a programmed period of time[6].

The pH detector is now lowered into the titrant solution that is collected in the beaker with the help of a motor and pulley arrangement. The pH probe takes a few seconds to show stable readings.

A counter is used to determine the number of times a drop of titre is added to the solution. Each drop corresponds to a predetermined volume. Every time we add a drop of titre into the reacting beaker the solution is stirred so that the reaction is uniform.

Check the pH of the solution. The algorithm to find the pH is explained in the following subsection. If the pH is still below 7, then repeat the above steps.

Once the pH has reached 7, the total volume of titre added to the solution is calculated by multiplying the counter value with the predetermined volume.

5.3 Algorithm for pH detection

1. Sample the pH glass electrode output.
2. Obtain 50 samples at a time.
3. Find the value that has occurred with maximum frequency in the sample set.
4. Set this value as current pH

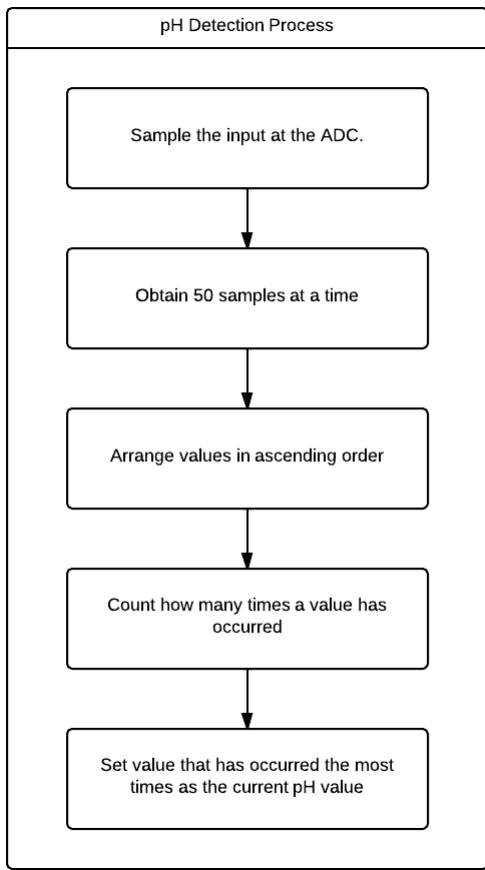


Figure 5.2: The process for pH detection

The pH electrode consists of two probes, a Glass Electrode and a Reference Electrode. The output of the reference electrode is connected to ground, while the glass electrode output is sampled.

A number of samples of the glass electrode output are collected. The pH probe provides an estimate of the pH value in terms of an equivalent voltage. Each time a drop of titre is added, there is a spike in the pH value. So the pH probe takes a few seconds to stabilize. However, there continues to be a small fluctuation in outputs. Hence, the values are searched for the output voltage that occurs the most number of times as the actual pH equivalent.

Chapter 6

Simulation & Experimental Results

The final implementation of the autotitrator system is shown in Fig. 6.1.

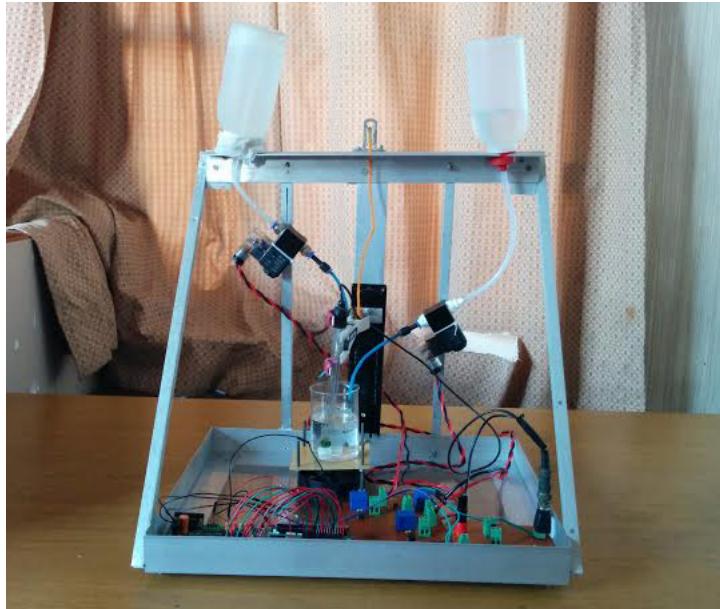


Figure 6.1: The designed Auto-titrator system

The solenoid valve used to implement the flow control module discharges a predefined volume of solution. The amount of solution discharged depends on the time for which the valve is opened. The relationship between the time for which the valve is opened and the liquid flowing through is summarized in Fig.6.2.

The pH electrode gives us outputs in the microvolt range. The microcontroller needs inputs in the range of 0-5 V. In order to improve the resolution, therefore, the pH electrode output must be amplified before it can be fed to the processor. The amplified output of the pH probe in solutions of various pH values have been summarized in Table. 6.1.

