SINKING SENSORS IN SOLUTION: A NOVEL HYDROPONIC ION CONTROL SYSTEM

by

MICHAEL ZHAO

(Under the direction of Mark Haidekker)

ABSTRACT

To mitigate concerns of nutrient deficiencies in recirculating hydroponic systems, a novel ion-specific controller utilizing a Raspberry Pi provides continuous monitoring, and automated correction of individual ion concentrations in a liquid reservoir. For the proof of principle, a selection of four ion-specific electrodes carry voltage information regarding $\text{K}^+$, $\text{NO}_3^-$, $\text{Ca}^{2+}$, and $\text{H}^+$ concentrations to a custom PCB where it undergoes filtering and amplification. Ion concentrations are detected in real time, and compared to a predefined concentration. If needed, an automated controller will precisely inject a liquid-ion solution into the main reservoir. This mechanism utilizes a linear slide with a stepper motor, and lead screw to cycle a syringe. Double-check valves connect this syringe with a high molarity stock ion solution, and the nutrient reservoir. Through this type of control system, ion concentrations are controlled to a grower set point.

INDEX WORDS: hydroponics, Ion-specific electrodes, ISE, Raspberry Pi, Recirculation, Soilless culture, ion-control, reservoir control
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This thesis is dedicated to my grandparents, who have always supported me in everything, and who have never allowed me to feel alone. My great-grandmother, whose indomitable spirit still lives through her children and grandchildren today. My mother, for her love, support, and tireless attitude toward life. My father for the opportunities he has created and values instilled. My uncle for treating me like his own son. My brother and my sister for allowing me to be their role model. My Sadie for always bringing a smile to my face.

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CHAPTER 1: EXECUTIVE SUMMARY

State of the art hydroponic reservoir nutrient controllers employed in the agricultural industry utilize a bulk measurement of nutrient concentration, represented by the electrical conductivity (EC) of the solution. This value approximates the reservoir nutrient concentration as a single combined measurement. Studies have shown that plant growth requires over a dozen specific ions for proper nutrition. When a bulk measurement is utilized, nutrient excesses in one ion may mask a deficiency in another. This problem is especially prevalent in reservoirs that utilize nutrient recirculation as part of their reservoir management. To prevent these nutrient deficiencies from arising, and thereby preventing optimal growth, ion specific electrodes (ISE) may be utilized to characterize ionic concentrations. In the new and improved method described in this thesis, the reservoir is polled for concentrations of key ions, rather than obtaining a single bulk measurement. Through real-time monitoring of these data, concentrations of major ions can be determined independently, and held at constant rates by a nutrient injection system.

Specific objectives of the project involve interfacing ion sensors for nitrate, potassium, pH, and calcium with an embedded controller; these ions are critical for
plant growth and significantly influence yield outcomes. These ions were chosen to provide proof of principle within a reasonable time frame and represent the three key macronutrients for plant growth. In addition, concentration data for these ions are used to automatically react and control ionic concentrations. This automated ion control system is predominantly targeted at growers utilizing recirculating reservoir management modalities of up to 1200 gallons, but can be scaled up for even larger size reservoirs. The controller has the means to self-calibrate by associating a ppm with a voltage to compensate for normal, routine degradation of the ion-selective electrodes.

Recirculating reservoirs are rarely fully emptied, and may be topped off daily with fresh water. Although it is ideally possible to calculate and adjust the nutrient solution to compensate for top off and nutrient depletion for long temporal periods (weeks), the myriad of cultivars and strains grown hydroponically present unique nutrient requirements and challenges in determining the specific strain requirements. Data on specific ion concentrations may easily be miscalculated during the multiweek growing process causing the grower to misgauge needed nutrients, and under-or overdose nutrients. In addition, topping off slowly dilutes initial reservoir concentrations, and during phases of heavy plant growth, it is possible for nutrient depletion to outweigh any nutrients the grower may supplement.
Reservoir control by a fully automated ion-controller may mitigate the effects of heavy ion depletion from growth, as well as keep reservoir ion concentrations held in a steady state. Grower setpoints parameters are software-selectable, which the feedback control system then uses to monitor reservoir concentration for changes. Should the reservoir deviate outside of this grower setpoint by a user-defined percentage, nutrient injection will occur and the program will attempt to rectify any nutrient deficiencies by addition of a specific ion.
CHAPTER 2: INTRODUCTION

2.1 Problem Statement

Hydroponic farming modalities are becoming more efficient in terms of water and fertilizer usage due to increased sensor application. Real time feedback from the field to the grower aids, decreases waste, allows for more stringent control of crop nutrients, and finally increases overall yield of the crop by preventing deficiencies. These feedback mechanisms can manifest themselves anywhere from moisture sensors implanted within the soil (1), to more advanced sensors, which may be electrical conductivity (EC) sensors embedded into a hydroponic reservoir. With the increase in usage of embedded technologies, and the complexity of control systems will increase.

Recirculating reservoir management is attractive to growers due to it’s nutrient conservation, as well as water conservation (2). However, over time, a common problem in recirculating management is the ”lack of information on managing the nutrient solution. (3)” This is due to the plants depleting nutrients during every recirculation cycle. If depletion was uniform across all ions, then growers could still track individual ion concentrations across recirculation cycles. However, due to differential depletion of ions depending on stage of plant growth, growers lose track of individual ion
concentration. The consequence of losing track of individual ion concentration is the possibility of nutrient deficiencies in between dosage periods, especially in periods of heavy plant growth where it may significantly impact final yield. Micronutrient concentration is often times in the order of between one to a few dozen ppm, and is especially susceptible to dropping to low levels. With heavy depletion, and daily topping off of freshwater, it is possible for ion concentration to drop below the ideal growing point (3). The original hydroponic formulation from Hoagland (Table 2.1) was targeted toward tomato and bell pepper, but since then, has been modified numerous times. Nonetheless, the ions present and their respective concentrations are still representative of the scale between macro, and micro nutrients (4).
Table 2.1: Concentrations of Ions in the Hoagland Solution

<table>
<thead>
<tr>
<th>Element</th>
<th>PPM</th>
<th>Classification</th>
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<tbody>
<tr>
<td>Nitrogen</td>
<td>210</td>
<td>Macronutrient</td>
</tr>
<tr>
<td>Potassium</td>
<td>235</td>
<td>Macronutrient</td>
</tr>
<tr>
<td>Calcium</td>
<td>200</td>
<td>Macronutrient</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>31</td>
<td>Macronutrient</td>
</tr>
<tr>
<td>Sulfur</td>
<td>64</td>
<td>Macronutrient</td>
</tr>
<tr>
<td>Magnesium</td>
<td>48</td>
<td>Macronutrient</td>
</tr>
<tr>
<td>Boron</td>
<td>0.5</td>
<td>Micronutrient</td>
</tr>
<tr>
<td>Iron</td>
<td>1-5</td>
<td>Micronutrient</td>
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<tr>
<td>Manganese</td>
<td>0.5</td>
<td>Micronutrient</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.05</td>
<td>Micronutrient</td>
</tr>
<tr>
<td>Copper</td>
<td>0.02</td>
<td>Micronutrient</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.01</td>
<td>Micronutrient</td>
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</table>

The ability to avoid nutrient deficiencies allows the plant to fully express their phenotype. Concentrations of micronutrients are sometimes less than 1 ppm, and Liebig’s law of the minimum states that growth is controlled by the limiting factor (5). This indicates that seemingly minor nutrient deficiencies can manifest themselves to
major differences in yield (6). One obvious solution to avoid this problem is to utilize a non-recirculating reservoir management. That is, the nutrient solution is only used once, and discarded. While this may ensure proper nutrient levels, it is also exceedingly wasteful as nutrient rich solution is discarded. Avoiding drain-to-waste, but also compensating for individual ion deficiencies allows for optimal growth without the guesswork of recirculation, and the water use inefficiency of drain-to-waste (7).

Furthermore, the ability to understand nutrient uptake characteristics is critical to understanding strain-dependent differences among individual cultivars. It is well known that nutrient use efficiency varies according to strain, as this property is subject to genetic control. For instance, two cultivars of maize were studied, and with increase in nitrogen application rates, an increase yield of over 10% was observed (8). For meaningful analysis of strain differences, information of specific nutrient application and depletion is necessary. Simply knowing how much fertilizer added each time, without knowing the depletion holds little useful information. Currently, growers and researchers can obtain this information through laboratory techniques, one popular modality is atomic absorption spectroscopy analysis, which proves to be expensive, and does not yield real-time data (9).
2.2 Project Goals

The design approach of this automated ion-nutrient controller focused on several key design components: sensing the ion signal, maintaining a threshold steady state by nutrient injection if necessary, producing real-time ion data to allow for in-depth strain analysis, and to provide long-term and stable analysis without data degradation. Each of these goals requires specific parameters and demands during the design process.

2.3 Target Users

There are two major users of this device: growers in the hydroponic industry, and researchers who wish to study nutrient uptake characteristics of plants. Specifically, the system described in this work is aimed at growers utilizing recirculating nutrient reservoirs. These include recirculating deep-water culture (rDWC), ebb-flow, top-feed drip, nutrient film technology (NFT), and aeroponics. In each of these modalities, the reservoir solution is used by the plants, returned to a central reservoir, and recirculated back onto the plants for reuse. Scientists and researchers would utilize the device to investigate differential nutrient uptake to phenotype plants, or to characterize genetic variation within cultivars.
In order to identify ion reservoir concentration, ISE’s are placed into the reservoir. These electrodes generate an analog, millivolt signal to be acquired by a custom acquisition board. The sensors themselves must be able to withstand continuous immersion in a liquid solution. Older generation ISE’s had ionophore degradation on the order of days to weeks. However, sensors with newest generation plasticizers have ionophore lifespans of six months and beyond (10). Furthermore, ISE’s with durable epoxy bodies and user replaceable membranes will be used to further expand the lifespan of the electrode. To provide the proof of principle, three representative ISE’s are monitored by the device described in this work: nitrate, potassium, and calcium. These ions are three of the most significant macronutrient ions from the Hoagland solution.
Figure 2.1: Block diagram illustrating the relationship between the electrodes, acquisition board, and controller.