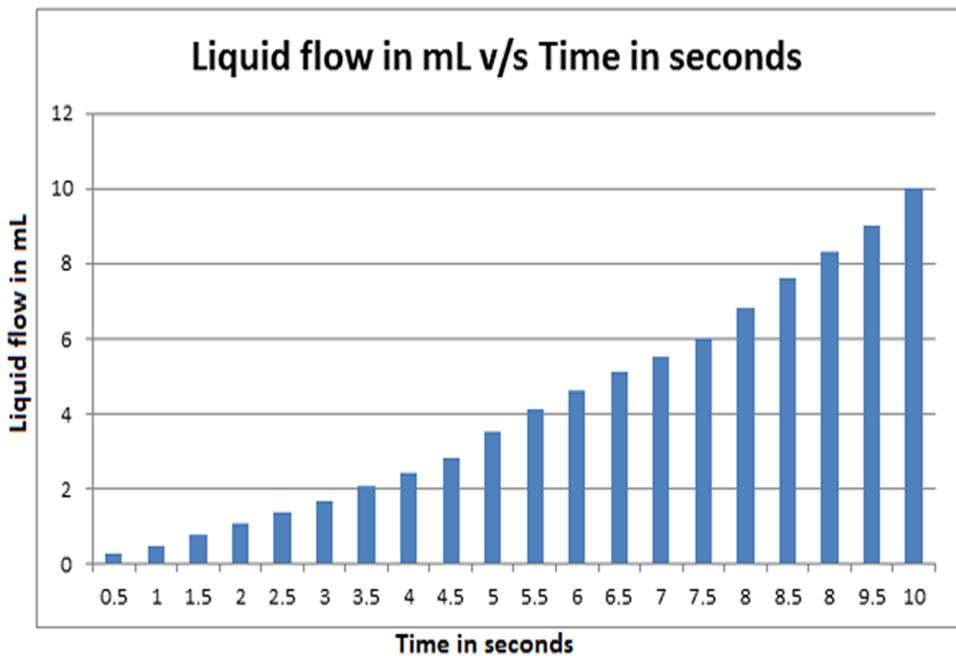


Figure 6.2: Liquid Flow v/s Time

Table 6.1: Voltage outputs given by pH probe

Solution Type	pH Range	Amplified Input to Processor
Acid	1 to 6.5	4.6 V to 3.6 V
Neutral	6.5 to 7.5	3.6 V to 3.2 V
Base	7.5 to 12	3.2 V to 2.7 V

As seen from the table, acidic samples showed voltage outputs above 3.6 Volts and basic samples showed voltage outputs below 3.2 Volts. A voltage range of 3.2 Volts to 3.6 Volts corresponded to a Neutral pH. On the basis of the above input voltages the pH was detected and used to find the end point. A neutral pH denotes the end-point of the titration operation.

A few bases of known normalities were titrated against acids of known concentrations. The normality of these basic solutions was calculated using the system. The normality of these bases were also calculated using classical titration method. The results are as tabulated in Table. 6.

Thus the system gave us satisfactory results within an error of approximately 10 percent. This is acceptable as the manual methods currently employed in small-scale applications have an average error of around 17 percent.

As stated earlier, the main purpose of the project is to design the auto-titrating system within a low cost. Table 6.3 shows a comparison of our system with respect to other com-

Table 6.2: Normality Outputs

Actual Normality	System output	Classical method
0.1 N	0.089 N to 0.11 N	0.083 N to 0.09 N
0.2 N	0.17 N to 0.25 N	0.18 N to 0.25 N

mercially available systems[12][13].

Table 6.3: Comparison of Costs of Auto-titrating systems

Auto-titrating System	Approx Cost in INR
Our System	Rs.5,000
Hanna Instruments HI84431	Rs.45,000
Hanna Instruments HI8453001	Rs.55,000
ALDRICH Z673951	Rs.80,000

Thus the cost of our system was approximately one-tenth of other commercially available systems.

The Specifications of our system are as follows:

1. Supply : 230 V , 50 Hz
2. Titrant Addition : Incremental
3. Titration flux : 0.5mL / sec
4. Distinguishability : 0.3 mL to 0.5 mL
5. pH range : 1 to 12 pH
6. Polarizing Current : 1 microampere
7. End Point delay : 100 to 500 seconds
8. Stirring : Magnetic Stirrer
9. Display : 16 x 2 Alphanumeric LCD
10. Titration : Potentiometric Titration

Chapter 7

Conclusion and Future Work

7.1 Conclusion

We have developed an automatic titrating system with sufficient accuracy in results for small scale applications such as in educational institutes and small industries. The system achieves adequate results for small scale systems however is not suitable for applications that require high precision. Also, as the end-point detection is based on pH only acid-base neutralization type titrations can be performed. Besides being cost effective, the system is easy to use and does not special training, unlike other commercially available systems. Also no temperature correction mechanism has been provided and hence the system must be operated at room temperature only.

7.2 Future Work

The system has a lot of scope for improvement. Future developments of this system have great applications if it is merged with advanced technology. Some of the future possible mechanisms are given below :

1. It can be coupled with other probes to provide more efficient outputs as well as extend its applications to other forms of titration reactions.
2. With the use of colorimetric and amperometric detectors, the auto-titrator can be used to perform a wide range of titrations.
3. The working of the system can be made faster by implementing dynamic titrant addition rather than the incremental titrant addition used here.
4. The use of piston syringes can improve the accuracy of titre sampling and thus improve the accuracy of system.

Chapter 8

Appendix

8.1 PCB Details

8.1.1 Board File of Isolation circuit used in Solenoid and Motor Driver

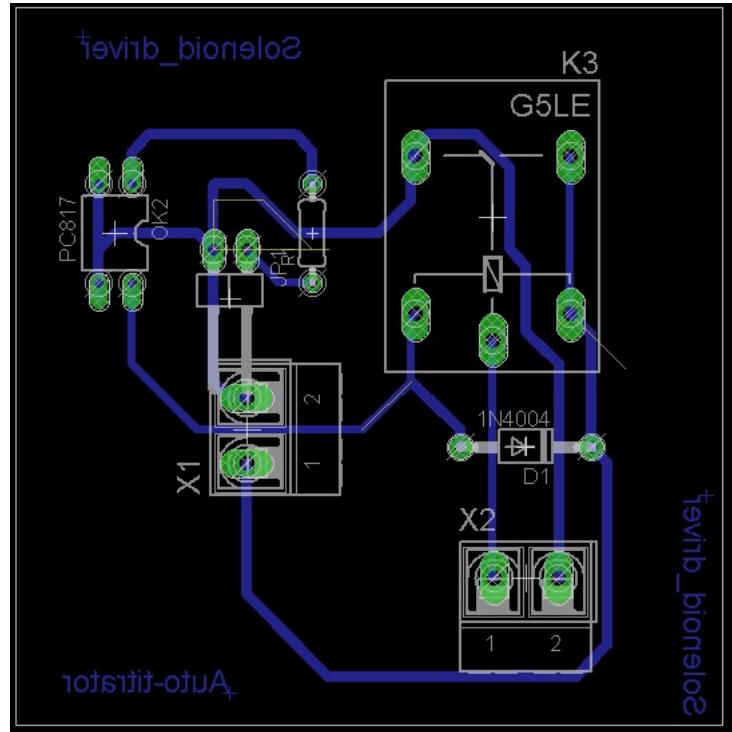


Figure 8.1: Solenoid and Motor Driver .brd file

8.1.2 Board File of pH interface module

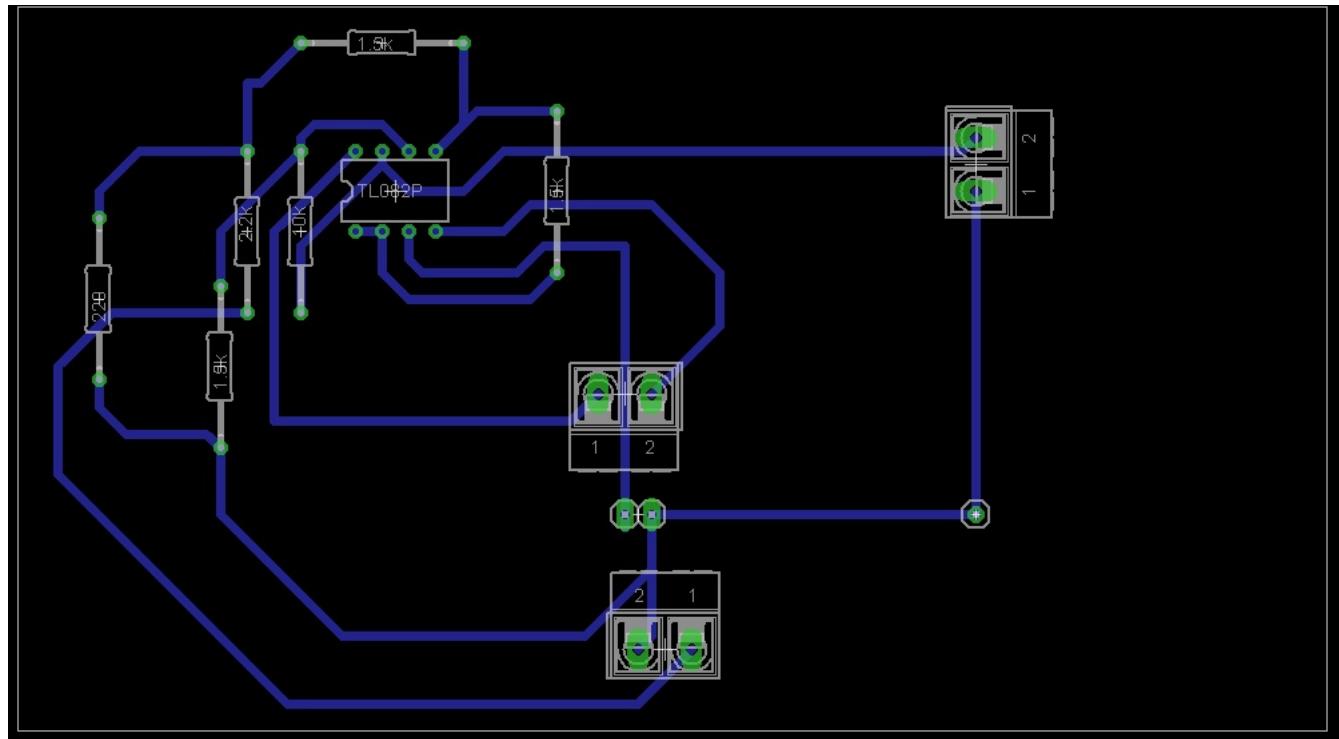


Figure 8.2: pH interface with TL082 .brd file

8.1.3 ATmega 8535 General Purpose Board

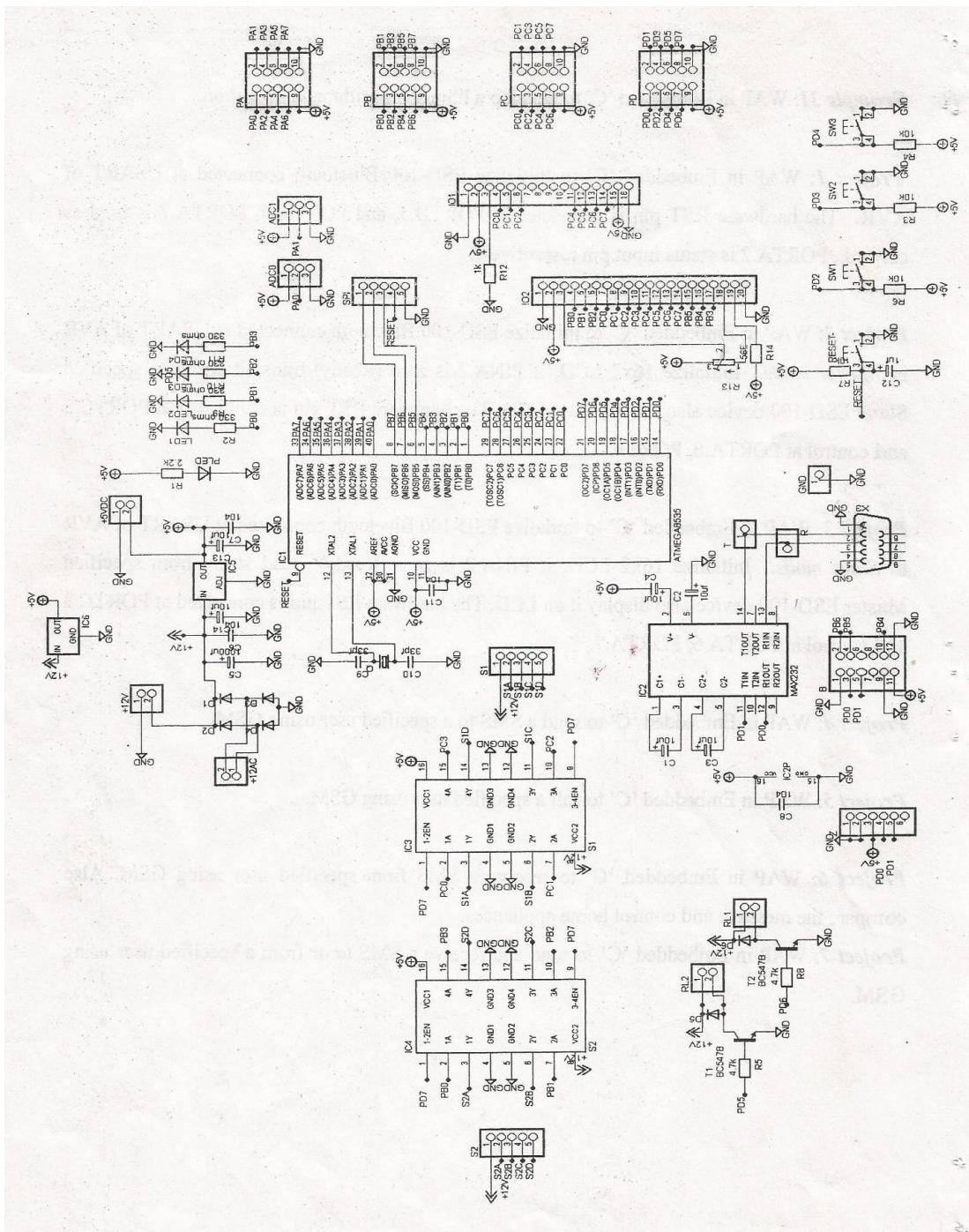


Figure 8.3: The Schematic Diagram of General Purpose Board

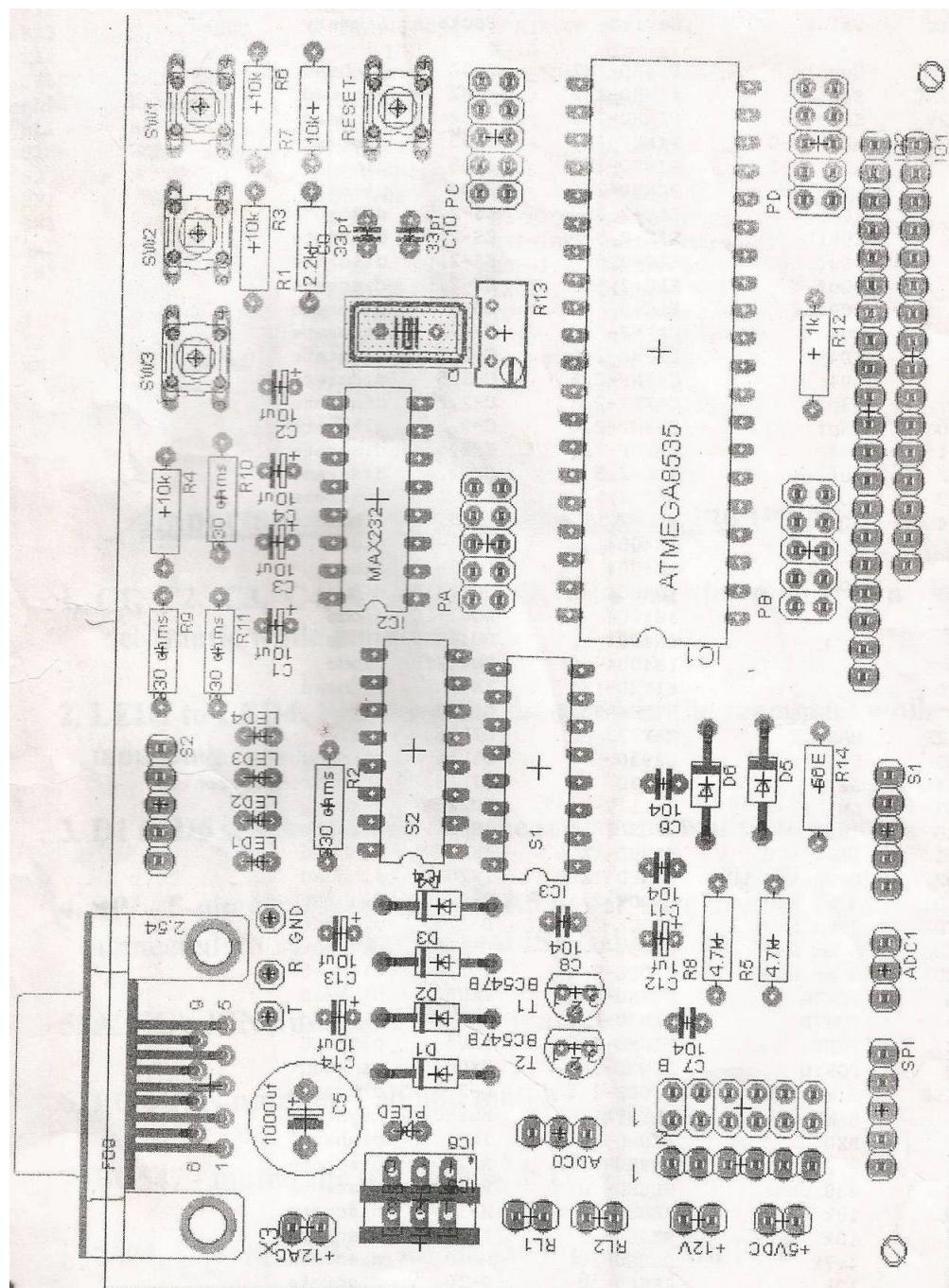


Figure 8.4: The Component Placement on General Purpose Board

8.2 Specifications of Components used

8.2.1 pH Probe

1. pH-range : 0 to 14 pH
2. Millivolt Range : 0 to +/- 1999 mV
3. Resolution : 0.01 pH
4. Repeatability : +/- 0.01 pH
5. Polarizing Current: 10 microampere