The voltage signals generated from these four ion sensors enters a custom PCB, passes through amplification, then filtering via a low-pass filter. In order to make the data readily available for analysis, these analog signals are converted to digital signals via analog-to-digital conversion, and sent to a Linux embedded computer known as the Raspberry Pi. Figure 2.1 above illustrates the relationship and control diagram of the electrodes, the acquisition PCB, and the Raspberry Pi controller. The resulting digital
signal from each ISE is then calibrated via a log-linear equation that correlates the potential in volts from the solution, to the logarithmic values of known concentrations to produce the ion-concentration in ppm for its respective ion. Through this calibration scheme, the voltage generated by each ion-specific electrode may be correlated to its respective concentration.

To determine if ion injection is necessary, each ion concentration is compared to a user determined threshold. If correction for a specific ion is indeed necessary, the processor computes the exact volume of an associated, highly concentrated, stock solution to add into the reservoir. The calculation of this volume is governed by the dilution equation. This volume is then converted to a format in which a syringe injector can accurately respond to.

The physical injection mechanism is done by a stepper motor, which is able to translate its precisely controlled rotational motion, into a linear travel. Since the diameter of the syringe is known, it is possible to calculate the volume dispensed per step, as each step will have an exact linear travel distance. Following ion injection, the Raspberry Pi interrogates the reservoir for updated ion concentrations. If all levels are within calculated thresholds, then a cycle is concluded, and nutrient injection was successful.
CHAPTER 3: BACKGROUND

3.1 Hydroponics: History and Modalities

3.1.1 Fundamentals of Hydroponics

Hydroponics can also be described as "soilless culture", which indicates that plants receive their nutrition utilizing mineral nutrient solutions. This may be with roots immersed directly in a nutrient rich solution, or inert mediums such as perlite or coco coir can. Principal benefits of these inert mediums are that they provide a development matrix for root growth, and an anchoring point for a well-developed plant. Common to all inert mediums is that all nutrients still must be received from an ion rich solution. This contrasts to how plant nutrition is supplied in soil based agriculture. In soil-based culture, nutrition is received from bound substrates released from a surrounding soil matrix during irrigation (11).

Historically, hydroponics has been employed by both meso-American cultures and in ancient Egypt. In both of these cases, underlying mechanisms of soilless culture were not known, but practical applications were explored. Better understanding of the underlying mechanisms of plant growth did not occur until the 1600’s; scientists discovered that plants grew better in dirty water than distilled water. Though scientists at the time did not know the reason for this phenomenon, it is now understood that this
was due to the lack of nutrient ions in distilled water. More formalized academic attempts at soilless culture includes Hoagland and Arnon’s work in releasing a hydroponic nutrient ingredient mixture that prescribes relative concentrations of relevant ions. This early work detailed a list of 12 nutrient ions, provided by ionic salts dissolved into water (4). Though initially Hoagland made the assessment that hydroponics offered only minimal improvements over soil, he did not consider the advantages rendered onto plant growth through high oxygenation, and lack of drought conditions. Furthermore, due to the fact that water is applied directly onto the root system, water use efficiency is much higher than soil conditions, and similar yields can be obtained with less water application. This makes hydroponics very attractive in the dry and arid conditions that make up a substantial portion of global climate (11). In addition, drought stricken areas such as the California Central Valley (Figure 3.1) could benefit substantially from water efficient soilless culture techniques in order to maximize water use efficiency.
As briefly mentioned above, water use efficiency is one advantage of soilless culture over traditional soil techniques. The technique comes with other major advantages, and some disadvantages, over soil based systems. The ability to move away from soil culture allows for less disease and pest formation. The physical mediums often employed in soilless culture can be sterilized prior to use, and due to their inert state,
do not readily support pathogen or microbial growth (13). Other advantages include being able to control nutrient dosing, which prevent nutrient shortages to some degree. In addition, additions of certain non-nutrient ions have been shown to reduce disease rates. Studies have shown that applications of potassium silicate decreases occurrence rate of powdery mildew in strawberries (14). The substrate itself may also have an influence over disease progression. Use of stone wool as a substrate decreases *Pythium aphanidermatum* in cucumber plants (15). This lack of disease spread is also aided by container mobility, it is also easier to control and possible pesticide or disease infections. Mobility means that diseased plants or pests (spider mites, thrips, fungus gnats) can be easily quarantined. This may also help reduce pesticide application rate.

Principally though, there are two major factors that make the use of hydroponic modalities attractive. Firstly, hydroponic modalities may produce much higher crop yields per unit area. This is due to a combination of reasons from increase in oxygenation, ease of uptake of nutrients from ionic solutions, low growth resistance as roots can easily grow in mostly porous hydroponic growth mediums. For example, zucchini plants grown in soilless systems featuring coco coir, perlite, and pumice as mediums featured high yield in total, and marketable fruit number (16). The second major advantage of hydroponics is the ability to be grown in environments where either water or soil is not available, or of insufficient quality for meaningful agricultural
cultivation. According to the FAO aridity map (Figure 3.2), a wide swath of the world, particularly the developing world, is characterized as dry and arid. The advantages of hydroponics in these environments cannot be overstated, as increases in water-use efficiency is highly desirable in order to conserve of limited water supplies. Of course there are economic considerations as well, as crop value must be high to overcome the high initial investment into hydroponics. Nonetheless, hydroponic culture allows growth of crops that may otherwise be unable to grow in that environment.

![Aridity map of the world according to the FAO](image)

**Figure 3.2:** Aridity map of the world according to the FAO. Wide swaths of the world are considered arid, and water-saving hydroponic measures could be implemented. In these environments, traditional soil based methods are not efficient (17).

These advantages do come with downsides. Increases in system complexity introduce multiple points of failure. This puts more responsibility on the grower than what typically accompanies soil-based modalities. Concentrations of specific ions must
be considered, as the grower is responsible for all plant nutrition. In addition, nutrient uptake is pH dependent, with uptake of nutrient varying according to the pH in solution. For optimal nutrient uptake, pH needs to be controlled between a well-defined limit, between 5.5 and 6.5 (18). Solution temperature is also an important factor as it influences levels of dissolved oxygen. These added parameters of consideration to the grower only highlight the importance of proper control systems in hydroponics.

3.1.2 Reservoir Management and Hydroponic Modalities

As nutrients in soilless culture are entirely contained within a liquid solution, how this liquid solution is managed is of the utmost importance. Two completely opposite methods are employed in reservoir management: simple drain-to-waste, and solution recirculation. The general difference between the two is such that in drain-to-waste, the nutrient solution is only flowed through the roots once, and is either discarded, or irrecoverable. This allows fresh nutrient solution to be used during each irrigation. The other major method is very much like its name suggests, that the nutrient solution is used once, and then pumped into a holding area, where it is used again. Plants will not absorb everything in the nutrient solution in a single pass, so it is more efficient from a water use standpoint to employ recirculation, and reuse the solution more than once. This form of nutrient recirculation is only possible in soilless culture, as organic microbes in soil cultures will cause problems with disease once recirculated. Although microbes exist in soilless culture as well, the extent and scale is much less than that in
organic methods due to a decrease in the complexity of deleterious bacterial systems (19).

Although recirculation is unequivocally more efficient than drain-to-waste from a water usage standpoint, the data show diverging results in terms of yield comparisons among several different crops. This could be related to how well these crops tolerate salinity stress. The ion Na\(^+\) tends to accumulate within hydroponic reservoirs, as plants do not absorb sodium, and in fact, actively exclude it from transfer into the plant (3). Water naturally contains trace amounts of sodium, and with weekly topping off of the nutrient reservoir, this has the affect of slowly concentrating sodium levels within the reservoir. In addition, simply increasing overall reservoir nutrient concentration may have a reverse effect, and actually cause a decrease in overall marketable yield. Overall, crops that are affected by variations in recirculation solution concentration, by the metric of marketable yield, include pepper (20), tomato (21), and roses (22). However, in these cases of tomatoes and roses, water savings were on the order of roughly 30% compared to “farmers practice” in open-irrigation systems.

In other crops, responses to recirculation feature a wide range of results. In some cases, comparable results to open fertilization was achieved, but only featured a 30-day study, insufficient for any meaningful amounts of sodium buildup to take place (23). Other studies on muskmelon exhibit a parabolic response, where yield is highest at
moderate nutrition amounts, and higher concentrations reduce yield (24). In less common cases such as strawberries, yields remain unaffected even when the plant is presented with a wide range of nutrient concentrations. These variations in nutrient concentrations caused the strawberry plant to uptake ions in different proportions, but final yield was unaffected (25).

Bugbee achieves long-term recirculation with addition of refill solutions added into the reservoir after certain amount of depletion occurs (3). The strength of the refill solution is calculated from a wide set of parameters including ambient humidity and transpiration to dry mass growth. Estimation of this parameter varies from 200-400 kg of water transpired per kilogram of dry mass plant growth. The specific ratio varies by the humidity of the air, as well as the CO₂ concentration of the air. Growers utilizing CO₂ supplementation should be aware that elevated carbon dioxide closes stomates past the 300 ppm level (26), so the transpiration to dry mass ratio decreases to about 200:1. This parameter is multiplied by the desired concentration of the element in the plant. For example, if the desired potassium concentration in the plant is 4%, and the transpiration to dry mass ratio is 300:1, then for every kilogram of plant growth, 300L of solution are required. Since the desired concentration of potassium is 4% in 1 kilogram, 40 grams of potassium are needed in the 300L refill solution, or 0.133 g/L. Dividing this value by the molecular mass of potassium will yield the concentration of
potassium in the refill solution. In this case, it is 3.4 mM of potassium. However, from the above studies, it is clear there is a wide crop response to nutrient levels in recirculating reservoirs. Each crop presents specific demands that uniform or general rules may not apply to, illustrated by the wide response of crop yield to lower or higher concentrations of solution concentration. Moreover, since the development of the refill solution must first target a known percentage of an ion in a plant, these parameters may not be known for new cultivars or strains. Thus, for maximum yield, the ideal percentage of each element in the final dry mass is unknown.

The effects of recirculation on final yield have been studied for a variety of crops. However, not discussed yet, are the methods and physical techniques employed for recirculating nutrient reservoirs. There are multiple techniques that are employed all with the target of recapturing the nutrient solution, each with its advantages and disadvantages. Some techniques seek to maximize oxygen reaching the plant roots, while other techniques aim to present sufficiently large volumes for root growth. This helps larger plants achieve efficient and large root networks with which to efficiently capture all of the solution inputs. In industry however, only certain techniques are used predominantly, while others are hardly seen anymore. As costs change, and prices of marketable crops fluctuate, certain modalities will be favored more than others. The importance of a flexible ion controller that can keep a medley of ions at different levels
may be able to successfully interface with a much wider selection of crops. In addition, the ability to control specific ion levels may help increase final yield by optimizing growth characteristics to each crop. In the following section, an overview of the most prominent recirculation modalities is provided.