8.2.2 JELPC 4V 210-08 Solenoid valve

SPECIFICATIONS			
MODEL	4V210-08-24	4V210-08-110	4V210-08-220
POSITION NUMBER	Two position five way		
EFFECTIVE SECTION AREA	16mm ² (CV=0.89)		
JOINT PIPE BORE	Inlet/Outlet=1/4" exhaust=1/8"		
WORKING MEDIUM	40 micron filtered air		
MOTION PATTERN	Inner Guide Type		
OPERATING METHOD	Inside Piloted		
PRESSURE RANGE (MPa)	0.15~0.8		
MAX PRESSURE RESISTANCE (MPa)	1.2		
APPLICABLE TEMPERATURE (°C)	-5~50		
SOLENOID OPERATION VOLTAGE	24VDC	110-130VAC	220VAC
VOLTAGE RANGE	±10%		
POWER CONSUMPTION	DC: 4W	AC:4.5VA	AC:4.5VA
INSULATION & PROTECTION CLASS	IP65/ F Class, IP65		
WIRING FORM	Lead Wire Connector Type		
LUBRICATION	NOT REQUIRED		
MAX ACTION FREQUENCY CYCLE/SEC	5 CYCLE/SEC		
RESPONSE TIME SEC	0.05		
SERVICE TIME	10 MILLION		

Figure 8.5: Solenoid Valve Specifications

8.2.3 ATmega 8535

1. High-performance, Low-power AVR 8-bit Microcontroller
2. Advanced RISC Architecture

- (a) 130 Powerful Instructions Most Single Clock Cycle Execution
- (b) 32 x 8 General Purpose Working Registers
- (c) Fully Static Operation
- (d) Up to 16 MIPS Throughput at 16 MHz
- (e) On-chip 2-cycle Multiplier

3. Nonvolatile Program and Data Memories

- 8K Bytes of In-System Self-Programmable Flash Endurance: 10,000 Write/Erase Cycles
- Optional Boot Code Section with Independent Lock Bits In-System Programming by On-chip Boot Program True Read-While-Write Operation
- 512 Bytes EEPROM Endurance: 100,000 Write/Erase Cycles
- 512 Bytes Internal SRAM
- Programming Lock for Software Security

4. Peripheral Features

- Two 8-bit Timer/Counters with Separate Prescalers and Compare Modes
- One 16-bit Timer/Counter with Separate Prescaler, Compare Mode, and Capture Mode
- Real Time Counter with Separate Oscillator
- Four PWM Channels
- 8-channel, 10-bit ADC
8 Single-ended Channels
- Byte-oriented Two-wire Serial Interface
- Programmable Serial USART
- Master/Slave SPI Serial Interface
- Programmable Watchdog Timer with Separate On-chip Oscillator
- On-chip Analog Comparator

5. Special Microcontroller Features

- Power-on Reset and Programmable Brown-out Detection
- Internal Calibrated RC Oscillator
- External and Internal Interrupt Sources
- Six Sleep Modes: Idle, ADC Noise Reduction, Power- save, Power-down, Standby and Extended Standby

6. I/O and Packages

- 32 Programmable I/O Lines
- 40-pin PDIP, 44-lead TQFP, 44-lead PLCC, and 44-pad QFN/MLF

7. Operating Voltages

- 2.7 - 5.5V for ATmega8535L
- 4.5 - 5.5V for ATmega8535

8. Speed Grades

- 0 - 8 MHz for ATmega8535L
- 0 - 16 MHz for ATmega8535

8.2.4 TL 082 Texas Instruments JFET Operational Amplifier

1. Low Power Consumption: 1.4 mA/ch Typ
2. Wide Common-Mode and Differential Voltage Ranges
3. Low Input Bias Current: 30 pA Typ
4. Low Input Offset Current: 5 pA Typ
5. Output Short-Circuit Protection
6. Low Total Harmonic Distortion: 0.003 percent Typ
7. High Input Impedance: JFET Input Stage
8. Latch-Up-Free Operation
9. High Slew Rate: 13 V/s Typ
10. Common-Mode Input Voltage Range Includes VCC+

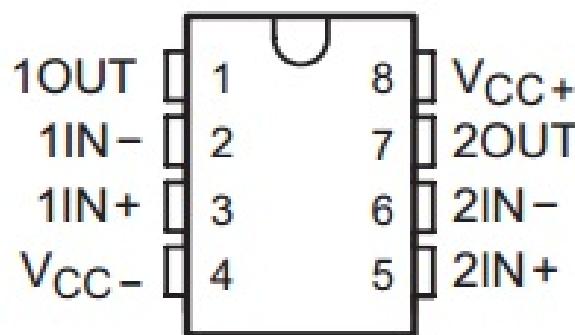


Figure 8.6: JFET Operational Amplifier TL082

8.2.5 PC 817 High Density Photo-coupler

1. Current Transfer Ratio: Min 50 % at $I_F = 5\text{mA}$, $V_{CE} = 5\text{V}$.
2. High isolation between input and output