**Ebb and Flow**

In this form of recirculating irrigation, plants are grown on a bed with an inert medium, usually perlite, gravel, clay hydroton pebbles, or some other medium that provides structural support. Liquid solution in a reservoir underneath the planting bed is pumped into the growth bed for a defined period of time, usually 5-20 minutes. The amount of liquid solution is such that it can submerse the growth medium up to six inches. The submersion time varies by substrate medium and volume, but needs to be long enough for solution to be drawn to the top root layer by capillary action of the medium. The substrate medium also determines the immersion depth. Some substrates present good drainage, but poor capillary action as measured by the hydraulic conductivity (gravel). In these cases, the flood depth must be longer, as well as deeper to compensate for the poor capillary action.

After a proper soak time corresponding to the properties of the volume as well as type of substrate, the nutrient solution is allowed to drain back down into the underlying reservoir. This drainage is a critical part of ebb and flow technique in terms
of oxygenation. In this case, the drainage of liquid into its underlying reservoir creates a form of vacuum pressure, which ambient air fills the gaps created by the draining solution bringing the needed oxygenation into the root system. This also adds to the importance in using an appropriate substrate. A tightly packed substrate could decrease oxygenation penetration into the lower depths of the root zone. This would influence plant growth by presenting limiting factors of decreasing oxygenation, which influences final yield. Figure 3.3 below shows the setup of a typical ebb and flow system.

Figure 3.3: Simple illustration of the ebb and flow modality. Nutrient solution from an underlying reservoir is pumped into an above tray, where it soaks the growth substrate for a prescribed time, and is allowed to drain back into a reservoir. This same solution is pumped back above periodically, thereby creating nutrient recirculation (27).

Typical downsides to the ebb and flow technique include problems with disease and pathogen spread. As the tray is drained, all of the excess water in the pots entirely
leaves and is returned back to the reservoir. Coupled with the typical long durations for flooding, and the risk of water based pathogens spreading is increased. To minimize this risk, the time of flooding should be kept to a minimum; prolonged periods of standing water should absolutely be avoided. Sometimes multiple tables will share a single reservoir with the solution pumped and drained sequentially. This especially increases the risk of a root based pathogen spreading.

**Top-feed Drip**

Top-feed drip was initially pioneered in the Israeli desert during the mid-1970’s (28). Although not typically used with recirculation systems, it is possible to combine top-feed drip with nutrient recirculation if implemented correctly. Current drip systems are classified as either microtube systems or inline systems. The discussion here will focus only on microtube systems. In this modality, individual containers are interfaced to the main reservoir via small diameter capillaries (<1/8”, ID), which are connected to a main pipe. Several of these main pipes can be connected together at the central junction to the nutrient reservoir. A high-pressure pump serves to deliver nutrient solution from a reservoir into the central junction, and finally to each container. To ensure uniform pressure and application rate throughout the system, a pressure compensated emitter is attached to the open end of every microtube (11). The below image (Figure 3.4) shows the reservoir, pump, and finally tubing that deliver nutrient solution into each pot.
Figure 3.4: Illustration of a top-feed drip system. A pump forces nutrient rich solution into a central tubing system, which has microtubes branching off from it. Liquid is forced through these microtubes onto plant sites where it irrigates the substrate. Recirculation is accomplished by collecting the runoff back into the central reservoir (29).

Recirculation in top feed drip is accomplished from collecting the combined runoff from all the containers and recirculating it back to a main reservoir via a float pump. With sufficiently inert substrates such as rockwool that come to the grower factory sterilized, it may be possible collect and reuse the runoff (30) (31).

**Nutrient-Film Technique (NFT)**

Nutrient-film technique appeared in the hydroponic industry in the early 1980’s, and creates plant growth by maintaining a layer of nutrient solution over the roots at all
times. In commercial practices, this is commonly accomplished by rows or gullies of
growth chambers, elevated at one end, and emptying into a main central reservoir at
the other (32). The width of these gullies is typically between 10-20cm. In NFT culture,
plants are started in netpots in an inert medium with roots growing exposed into the
gully. Oxygenation is also not an issue as the roots are exposed to the air in each
growth gully. A constantly running nutrient stream provides fresh nutrients constantly.
The height of this nutrient stream is just enough to cover the gully, about one to two
centimeters. There is no more need to determine flood times, and no more need for
stagnant water to sit compared to the ebb and flow technique. The pump is constantly
running and providing a fresh nutrient stream across the roots (Figure 3.5). Due to
inputs being constantly given to the plant, and oxygenation not being an issue, plant
growth is particularly robust in NFT systems (33). This somewhat mitigates the
problems of ebb and flow culture, namely disease/pathogen spread, by not completely
inundating, and subsequently emptying the entire container. However, disease spread is
a risk in NFT culture and should be carefully monitored by checking both root status,
and leaf health.

Variables for control include the slope rate of the gullies. This determines the
flow rate of the nutrient solution. Slower flow rates could induce nutrient deficiencies for
plants further downstream. The slow stream would cause upstream plants to absorb
most of the key ions from the nutrient stream, especially potassium. Thus, yield differences have been observed with flow rates that are too slow (34). Usually 2-4% slope will produce a flow rate that will not influence final yield, and carries optimal oxygenation (35).

Figure 3.5: Example of an NFT system. A sloping gully carries nutrient solution down to the reservoir by gravity, where roots uptake the nutrients during the drainage process. A pump recirculates the solution from the underlying reservoir, back into the gullies. The slope rate determines the oxygenation in the solution, and extra oxygenation can be supplied by an airpump (29).

However, this design is subject to its own constraints and limitations. The NFT system features very little buffers to failure. A power outage of a few hours could be enough to wilt entire plants. The entire system is dependent on the constantly moving
stream, and disruptions to this stream could cause adverse impact to the plants. Since roots are maintained in air, there is very little growth medium to provide a barrier to the environment. This causes roots to be particularly sensitive to changes in ambient temperature. High temperatures make roots more prone to root rot, and since NFT system recirculate the nutrient reservoir, this could very easily infect all plants in a reservoir. This root rot is not a subject to be taken lightly. For example, spinach that has contracted root rot in a NFT system was treated with three different types of biofungicides, as well as potassium silicate, which all proved to be unsuccessful (36).

**Recirculating Deep-Water Culture - rDWC**

Deep-water culture (DWC) has been employed in soilless culture since the inception of the science. It was mentioned briefly that both meso-American and Egyptian societies employed soilless culture (11). Specifically, they both employed deep-water culture. In either of these societies, farmers filled rafts with soil, planted the seed, and allowed the basket to float on a lake. The roots of the plant would quickly grow past the limitation of the bucket, and directly enter the underlying lake. This form of raft culture represented a primitive form of deep-water culture. In modern times, this technique is modified such that plants are grown in a nutrient solution filled bucket with a net pot. Minimal amounts of inert medium are used to physically anchor the plant, but plants roots reach directly into the solution rich bucket. Unlike ebb and flow, in deep-water
culture, the liquid solution is never removed from the roots, and the roots stay constantly immersed in the liquid solution. This modality also helps counters the buffer difficulties of NFT by introducing large water volumes per grow bucket. Today, typical volumes of three gallons per bucket are used for growing. Because of the large volume and the high specific heat capacity of water, environmental temperature fluctuations are moderated, and the roots thus protected to some extent from those temperature fluctuations (Figure 3.6).

![Image showing a recirculating deep water culture.](image)

**Figure 3.6**: Image showing a recirculating deep water culture. Pipes connect each bucket with each other, and connect back to the central reservoir. Large volumes of water in each bucket buffer the temperature much better than NFT, and allow roots to be shielded from environmental swings. An air pump adds oxygenation to each bucket individually (37).

Without proper aeration, root systems in deep-water culture do not get enough oxygen. The oxygen in the buckets is quickly depleted by the roots in solution, and
impedes optimal development (38). To overcome this, oxygen supplementation is needed from external air pumps. In addition, nutrients can be quickly used up by the plant from the limited solution in each bucket. Also, due to the nature that each bucket is self-contained, pH levels may fluctuate between bucket to bucket.

To ensure better consistency, and uniformity through each DWC bucket, recirculating deep-water culture (rDWC) was introduced. Whereas in regular deep-water culture, each bucket has its own, separate liquid solution, all volumes are combined in rDWC. Individual buckets are connected to each other, as well as to the control bucket. The control bucket is connected through the central reservoir via a float valve. Through this interconnection, the liquid solution is kept constantly recirculating. This recirculation churns the water and introduces consistency of the pH, as well as introduces fresh nutrient solutions to each bucket. Utilizing rDWC prevents nutrient deficiencies from forming in individual buckets. However, similar to regular DWC, oxygenation must be provided at acceptable levels through use of air pumps and air stones to properly disperse the oxygen (39).

**Aeroponics**

Aeroponics is a subset of hydroponics that utilizes a mister or atomizer nozzle to spray a nutrient rich solution over plant roots. Roots are placed in a volume where they are constantly misted over by the nozzles. This volume is enclosed in a triangle-like
construct with polystyrene or plastic. This volume is sealed off from the outside, and is typically self-contained with the pump inside this volume. Plants are held on surface above exposed to the light, while roots are enclosed below (Figure 3.7). Inside this enclosed volume, relative humidity is very high at 100%. Unlike other hydroponic modalities, these plant roots are not held in an inert medium, and instead are free to be misted over. A very high-pressure pump is used to deliver particles between 20-50 micrometers wide (40). Due to the small particle size of the fine mist, the oxygenation delivered utilizing aeroponics is much higher than simple NFT or top-feed drip. As mentioned above, root absorption of oxygen from air is more efficient than absorption of oxygen from solution. The increase in oxygenation conveys an advantage to the plant in terms of fast root formation, as well as increased yield. A study comparing aeroponically grown lettuce with NFT grown lettuce showed higher yield in the aeroponic system, likely due to the oxygen available to the plant (41).
Figure 3.7: Aeroponics setup with end caps removed to expose roots. The roots are exposed in the triangle like enclosure, inside (not shown) are high-pressure misting pumps that deliver a fine mist to coat the plants. The misting allows for increased oxygenation to be delivered to the plant roots, which allows for faster root formation and plant growth (42).

Downsides of aeroponics are similar to the downsides of NFT, in the sense that the system is very poorly buffered. Only a fine film separates the delicate and fragile plant roots from the outside air. The poor buffering capability of this thin film highlights the importance of a consistent power supply. A disruption to the power usually means that there will be unavoidable damage to the root system. In other modalities, such as rDWC, disruptions to the water supply could take hours to days to manifest themselves due to buffering capabilities of the existing water. In aeroponics, desiccation of the roots is very fast, as there is absolutely no media, or even a bare layer of liquid to buffer the roots. Like in NFT, the risk of root rot is also possible. With little
water volume to buffer root temperature, as well as increase root volume coverage from the fine mist, fast growth of harmful pathogens such as *Fusarium* and *Pythium* is possible if the pathogens are not properly managed and monitored early. In fact, aeroponic systems are so prone to root rot if managed poorly, that they are often used in academic environments to study effects of root rot. Commercialized evaluation systems to mass screen genotypes for root rot employ aeroponic misters to achieve efficient infection of all plants, and to decide if certain genotypes are more resistant to root rot (43). Lastly, possibly the primary reason that aeroponics is not used more frequently in industry is the lack of penetration depth from the mist. For initial stages of plant growth, the fine aeroponic mist is excellent for filling the entire surface area of the exposed roots, which provides optimal nutrition and oxygenation. However, when plant root density increases, the aeroponic mist often incapable of penetrating deep into the root layers, especially the central roots. Due to these issues in penetration, aeroponics most often used as a tool to aid plant cloning or early vegetative stages.

**Deep-Flow Technique**

To improve upon the lack of buffering in both NFT and Aeroponics, deep-flow technique (DFT) was developed in response. Advantages of the NFT and aeroponic techniques include a stream of fresh flowing nutrient solution over the roots, which provide excellent nutrition to the plant. However, both techniques are too sensitive to
external factors, which include temperature extremes, as the roots only are shielded from the air by a thin water layer.

In the deep-flow technique, the water depth is kept between 5-15cm in a sloped trough, while plants are grown in small net pots above. Typically, holes are punctured in a polystyrene raft, and pots placed into these holes. An adjustable pipe is fitted in the trough vertically, which connects the trough with its underlying reservoir. This pipe also determines the depth of the water in each trough. Each reservoir could have a few, or up to several dozen trough’s emptying into it. The widths of these troughs are between 100-150cm, so the volume of water within a trough is substantial (Figure 3.8). Once a root system forms in the net pot, the roots quickly penetrate to the outside, and contact the flowing water stream. Unlike in NFT where only a shallow stream of water is kept flowing over the roots, the approach is fundamentally different in DFT. The DFT approach to growth depends on a massive amount of water.
Figure 3.8: Example of a typical growth bed for deep-flow technique. The white covering over the wide troughs is punctured and net pots placed over each whole. The trough width is much wider than NFT, and water level is substantially deeper. Recirculation forces nutrient solution emptying into the underlying reservoir, back onto the top of the sloped trough, where gravity pulls it back down over the roots of the plants (44).

Although the nutrient uptake by the overlying plants consists of only a relatively small fraction of the overall solution, the large volume of water has other benefits to the plant. The large volume increases buffering capabilities much more when compared to traditional NFT or aeroponic techniques. The primary benefit of this increased buffering is the resistance to large temperature swings or extremes in daily temperature. This makes DFT very popular in hot, but not necessarily dry regions (45). The large water volume needed for recirculation renders DFT a poor choice in arid environments, as the water use of this technique is high. However, the large volume of water makes nutrient control simpler, as plants will take longer to deplete the larger volume of water.
Hybrid Techniques

Approaches have been taken to combine different modalities in order to extract the best advantages of both. One major example is known as the Ein-Gedi system developed in 1980 by Soffter and Levinger, often referred to as aerohydroponics (46). In this type of system, three modalities are combined, including the slope and constant water movement of NFT, the water volume of DFT, and misting effect of aeroponics. Both NFT and aeroponics share disadvantages in the fact that both of the systems are very poorly buffered. However, both have their major respective advantages. Ein-Gedi technique takes advantage of the constant fresh nutrient stream of NFT and the high root surface area covered by aeroponics. Furthermore, an advantage of DFT is brought in as well, with bulk water flow of a height between 5-15cm, but with the width of a typical NFT trough. This allows for bulk movement of water to increase the buffer volume available to the plant, but avoids the typical massive amounts of flowing water associated with DFT.

In the Ein-Gedi technique, plants are grown in net pots in a modified NFT trough. However, unlike NFT, instead of depending on a pump to move water to the elevated end of the trough, a high-pressure water line is utilized. A pump moves water into this water line, which stretches from one end of the trough down to the other. Emitters are spaced out evenly on this water line, with the nozzles matched up to the
net pot sites. When the pump is turned on, rather than depending on gravity to drive the flow of water down the gully, emitters spray out the nutrient solution directly onto the roots. The runoff from these emitters, is then collected inside the trough, and finally is allowed to stream down the entire length. An adjustable vertical pipe similar to DFT is placed at the drainage end of the trough, where the solution returns back to the reservoir (Figure 3.9). The height of this pipe is adjustable, and thus, the water level in each trough can be controlled. The water level in the trough rises to the height of the pipe, before draining and recirculating back to the central nutrient reservoir (46).
Figure 3.9: Aeroflo 60 site system from General Hydroponics. An example of aerohydroponics. Emitter nozzles line the length of the trough, with the nozzle placement corresponding to planting sites. A pump recirculates solution from the lower reservoir into the upper growth troughs.

The adjustable pipe allows for the water level to be raised up, and thus, allows for bulk water a flow. This bulk flow overcomes the buffer issues of both NFT and aeroponics, and allows the system to better withstand temperature fluctuations. The problem with nutrient depletion on sites downstream of the NFT trough is overcome by aeroponics, as the nozzle emitters directly spray nutrient rich solution onto the roots. Recall that an issue with NFT is nutrient depletion, especially of mobile ions like potassium, by upstream plants. By utilizing an aeroponic emitter, fresh nutrients are
supplied to every plant individually. In this manner, nutrient uptake is not solely
dependent on a steadily depleting NFT stream. Lastly, the downsides to aeroponics are
mitigated as well. Issues with only superficial penetration, and not being able to entirely
cover thick root systems are entirely overcome. Although superficial roots are still able
to uptake efficiently from the aeroponic mist, deep roots are able to receive nutrition
from the NFT/DFT hybrid technique. In terms of pathogen resistance, Ein-Gedi
technique helps mitigate root rot problems commonly associated with elevated
temperatures. In aeroponics especially, and to a lesser degree in NFT, open root systems
are easily affected by elevated temperature. The increase of water buffer decreases the
effect of high temperature on plants, and consequently, lowers the possibility of root rot
occurring. High water use associated with DFT is also avoided. In the DFT scheme,
growth rafts are used, which means that the total surface area of water exposed to air is
much higher. This increases evaporation and overall water use is much higher. By
consolidating the DFT scheme into compact growth troughs, rather than the wide
troughs typically associated with DFT, evaporation is much lower. This makes the Ein-
Gedi system more suited toward arid or drought stressed environments.
3.1.3 Choosing a hydroponic modality

With the diversity in the types of modalities, it is not easy to decide an optimal hydroponic modality. However, with nearly all variations of soilless culture, electricity is needed to perform nearly all bulk movements of water. It is this water movement that is so critical to life, and success in hydroponic modalities. Fresh water brings fresh nutrients, oxygen, as well as prevents salinity buildup that is so detrimental to final yield (47). To determine the optimal growth modality, a number of variables should be carefully weighed. Especially the cost-benefit analysis in comparing the cost of energy, to the qualitative or quantitative advantages a change in modality could bring. The difference in energy use among different modalities certainly exists, with perhaps top-feed drip presenting the lowest power use, and Ein-Gedi technique the highest. The advantages that a change in modality could bring include increases in nutrient use efficiency, oxygen uptake, water availability, and decreases in pathogens. Variables to consider include water availability, cost of inputs such as water and electricity, environmental parameters such as temperature and relative humidity, and lastly crop specific demands.

With the amount of variables to be considered, there is no easy, or direct answer to the "optimal" or "best" hydroponic modality. It is a careful balance between managing inputs, and maximizing outputs. Recirculation provides efficient use of nutrients, though at a cost of not obtaining maximized yield or increased risk of disease. Automated ion
control helps decrease the effects of slow nutrition depletion in crops, and maintains key ions at specified levels. In addition, individual ion sensing provides the grower with in depth information on which to base decisions.

3.2 Electrochemical Sensors: Theory and Application in Agriculture

3.2.1 Classes of Electrochemical Sensors

The quality of any good control system depends on the quality and accuracy of the incoming information. For accurate decisions to be made at a processor level, in regards to whether nutrient injection is necessary, the incoming information regarding the concentration of that ion must be accurate. To detect these concentrations, sensors have been developed to reliably detect its ion using a wide variety of modalities. In general though, the functioning principle of these sensors is grounded in the fundamentals of electrochemistry.

Electrochemical sensors are a broad class of sensors that exploit chemical principles in order to generate an electrical response. These sensors can be broadly classed into potentiometric, voltammetric, and gas sensors (48). Still others existing outside these three include ion-selective field effect transistors (ISFET) and light based sensing solutions. Though there are stark differences between the operating principles of these sensors, the unifying thread is the generation of an electrical signal, which is correlated with a relative concentration of a chemical. That is to say, varying
concentrations of the relevant chemical will produce corresponding variations in an electrical signal. Through careful calibration of the electrical signal, it is possible then to determine the absolute concentration of that chemical in a sample. The usage of electrochemical sensors is extremely broad, and applications are found in agriculture, biochemistry, manufacturing, and the energy industry among others. Chemicals that can be sensed by electrochemical sensors include biological species, complex molecules, as well as singular ions. Much research has been focused onto the latter, and the scope of this document will focus on ion-selective sensors. As the main focus is on agricultural applications, only relevant sensors to the agriculture industry will be discussed. The main applications of gas sensors are air sampling, and due to the plants receiving nutrition in soilless culture through liquid solutions, the discussion of gas sensors is not relevant in the scope of this topic.