8.3 Embedded C Codes

8.3.1 Code for LCD initialization and Display

```
include <mega32.h>
include <delay.h>

/*****************/
void dsp (char , char );

void dsp_hex(int);

void dsp_int (int);

void dsp_s(char* );

void lcd_init();

void lcd_clear();

/****************/

void dsp(char a,char cmnd)
{ char temp=(a0xf0);

a=a<<4;

if (cmnd=='c')
{ PORTC=0x04;
delay_ms(1);
PORTC=(temp||0x04);
delay_ms(1);
PORTC=0x00;
delay_ms(1);
PORTC=0x04;
delay_ms(1);
PORTC=(a||0x04);
delay_ms(1);
PORTC=0;
}

if (cmnd=='d')
{ PORTC=0x05;
delay_ms(1);
PORTC=(temp||0x05);
delay_ms(1);
```

```
PORTC=0x00;  
delay_ms(1);  
PORTC=0x05;  
delay_ms(1);  
PORTC=(a||0x05);  
delay_ms(1);  
PORTC=0;  
}
```

```
}
```

```
void lcd_init()  
{  
DDRC=0xFF;  
PORTC=0x00;  
delay_ms(50);  
dsp(0x2c,'c');  
delay_ms(50);  
dsp(0x2c,'c');  
delay_ms(50);  
dsp(0x2c,'c');  
delay_ms(50);  
dsp(0x2c,'c');  
delay_ms(50);  
dsp(0x2c,'c');  
delay_ms(50);  
dsp(0x2c,'c');
```

```
delay_ms(50);  
dsp(0x06,'c');  
// lcd init ends  
delay_ms(50);  
dsp(0x14,'c');  
delay_ms(50);  
dsp(0x0f,'c');  
delay_ms(50);  
dsp(0x01,'c');  
delay_ms(50);  
dsp(0x02,'c');  
delay_ms(50);  
}
```

```
void lcd_clear()
```

```

{
    dsp(0x01,'c');
    delay_ms(10);
    dsp(0x02,'c');
    delay_ms(10);

}

void dsp_hex(int a)
{
    char temp=a;

    temp >>=4;
    if(temp<0x0a)
        temp+=0x30;
    else
        temp+=0x37;

    dsp(temp,'d');

    a=0x0f;
    if(a<0x0a)
        a+=0x30;
    else
        a+=0x37;
    dsp(a,'d');

}

void dsp_int(int a1)
{
    char c;
    char b;
    char a;

    a=a1/1000;
    if (a!=0)
    {
        dsp(a+0x30,'d');
    }
    b=a1/100;
    if (b!=0)
    {
        dsp( b+0x30,'d');
    }
    c=(a1&0000);
}

```

```

dsp((c/10)+0x30,'d');
dsp((c%10+0x30),'d');

}

void dsp_intl(int a1)
{
char c;
dsp( (a1/100)+0x30,'d');
c=(a1%100);
dsp((c/10)+0x30,'d');
dsp((c%10+0x30),'d');

}

void dsp_s(char* d)
{
int i=0;
while(d[i]!=0)
{dsp(d[i],'d');
i++;
}
}

```

8.3.2 Code for Flow Control

```

int i=0;
int drop=0;
void titrant_clr(int time1)
{
lcd_clear();
PORTA=0x04;
dsp_s("VALVE 1 OPEN");
delay_ms(time1);

lcd_clear();
PORTA=0x00;
dsp_s("VALVE 1 CLOSE");

}

void titre_clr(int time2)
{
lcd_clear();
PORTD=0x04;
dsp_s("VALVE 2 OPEN");

```

```

delay_ms(time2);

lcd_clear();
PORTD=0x00;
dsp_s("VALVE 2 CLOSE");

}

void main(void)
{
PORTA = 0x00;
DDRA = 0xF6;
PORTD = 0x00;

DDRD = 0xF6;

lcd_init();

while(1)
{
titrant_clr(125);
delay_ms(125);
titre_clr(0.25);
drop++;
delay_ms(125);
lcd_clear();
dsp_s("drop =");
dsp_int(drop);
delay_ms(250);
}
}

```

8.3.3 Code for ADC Initialization

```

ifndef
define ADC_INC

include <mega32.h >
include <delay.h >

/***********************/

void adc_init(char );

char adc_get (char );

```

```

int adc_get_int(char);

/*****************/
char ladj=0;
void adc_init(char vref)
{
DDRA=0x00;
PORTA=0x00;
ADMUX=0;
ADCSRA=0x83;

    if(vref==0)
    //AREF
    ADMUX=0;
    else
    {
if(vref==1)
//AVCC
ADMUX=0x40;
    else
if(vref==2)
// INT REF
ADMUX=0xC0;
    }

}

char adc_get (char ch )
{
char temp=0;

ADMUX=0xf0;
ADMUX|=ch;

    if(ladj==0)
{ADMUX|=0x20;
ladj=1; }

ADCSRA|=0x40;

while(!(ADCSRA&0x10));

```

```

        temp=ADCH;
ADCSRA|=0x10;

return temp;

}

int adc_get_int(char ch)
{
    int temp=0;
    char t;

    if(ladj==1)
    {ADMUX=0xD0;
    ladj=0; }

    ADMUX|=ch;
    ADCSRA|=0x40;
    while(!(ADCSRA&0x10));
    t=ADCL;
    temp=ADCH;
    temp=temp<<8;
    temp+=t;
    ADCSRA|=0x10;
    return temp;

}

endif

```

8.3.4 Code for pH detection

```

include <adcmur.c >
include <valveclr.c >
include <mega16.h >
include <delay.h >
include <stdlib.h >
include <math.h >
define ADC_VREF_TYPE 0x40

```

```

    int a=0;
    unsigned char s;
    float temp,arr[50];
    char lcd_volt[7];
    float total;