There are fundamental differences in the operational principle of potentiometric and voltammetric sensors. Though they share characteristics between them, the differences and mechanisms utilized between the two classes are not similar. In the potentiometric approach to ion sensing, a PVC membrane is utilized, which contains an ionophore that is highly specific to only a single ion. The solution comes into contact with the ionophore side of the membrane, with only the specific ion able to bind onto the ionophore. On the other side of this PVC membrane is a reference electrode
surrounded by a highly specific reference solution in terms of concentration. The difference between the outside solution voltage, and this inner reference voltage, creates a potential across the ionophore membrane. It is this potential that is recorded and analyzed. This topic is discussed in more detail in section 3.2.3.

Varying solution concentrations of the measurement ion produces variations in potential, which can then be correlated to the concentration of that ion. A reference electrode measures this potential, and is composed of materials that have stable half-cell components, and moreover, produce consistent variations in voltage with changes in temperature. Furthermore, the reference electrode needs to produce a fixed and reproducible electrode potential when combined with the reference solution. This increases precision and accuracy of the measurement system (49). Other implementations bypass the internal reference solution entirely, and only utilize a reference electrode. This electrode requires a stable, and nonreactive material, and is therefore frequently made of platinum. This electrode is dipped into the solution directly, and develops a reference potential to the ion to be measured. Any changes to this ion concentration will directly influence the reference potential. The hallmark of potentiometric sensing is that it is a passive sensing technique as only the potential is measured. This means that no external current needs to be applied to the electrode (50).
Voltammetric sensing modalities are not considered a passive modality and require external inputs. The operating principle is opposite that of potentiometric measuring mechanisms. In this mechanism, information about an ion concentration is obtained by measuring the current as a response to a varying potential. It is also possible to hold potential constant, and measure the subsequent current while ion-concentration varies. Unlike potentiometric sensing, three electrodes are utilized including a working electrode, a reference electrode, and an auxiliary electrode. The working electrode makes contact with the solution and applies a controlled electrical potential. This electrode also facilitates the current transfer between and from the solution (51). The auxiliary electrode complements the reference electrode by matching the current found in the reference electrode. This is to balance the reaction occurring at the reference electrode (52). The last electrode is the reference electrode, which is unique in the fact that it is the only electrode without a need to pass current. This electrode is a half-cell with a known reduction potential, and it is needed in order to provide a stable reference against which the working and auxiliary electrodes are measured against (51). A half-cell electrode is one that is immersed in the electrolyte solution, and naturally generates a voltage due to the formation of a Helmholtz double layer (53). The electrodes themselves are coated with a membrane containing an electroactive species, as well as an ionophore, and a supporting electrolyte dissolved in a plasticizer.
A potential is applied at the working electrode surface, and the resulting current is measured (54). The actual probing mechanism is investigating the half-cell reactivity of the ion. The strength of this resulting current is related to the concentration of that ion in solution.

Generally, potentiometric sensors are much more cost effective than voltammetric sensors. This is due to the fact that voltammetric sensors require more electrodes than potentiometric techniques. Materials used in electrode, and especially reference electrode fabrications are often of expensive silver or platinum. In addition, voltammetric systems have to be able to handle electrical current flowing both into, and out of the electrodes. In potentiometric sensors, only a single potential needs to be established, and thus, current flow is only one way.

Other sensing modalities that are less commonly used compared to voltammetric and potentiometric methods include ion-selective field effect transistors (ISFET). The operating principle of this type of ion sensor is similar to that of a MOSFET. With variations in the ion-concentrations, a corresponding current through the FET channel changes accordingly. The specific construction of an ISFET is similar to that of an electrical MOSFET with the source and drain corresponding between both types. In the ISFET, the gate connection is separated from the chip in the form of “a reference electrode inserted in an aqueous solution which is in contact with the gate oxide. (55)”
The pH of the sample determines its threshold voltage, but once the voltage is formed, a current will begin to flow through the transistor (55). Like both voltammetry and potentiometry, ISFETs still rely on a reference electrode in order to verify the strength of the chemical gradient. With increasing amounts of ions, the current flow from the source to the drain will be increased, and thus, the concentration can be related to the current.

Still other approaches to ion sensing have utilized light based modalities such as fluorescence or absorption sensing. The advantage to this form of modality is that the need for costly reference electrodes is taken away and mitigated. Currently, many of the problems with ion-selective electrodes utilizing reference electrodes are caused by the presence of this electrode. This includes the propensity of the leakage of the solution surrounding the reference electrode, as well as the bulkiness and fragility of this same electrode. Breakdown of the reference electrode presents a risk in pharmaceutical industry, as well as agricultural industries as electrode debris and toxic heavy metals can leak into the substrate (56). A light based sensing modality (optode) present advantages in this area. Without a reference electrode, the cost of the sensor is lower from a physical standpoint. Optode sensing modalities require an ion-selective membrane, a spectrometer, and an emitting source. Spin coating typically creates the membrane, and it serves the critical role of separating the sample to be measured from a
chromoionophore solution. The diffusion of the ion across the membrane induces a color change in the chromoionophore solution. An emitting light source measures the absorbance across a spectrum, with the absorbance at each wavelength attenuated by the sample concentration. A higher ion concentration induces an absorbance at a select wavelength differently to a low-ion concentration at the wavelength (57).

Still other modalities for measuring ion-concentrations are not classically traditionally considered sensors, as there is an irreversible change in chemical binding. For example, measurement of Fe$^{2+}$ ions in solution can be done with potassium ferricyanide. In the presence of this compound, the color change is immediate and abrupt, and turns into a deep color of blue. Comparing the absorbance at 700nm results in the differentiation of iron concentrations based on the strength of the color change (58).

3.2.2 Evolution and Variations of Potentiometric Electrodes

The ease of use, and relative cost efficiency of potentiometric sensors has seen them adopted rapidly, and potentiometric ion-selective electrodes are the most widely used ion sensors of all the types. Just in the US, valinomycin based ISE’s are used to make 200 million clinical K$^+$ assays every year (59). However, even among potentiometric electrodes, there are distinct differences in class and operational type. The operating principle is the same; a bulk membrane is impregnated with an ion carrier, permeable to either a single or to multiple ions (50). However, differences in this bulk membrane, as
well as degradation characteristics of the ion carrier all influence final quality. Though the general design is the same, there is a substantial variation in quality. Relevant parameters in the characterization of potentiometric electrodes include response time, sensitivity, specificity, detection limits, measuring ranges, pH ranges, and operational lifespan.

One of the first ISE’s to be commercially available was sensitive to the calcium ion, Ca\(^{2+}\). The development of the Calcium electrode mirrors the development of similar ion probes such as NO\(_3^-\) and K\(^+\). From their initial appearances up to now, numerous advances have been made in the ion carrier, with hundreds of potential ionophores discovered. As expected, first generation commercial implementations of these ion-selective electrodes were met with problems in poor lifespan and fast degradation of the ionophore (60,61). Improvements in the fabrication practices and ionophore stability have significantly boosted overall sensor lifespan. This is plainly visible in literature regarding sensor capabilities. First generation calcium sensors had a lower detection limit at 10\(^{-3}\) M, while newest generation calcium sensors have a lower detection limit of 10\(^{-7}\) M, an improvement on the order of several magnitudes (62,63)

This same trend is no different in ions such as potassium. Early experiments with potassium ion-selective electrodes showed lifespans of around one-week (64). However, in recent experiments with potassium, solid-state potentiometric electrodes show
lifespans on the order of months to years (65). Improvements often focus on stability of
the bulk membrane, with several changes in electrode design to optimize and lessen the
chemical stress on this membrane. Further, improvements in specificity and selectivity
of ions have been made in the ionophores themselves, with newer ionophores being
highly specific to their associated ion. This improvement is very important, as typical
measuring environments will consist of a multitude of competing ions for binding spots
onto the membrane. Only with highly specific ionophores can the electrode display
proper sensitivity to relevant ion to be measured.

Potentiometric ISE’s come in different physical forms, typically either glass body,
or epoxy body. The selection of body material depends on electrode application. In
extreme sensor environments, such as areas of extremely low or high pH, temperature,
reactive substrates, and otherwise caustic environments, a glass body is normally
employed for its low reactivity. However in field environments where soil may be
measured, or where the electrode will be experiencing heavy use, then epoxy bodies are
more utilized. Glass bodies allows usage in environments of up to 100° C while epoxy
bodies can typically only withstand up to 80° C. Use of the body material does not
change performance, but only governs durability, and usage environments. Tip shape is
also important in terms of usage environment. For soil monitoring, many of the ion-
selective electrodes have a shielded hood in order to prevent damage to the sensitive
ionophore membrane (66).

Usage life of the ion-selective electrode is also limited according to its electrode type. Both epoxy and glass body electrodes are differentiated according to either single, or double junction electrodes. Single junction electrodes are the most simple and common type of electrode. In the example of the potassium sensor, the reference electrode is contained within a glass or epoxy housing, with an external junction contacting the outside solution. The reference electrode is a silver wire coated with a layer of silver chloride and is surrounded by a 4M solution of KCl saturated with AgCl. The lower end of this electrode is sealed with an ionophore-impregnated bulk membrane, which contacts the external test solution.

The double junction design is different, and consists of a two-housing design. The reference electrode is housed in a separate tube filled with a silver electrolyte within the main electrode housing. An inner junction connects the reference electrode with the main epoxy housing that holds the silver-free electrolyte. This main epoxy housing comes into contact with the outside solution through an external junction containing the ionophore. The outer silver-free solution forms a salt bridge between the inner reference system and the outer test solution. This solution is carefully chosen to minimize contamination of the inner electrode. Typical solutions for outer fill solutions include ammonium sulphate for the nitrate ISE’s, as well as sodium chloride for
potassium ISE’s (67). The primary benefits of double junction electrodes are that with the conventional single junction design, outside substances are more likely to diffuse through the bulk membrane and contaminate the silver wire. The double junction design introduces another membrane in which outside contaminants have to diffuse through, which increases operational lifespan of the sensor (Figure 3.10). Although the extra internal junction is more difficult to manufacture and increases cost, usage life of double junction electrodes exceed that of single junction (68).

Figure 3.10: Single vs Double Junction Electrode. Double junction electrodes have a separate inner tube containing the reference junction, so any contamination of the reference electrode requires diffusion through two different junctions. This increases lifespan(66).
Other increases in lifespan are related to advances in the bulk membrane. As mentioned above, lifespans of early ion-selective electrodes were limited to a few days with membranes primarily manufactured from PVC. In this design, ionophores specific to various ions were combined with plasticizers and incorporated into PVC for structural support. For example, the first ionophore utilized with the potassium ion was valinomycin. Interestingly, this ionophore was utilized first in biology as an antibiotic, but the inner hexagonal ring is approximately similar to the diameter of a \(\text{K}^+\) ion, which allowed for a novel use of this antibiotic as an ionophore (69). However, this diameter also allows other small ions to pass through and cause errors with potassium determination. In addition, the ionophore membrane degrades over time, leading to a limited lifespan. To improve selectivity as well as lifespan, other membranes were developed including crystal-membrane electrodes. Fluoride was the first element to build on this sort of crystal membrane. This implementation of the selective membrane exhibits 100% selectivity for the \(\text{F}^-\) ion, and only experiences interference from the \(\text{OH}^-\) (70,71). Similar to crystal membrane electrodes, other forms of solid-state electrodes exist based on compressing a polycrystalline pellet. Electrodes sensitive to the bromine ion typically utilize this compressed pellet form of bulk membrane (72). Solid state ion-selective membranes also are able to detect ions that impregnated PVC electrodes cannot.
Development of a phosphate electrode has been long hampered by the fact that the high hydration energy of phosphate means that ion-selective electrodes have poor selectivity for the phosphate ion. Furthermore, the phosphate ion is near the bottom of the Hofmeister selectivity series, which indicates it shows the lowest selectivity response toward anions because the free energy of the phosphate ion is very low (73). While ISE’s sensitive toward the phosphate ion have been made, typically all have suffered from very poor lifespan due to the inherent properties of phosphate, and the tendency toward hydrolysis in the bulk membrane (74). Solid-state membranes bypass this hydrolysis effect and are the first type of phosphate electrodes to show long-term stability. Crystal membranes consisting of aluminum powder, aluminum phosphate, and powdered copper exhibited excellent sensitivity to the phosphate ion. More importantly, the lifespan of this solid-state phosphate sensor was on the order of months (75).

3.2.3 Operational Principle of Potentiometric Sensing: The Nernst Equation

Determination of a concentration starting from the electrical potential has its basis in the Nernst equation. This equation was described by Walter Nernst in the 1800’s and relates the concentration gradient to the electrode potential. What this means is that once a concentration gradient is established across a membrane, ions will diffuse across this membrane from regions of high concentration to low concentration. In steady-state, the movement of ions is exactly balanced by an electrical charge that opposes this movement. In this way, equilibrium is established across a membrane, but the
consequence is a potential.

The voltage of the cell is described by Equation 3.1 gives the total cell potential, $E$, in terms of the standard cell potential of the analyte solution ($E^\Theta$), the constant ideal gas constant $R$, the temperature in Kelvins ($T$), number of moles transferred in the cell reaction ($z$), the Faraday constant ($F$) and reaction quotient ($Q$):

$$E_{cell} = E^\Theta_{cell} - \frac{RT}{zF} \ln Q \quad (3.1)$$

At room temperature, the term $\frac{RT}{F}$ reduces down to a single constant of 25.693mV. The standard potential of the analyte solution is the combined potential of all the other ions that are not being measured. The reaction quotient $Q$ can be written as an equilibrium, $[X]_{out}/[X]_{in}$, where $[X]_{out}$ is the concentration of ion species X within the electrode; $[X]_{in}$ is the concentration of ion species in the analyte. As the measurement electrode, and the concentration of the ion species within the electrode is constant in every measurement Equation 3.1 can be simplified into:

$$E_{cell} = E^\Theta_{cell} - \frac{RT}{zF} \ln [X]_{in} \quad (3.2)$$

Derivation of the Nernst equation can be done based on first principles, specifically the first law of thermodynamics and Gibbs free energy. A spontaneous reaction such as diffusion will be accompanied, and counterbalanced with positive potential $E$. This relationship can be seen by first rearranging the equation 3.1 into:

$$zFE_{cell} = zFE^\Theta_{cell} - RT \ln Q \quad (3.3)$$
In addition, for a reaction system at equilibrium, the Gibbs free energy equation can be expressed at:

\[ \Delta G = \Delta G^0 + RT \ln Q \]  \hspace{1cm} (3.4)

The Gibbs identities:

\[ \Delta G = -nFE \]  \hspace{1cm} (3.5)

\[ \Delta G^0 = -nFE_{cell}^{\Theta} \]  \hspace{1cm} (3.6)

Can be substituted into equation 3.4, and once simplified, will yield equation 3.1

3.2.4 Calibration and characterizing ion-selective electrodes

Determination of a concentration from the total cell potential requires careful calibration of the sensor. The presence of interfering ions as well as temperature differences of the analyte solution requires that calibration of the electrode be done before measuring. This calibration is performed by immersing the electrode in a series of solutions with known concentrations, and then subsequently plotting the millivolt reading from each sensor versus the log of the activity. Since activity is very difficult to determine in complex solutions, a simplification is generally done in weak solutions (of less than 0.01M) and concentration is plotted instead. However, in high ionic strength solutions, the true activities of the ions must be used. This complicates matters a bit, as estimation of ion activities requires careful experimental measurement. To mitigate this effect somewhat, if the application of the sensor is in a high ionic concentration solution, the higher activity rate is simulated with addition of ionic strength adjustment buffer.
This creates a calibration curve more similar to that ion activity in a high strength solutions (68). In any case, the ideal calibration curve is a linear relationship that directly relates analyte concentration with membrane potential. By determining the x-intercept and y-intercept of the linear equation, a calibration curve for the electrode will be produced.

As mentioned before, each electrode has an inherent detection limit. This detection limit is a lower, and upper bound of ion concentration that can be detected by the ion-selective electrode. This detection limit is determined mathematically from the slope. As mentioned above, the membrane potential generally follows a linear relationship with log ppm. However, at extreme detection limits, the slope of the response flattens out. Figure 3.11 shows IUPAC specifications, where the membrane potential of the response no longer changes with variations in concentration, then the upper and lower limits of the slope are defined (76).
Figure 3.11: Definition of both the upper and the lower detection limits. IUPAC standards set the detection limits when the slope no longer changes to voltage. The variable “a” is the concentration of the analyte solution. The y-axis, EMF, is the electromotive force, and is measured in volts. The linear slope is formed from the log of the concentration plotted against the voltage (59).

Setting a single set of standards for testing ion-selective electrodes is important in the fact that comparisons across the literature are made easier. Just as IUPAC has specifications on upper and lower limits of detection, there are also specifications regarding response times of electrodes. Response time is measured as the difference between two time points. The first is the instant that the analyte solution and ISE make contact. The second time point is defined as when the potential of the cell reaches its steady state value with an acceptable deviation of 1mV. On a typical nitrate electrode, this translates into roughly 3.5 ppm. Factors influencing response time are ion
exchange efficiency at the interface, as well as the diffusion speed of the analyte. Plasticizer material and content influences diffusion speed, and newer generation non-solid state ISE’s have much better response times than previous generation (59).

No ion-selective electrode is completely sensitive toward one single ion. Interference occurs from other ions influence readings. In the case of valinomycin, its central ring is approximately the same diameter of the K$^+$ ion. However, if other similar sized ionic species were also present, then potential interference could occur and the overall detection ability for the potassium ion would be decreased. The measurement of interference by another ion in the solution is measured by a selectivity coefficient. If an electrode is specific toward ion A, but interfered with by ion B, a selectivity coefficient of 0.1 would indicate that the electrode membrane is ten times as sensitive to ion A vs. B. Modern ion-selective electrodes are engineered with their membranes such that they can successfully operate in an environment with a multitude of interfering ions. For example, current generation nitrate ionophores are accomplishing their recognition through an amide-based dendritic molecule. This ionophore presents high specificity to the nitrate ion even in the presence of 11 other interfering cations and anions. Selectivity coefficients for the 11 ions ranged from $10^{-2}$ to $10^{-3}$, indicating no or minimum interference with the performance of the electrode (77).
3.2.5 Ion-Specific Electrodes in Agriculture

Early academic efforts in soilless culture attempted to detail exact mechanisms of plant nutrition, and uncovered a finite group of ions that are important to plant growth. Recall that the Hoagland solution provided a basic recipe for plant growth by the addition of salts to a liquid solvent such as water. In solution, these salts would dissolve and break apart into their respective charged ions. Plants then uptake these ions through their roots, and utilize them for synthesis of complex molecules.

The charges these ions carry can be probed, by a method called electrical conductivity sampling. More dissolved ions, and thus higher nutrient concentrations, can conduct electricity more easily. In a conductivity sensor, a current is applied, while another probe measures the subsequent voltage drop (78). A solution with very few, or no dissolved ions such as DI water, is a very poor conductor of electricity. This method probes the combined response of all the ions in the solution, rather than the specific concentration of any individual ion. Disadvantages of this technique include differential contribution of individual ions to the final measurement. Micronutrients contribute less than 0.1% to final electrical conductivity, and since differential uptake occurs, EC past the first few hours will just probe the calcium, magnesium and sulfate in the solution (3). The prevalence of EC based control systems suggest that sampling and understanding the nutrient reservoir is an important goal. The advent of reliable, long-lifespan ion-specific electrodes has lowered the barrier to entry in terms of studying
reservoir ion contents. Based on the limitations of EC, individual ion data is much more accurate and leads to more effective decision-making. Relevant ions for control are based on the salts that comprise the Hoagland solution. Commercially available ion-selective electrodes that are relevant to agriculture include electrodes to sample, sodium (Na⁺), nitrate (NO₃⁻), ammonium (NH₄⁺), copper (Cu²⁺), potassium (K⁺), calcium (Ca²⁺), chloride (Cl⁻), pH (H⁺), and to some extent magnesium (Mg²⁺).