```

```

float normal;
float vol1 = 60.0 ;
float nor1 = 1.0;
unsigned int j,k;
int count=1;
int cval=0;
int c1=0;

    int detect()
{
while(a<50)
{
arr[a++]=adc_get_int(0);
}

/*find pHvolt i.e. the voltage equivalent for given pH value*/
for(j=1;j<50;j++)
for(k=1;k<50;k++)
{
if(arr[j] >arr[k])
{
int t1=arr[j];
arr[j]=arr[k];
arr[k]=t1;
}
}
count=1;
cval=0;
c1=0;

//Sort all values in ascending order
for(j=1;j<50;j++)
{if(arr[j]==arr[j+1])
count++;
else
count=1;
//Find value occurring maximum times
if(count >c1)
{
c1=count;
cval=arr[j];
}
}

a=1;
return(cval);

```

```
}
```

8.3.5 Code to stir the mixture

```
asm
.equ _lcd_port=0x15;PORTC
endasm
```

```
    include "adcmur.c"
include "lcdmur.c"
include "mega16.h"
include "delay.h"
include "stdlib.h"
include "math.h"
```

```
void stir()
{
lcd_clear();
PORTB=0x10;
dsp_s("STIR ON");
delay_ms(675);
```

```
    lcd_clear();
PORTB=0x00;
dsp_s("STIR OFF");
```

```
}
```

8.3.6 Code for complete process

```
include "mega8535.h"
include "phD.c"
include "stir.c"
```

```
int y;
int drop=0;
int n2;
int v2;
int n1 = 0.1;
int v1 = 60;
```

```
void main()
{
while(1) {
//remove air bubbles from both supplies
```

```

titre_clr(1250);
delay_ms(500);
titrant_clr(1250);
delay_ms(1250);

        //start titration
//lower the detector
PORTA=0x10;

        //collect the titrant
titrant_clr(3750);
//collect titre drop-by-drop.
//check pH after every drop to search for end point
titrant_clr(1);
y = detect();
while(y<500)
{
    titre_clr(1);
    drop++;
    stir();
    delay_ms(125);
    detect();
}

        dsp_s("Drops =");
dsp_int(drop);
delay_ms(250);

v2=drop*0.1;

n2=n1*v1/v2;

lcd_clear;
dsp_s("Normality = ") ;
dsp_int(n2);
}
}

```

Chapter 9

Photo Gallery

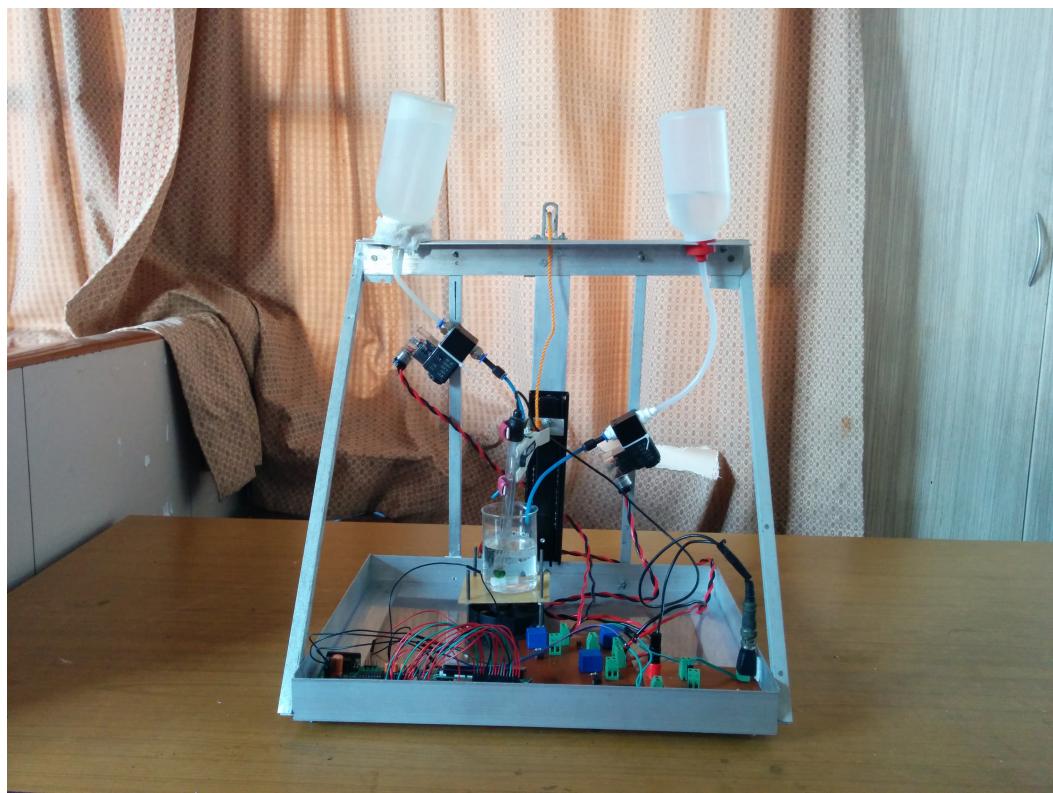


Figure 9.1: Final Implementation of System

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