Plant nutrition is generally divided into two classes of nutrients; macronutrient elements are nitrogen, potassium, and phosphorus. While the remaining relevant elements for plant growth are considered micronutrients (Table 2.1). It is important to target macronutrient ions in order to maximize the relevant information for the grower. Due to the difficulties of manufacturing a phosphate electrode, only two macronutrient ions provide opportunities for long-term monitoring, nitrate and potassium. Although ammonium is also considered a supply of nitrogen, in practice, disproportionate application of ammonium affects final yield. For example, in hydroponically grown strawberries, maximum yield was obtained from a 0.25 to 0.75 ratio of ammonium to nitrate. Increasing ammonium ratio to 0.75 resulted in decreases of fresh and dry weight, as well as declines in leaf area (79). Thus, for long term monitoring of the nitrogen ion, it is more relevant to use nitrate rather than ammonium as a marker for nitrogen nutrition. Micronutrients that are relevant to monitor include calcium, copper,
and sulfide. However, since copper and sulfide are found in only trace amounts, it may push the detection limits of the electrode. Due to this physical limitation, calcium may be a more reliable ion to monitor. The alternative candidate is magnesium, but is hampered by electrode characteristics. Commercially available magnesium electrodes are often sampled in conjunction with calcium as part of a "water hardness" electrode. If a water hardness electrode is used in conjunction with calcium electrode, it may be possible calculate the concentration of magnesium based on the Goldman-Hodgkin-Katz voltage equation (Equation 3.7), which is itself derived from the Nernst equation. In this equation, the total cell potential of a membrane permeable to multiple ions can be calculated with $E$ being the total membrane potential, the universal gas constant ($R$), the temperature in Kelvin ($T$), Faraday constant ($F$), the permeability of each ion ($P$), and the molar concentration for each ion in both the inside membrane (electrode) and the outside membrane (analyte):

$$E_m = \frac{kT}{F} \ln \left( \frac{\sum N P_{M^+} [M^+]_{out} + \sum N P_{A^-} [A^-]_{in}}{\sum N P_{M^+} [M^+]_{in} + \sum N P_{A^-} [A^-]_{out}} \right) \quad (3.7)$$

Water hardness electrodes are more permeable to calcium than magnesium, which is why the GHK equation must be used as opposed to any simplifications. It may be obvious to determine the concentration of magnesium by subtracting the ppm of $\text{Ca}^{2+}$ as measured by the singular electrode, from the combined ppm of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ from the water hardness electrode; however, doing so will result in measurement errors.
due to membrane preference for the Ca\(^{2+}\) ion. Due to this difference in permeability, the GHK equation must be used to determine magnesium concentration. Information from the dedicated Ca\(^{2+}\) electrode is combined with the total electrical potential from the water hardness electrode, and the permeability parameter constant to determine an accurate estimate of magnesium. Due to this added complexity in monitoring the magnesium ion, calcium may be a more suitable micronutrient to monitor.

A final ion that could be monitored is Na\(^{+}\). This ion is not necessary for plant growth, and plants do not absorb Na\(^{+}\) at all. In fact, guard cells in the plant actively exclude uptake; however, it can be utilized as an important marker for reservoir change. Over time, in recirculating reservoirs, salinity will increase as plants continue to exclude the sodium ion. Elevated salinity can decrease yield and this effect has been observed in both lettuce and tomato. The mechanism is hypothesized to be osmotic adjustment as the plants adapt, and this decreases the water content of fruit (80,81). Thus, with proper monitoring of the sodium ion, it can be made into a relevant ion in order to have a quantitative indicator of when nutrient changes are needed.

The dissociation of salts into ions in a liquid solution makes it highly relevant to track the concentration of these ions in solution. Though the Hoagland solution prescribes a list of about a dozen ions that are integral for plant growth, not all ions are available commercially in regards to electrode sensors. Commercial availability of ISE’s,
physical limits placed by low ion concentrations, and added complexity in computationally determining concentrations has limited viable ion-selective electrodes in agriculture to a handful.

3.3 Mineral Uptake and Automated Control Systems in Agriculture

3.3.1 Uptake and Ion Mobility

The previous discussion on ions is paramount, as plant roots uptake all of their nutrients in their inorganic form. In traditional soil based agriculture, organic minerals are disassociated into their inorganic ions by the hydrolysis caused by water. It is only then are these inorganic ions transported into the cell via active transport. This transport process is critical to plant growth and ensuring nutrition requirements are met. Typically, plants to have to move the ion of interest against the concentration gradient. Concentrations of ions like potassium are often over 10,000 as concentrated in the roots vs. the surrounding environment (82). This huge concentration gradient forces the plant to utilize efficient chemiosmotic active transport mechanisms. Proton pumps powered by H⁺ and ATPase open and close active transport channels. ATP is used to power these transport pumps, and H⁺ is transported from the inside of the cell to the outside. An enzyme known as ATP-ase removes a phosphate group, an exothermic reaction, to open the pump to allow ions in. Only through this active transport process, can the cell obtain needed ions for growth, as the extracellular concentration of that ion
is orders of magnitude lower compared to the intracellular concentration.

It is also immediately obvious why pH is so important to plant growth and uptake. Plants do not receive any nutrition from the pH ion, H\(^+\); instead the pH determines the ion absorption characteristics of the plant. Since each transport pump depends on pumping the H\(^+\) ion outward, the availability of this ion influences mineral uptake. Transport pumps are very specific towards their ion, and the majority of these pumps show ideal operation at slightly acidic pH. At low pH, or high pH, many of these active transport channels no longer functions at optimal efficiency, and transport processes all together cease. Optimal pH to maintain the optimum transport is 5.8 in hydroponic media (3). Failure to maintain this pH level is not catastrophic unless for prolonged periods of time, which may lead to nutrient deficiencies from transport pumps not working.

As transport is mostly an active process, plants decide what nutrients are needed, and what is sufficient. This concept is known as nutrient mobility. The macronutrients are typically very mobile, and both nitrate and potassium are quickly absorbed. Studies done with potassium mobility in soil have demonstrated that fixation of the ion into the plant occurs rapidly during the first eight hours, while after four days, very little uptake is observed (83). Other ions are less mobile. Calcium uptake in plants is gradual and unlike both nitrate and potassium, is not immediately taken up into the roots. The
uptake of calcium is actually quite a complex process, with two channels available to plants for calcium. One is suited for nutritive and signaling functions, while the other is limited to a signaling function (84). Together, these two pumps carefully regulate the membrane potential of the cell during periods of net ion flux. Measurements of membrane voltage show that plants can occupy one of two states, either the P-state where pumping occurs, or the K-state where the membrane potential is roughly similar to that of the K$^+$ ion. While the membrane exists in either of these states, the potential relatively stable (85). One hypothesis is that these channels are closed all the time. This could be the case in static cells; however, in dynamic cells experiencing net ion uptake like root-hair cells, cells must carefully balance membrane potential by counterbalancing the influx of ions, with the efflux of other ions (86). To balance out the net influx of Ca$^{2+}$, another positively charged ion must be pumped out in order to electrically counterbalance this influx, and maintain membrane potential. In the case of the dual Ca$^{2+}$ channels, a potassium pump moves K$^+$ outwards. Although this mechanism is specifically outlining the activity of the Ca$^{2+}$ pump, the same principles here apply to other voltage-sensitive transporters that mediate uptake of other ionic species.

Disregarding the concept of ion-mobility can easily lead to fatal dosing and poor control of the system. Over addition of nutrients can actually lead to nutrient deficiencies. Plants absorb potassium quickly as it is a mobile nutrient, but
oversupplying potassium can lead to deficiencies in both Ca$^{2+}$ uptake, as well as Mg$^{2+}$ uptake due to the similarity in charge (3). Similar risks with toxicity exist also in the nitrate ion. Its highly mobile nature means that uptake is rapid, so overdosing the system could lead to poor consequences. Calcium supply should also be carefully controlled and regulated. Plants uptake calcium passively so with oversupply, it is easy for the ion to accumulate in nutrient reservoirs.

3.3.2 Current Advancements in Detection and Control Systems

Several approaches have been made already to attempt ion-sensing in liquid solutions, and still others have attempted the problem of correction. A Spanish sensor company named Libelium has developed a Smart Water sensor, with built in wireless capabilities through cellular, and low-power radio (Zigbee) frequencies. This sensor detects a variety of parameters, but utilizes a bulk electrode to sample a variety of nutrients. It is not known if this is a combined measurement, and the developer does not give further information. However, this sensor does not attempt nutrient injection or rectification.

Other attempts have been made at systems that do perform nutrient injection. One such system is the PurGro system. In this system, pH control and bulk EC control is performed. Four containers hold solutions: two for EC control, and two for pH control. Once the EC falls below a certain level, the system attempts nutrient injection via opening solenoid valves, and adding commercially available liquid hydroponic solution in set amounts. The problem with this approach is that the grower is limited to
only two part solutions, as there are only two chambers. Furthermore, the container volume is limited, and only reservoirs of smaller sizes can be controlled. Overdosage is a potential problem as the sensor is limited to EC measurement. Although the EC sensor allows the grower to gain a general picture of nutrient availability in the reservoir, it cannot provide details on nutrient depletion caused by differential nutrient uptake, and specific ion deficiencies may still occur.

Another similar device built by Sustainable Microfarms, also utilizes EC to perform sampling. Nutrient solutions are interfaced directly into a specialized bottle cap, and solution is drawn into the device and injected into the system. The bottle size is limited to the quart size, and the maximum controllable reservoir size is approximately 100 gallons. This system has the same limitations as the PurGro system as ion deficiencies can still manifest themselves with EC measurement systems.

More complex dosing systems for single element fertilizers exist as well, but currently, these systems are extremely expensive, and do not provide feedback. Mixtures of ions are injected into holding tanks, where they are mixed and utilized as the fertilizer. Weekly recirculation may inject a finite amount of each nutrient to attempt to compensate for estimated depletion during recirculation. However, the differences between crops, as well as between cultivars make gauging for nutrient uptake
difficult. No real-time control of the nutrient solution is performed, and no ion selective electrodes are used to provide feedback to the controller.
CHAPTER 4: MATERIALS AND METHODS

Each of the described control systems have a shortcoming, which highlights the need to have 1) cost effective, 2) long term, 3) feedback controlled, and 4) automated control systems. Such a system would utilize cost effective potentiometric ion-selective electrodes to provide long-term monitoring of the reservoir in terms of its relevant constituent ions. A processor reacts to this feedback and performs ion injection if necessary to correct any deficiencies, or to hold nutrient concentrations inside a defined range.

To build a successful injection system for use in commercial, recirculating hydroponic reservoirs, specific design requirements must be taken into account including environmental considerations of a grow house, as well as scalability of the device to accommodate a wide range of reservoirs. These requirements, as well as the aforementioned goals, form the bulk of the engineering design considerations of a liquid-ion injection system.

4.1 The Frame

The frame is meant to provide a fixture point for the stepper motor drivers, as well as provide a point to attach and fix the syringes containing the stock solution. The frame
consists of the aluminum extrusions arranged in the rectangular shape, as well as the cross braces that the syringe holders attach too. A primary design consideration of the frame was developing a support that can withstand high moisture environments without noticeable degradation. Since this device will be in close contact with liquid solutions, waterproof materials are of paramount importance. In addition, the frame must provide proper structural support to the injectors and other parts placed onto it. There are a total of five injectors fixed onto this frame corresponding to each ion (\(\text{NO}_3^-, \text{K}^+, \text{Ca}^{2+}, \text{and H}^+\)). Though there are four ions, five injectors are needed as pH control requires ability to raise, and drop. The following table (Table 4.1) indicates the complete bill of materials necessary to build the frame.
Table 4.1: Bill of Materials for the Frame

<table>
<thead>
<tr>
<th>Description</th>
<th>Part Number</th>
<th>Material</th>
<th>Source</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>500mm extrusion. T-slot. 2040</td>
<td>26042-01</td>
<td>Anodized Aluminum</td>
<td>Inventables</td>
<td>2</td>
</tr>
<tr>
<td>1000mm extrusion. T-slot. 2040</td>
<td>26042-02</td>
<td>Anodized Aluminum</td>
<td>Inventables</td>
<td>2</td>
</tr>
<tr>
<td>1000mm extrusion. T-slot. 2020</td>
<td>26039-01</td>
<td>Anodized Aluminum</td>
<td>Inventables</td>
<td>2</td>
</tr>
<tr>
<td>Aluminum Extrusion End Cap. 2040</td>
<td>26047-02</td>
<td>ABS Plastic</td>
<td>Inventables</td>
<td>4</td>
</tr>
<tr>
<td>M5 Pre-Insertion Extrusion Nuts</td>
<td>25281-02</td>
<td>Low Carbon Steel</td>
<td>Inventables</td>
<td>140</td>
</tr>
<tr>
<td>M5 Socket Head Screw, 8mm</td>
<td>91290A222</td>
<td>Alloy Steel</td>
<td>McMaster</td>
<td>104</td>
</tr>
<tr>
<td>M5 Button Head Screw, 8mm</td>
<td>91239A222</td>
<td>Alloy Steel</td>
<td>McMaster</td>
<td>16</td>
</tr>
<tr>
<td>Corner-Plate (Double)</td>
<td>5537T209</td>
<td>Anodized Aluminum</td>
<td>McMaster</td>
<td>4</td>
</tr>
<tr>
<td>4x1 Aluminum Plate for 2020</td>
<td>5537T174</td>
<td>Anodized Aluminum</td>
<td>McMaster</td>
<td>4</td>
</tr>
<tr>
<td>Extended 90 degree Bracket</td>
<td>5537T187</td>
<td>Anodized Aluminum</td>
<td>McMaster</td>
<td>4</td>
</tr>
</tbody>
</table>
The assembled frame as rendered by Solidworks is shown in the below Figure 4.1:

Figure 4.1: Assembled Frame rendered from a SolidWorks model. The frame is constructed from extruded aluminum, and consists of the rectangular structural support, as well as the cross braces in the middle for both added rigidity, and to provide a point for all pieces to fix onto.

4.2 The Injector

Five syringe injectors handle nutrient injection. These are powered by a linear slide assembly, driven by a stepper motor, a lead screw, and a lead screw nut. The stepper motor is of NEMA17 size with 200 steps/revolution. This rotational motion is translated to a linear motion utilizing a Tr8x8(P2) ACME threaded lead screw of 8mm diameter in conjunction with a lead screw nut. It is possible to calculate the required amount of steps per unit distance according to the below equation 4.1 where $V$ refers to the
volume per step in microliters, $M$ is the microstep factor, and $N$ is the total number of steps, $D$ is the syringe diameter in cm, and $p$ is the pitch in mm/revolution:

$$\Delta V = \frac{\pi p D^2}{8M} * N \quad (4.1)$$

With no microstepping, each step with this motor translates into 25 steps per millimeter traveled. Given that the syringe has a known diameter, it is then possible to calculate the volume delivered per step. The following table 4.2 indicates the entire bill of materials needed to build five injectors:

<table>
<thead>
<tr>
<th>Description</th>
<th>Part Number</th>
<th>Material</th>
<th>Source</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
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<td>Carriage Plate</td>
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<td>Anodized Aluminum</td>
<td>Inventables</td>
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</tr>
<tr>
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<td>Alloy Steel</td>
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<tr>
<td>Dual Bearing V-Wheel Kit</td>
<td>25203-02</td>
<td>(KIT)</td>
<td>Inventables</td>
<td>20</td>
</tr>
<tr>
<td>Lead Screw Nut (ACME)</td>
<td>Tr8*8(p2) Metric Acme</td>
<td>Delrin</td>
<td>Openbuilds</td>
<td>5</td>
</tr>
<tr>
<td>M5 Nut</td>
<td>90591A146</td>
<td>Alloy Steel</td>
<td>McMaster</td>
<td>10</td>
</tr>
<tr>
<td>M5 Locknut</td>
<td>90576A104</td>
<td>Alloy Steel</td>
<td>McMaster</td>
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<tr>
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<td>91239A232</td>
<td>Alloy Steel</td>
<td>McMaster</td>
<td>30</td>
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<tr>
<td>M5 Washer</td>
<td>91166A240</td>
<td>Class 4 Steel</td>
<td>McMaster</td>
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<tr>
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<td>91166A240</td>
<td>Aluminum</td>
<td>McMaster</td>
<td>10</td>
</tr>
<tr>
<td>Item Description</td>
<td>Part Number</td>
<td>Material</td>
<td>Supplier</td>
<td>Quantity</td>
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<tr>
<td>----------------------------------------</td>
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<td>-------------------</td>
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<td>Aluminum</td>
<td>McMaster</td>
<td>5</td>
</tr>
<tr>
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<td>Inventables</td>
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</tr>
<tr>
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<td>Aluminum</td>
<td>Inventables</td>
<td>15</td>
</tr>
<tr>
<td>Shim Washer (M5). 1.5mm</td>
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<td>Stainless Steel</td>
<td>McMaster</td>
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</tr>
<tr>
<td>608ZZ Flanged Bearing</td>
<td>30169-01</td>
<td>Alloy Steel</td>
<td>Inventables</td>
<td>5</td>
</tr>
<tr>
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<td>93657A700</td>
<td>Nylon</td>
<td>McMaster</td>
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<td>M3 Socket Cap Screw, 10mm</td>
<td>91290A115</td>
<td>12.9 Alloy Steel</td>
<td>McMaster</td>
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<td>Aluminum</td>
<td>Inventables</td>
<td>5</td>
</tr>
<tr>
<td>M3 Washer</td>
<td>93475A210</td>
<td>18-8 Stainless</td>
<td>McMaster</td>
<td>15</td>
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<td>30158-01</td>
<td>303 Stainless</td>
<td>Inventables</td>
<td>10</td>
</tr>
<tr>
<td>Shim Washer (M3). 1.5mm</td>
<td>98089A101</td>
<td>Stainless Steel</td>
<td>McMaster</td>
<td>15</td>
</tr>
<tr>
<td>M3 spacer. 6mm</td>
<td>93657A708</td>
<td>Nylon</td>
<td>McMaster</td>
<td>15</td>
</tr>
<tr>
<td>Syringe Holder</td>
<td>Custom</td>
<td>General Purpose</td>
<td>---</td>
<td>5</td>
</tr>
</tbody>
</table>
The parts to the Bill of Materials are shown assembled in the below Figure 4.2.

**Figure 4.2: Assembled Linear Slide.** Lead screw nut that fixes each linear slide is not included on this rendering. The lead screw nut threads into the ACME lead screw, and is attached to the carriage plate. The carriage plate is fixed to the frame shown in Figure 1.

Each of the five injectors is assembled in the exact same manner. The syringe is fixed to a custom fabricated plate (not shown), which attaches to the end opposite that of the stepper motor. Backlash is negligible here as the syringe only injects in one direction, but if necessary, anti-backlash nuts can be fixed to the lead screw nut alleviating this potential issue.
4.3 The Circuit

The analog signal being received from the ion-selective electrodes must first undergo conditioning before it is ready to be processed by the digital processor. Each signal first is amplified using instrumentation amplifiers due to the high input impedance from each electrode. The instrumentation amplifier used here is the INA116P, which has an extremely high input impedance range, which minimizes any error caused from the impedance of the electrodes. A resistor is used to set the amplification gain, and follows the amplification formula of the INA116P where $G$ is the gain, and $R_G$ is the size of the gain resistor in ohms:

$$G = 1 + \frac{50k\Omega}{R_G} \quad (4.2)$$

A 3300kΩ resistor is used, and the resulting amplification is 16.15 times. This gain is needed in order to make processing of the low voltage analog signal easier, as well as increase the precision of the measurement. Following amplification, an operational amplifier filters the signal since analog signals need to be bandlimited to the Nyquist frequency before sampling. To keep this output voltage value stable, hardware filtering is employed via an operational amplifier in a Sallen-Key filter topology. This topology (Figure 4.3) is in a lowpass configuration, with high frequency signals filtered out. Electrodes and chemical concentrations are typically low frequency signals, so a cutoff frequency of 0.6 Hz is employed (87). This indicates that frequencies above 0.6Hz are
filtered out by the operational amplifier in this type of configuration. The figure below shows the generic configuration of a Sallen-Key filter in lowpass configuration:

![Sallen-Key Filter Diagram](image)

**Figure 4.3: Low-Pass Filter in Sallen-Key configuration.** The ratio of \( R_1/R_2 \) to \( C_1/C_2 \) determines the filtering voltage (88).

The generic equation for this type of circuit is described with the \( Q \), the quality factor, the angular frequency \( \omega \), and the attenuation \( \alpha \):

\[
Q = \frac{\omega}{2\alpha} = \frac{\sqrt{R_1R_2C_1C_2}}{C_2(R_1+R_2)} \quad (4.3)
\]

The quality factor chosen was 0.5, and the cutoff frequency was selected as 0.6Hz. Resistors \( R_1 \) and \( R_2 \) were calculated to be 2.6M Ohms, while \( C_1 \) and \( C_2 \) were found to be 0.1uF. This configuration of Sallen-Key filter attenuates 40 dB/decade above the cutoff of 0.6Hz, and thus 60Hz electromagnetic interference (EMI) is suppressed by a factor of 1:10000.

Following the filtering process, the signal is then sent through analog-to-digital conversion (ADC) through the MCP3008, before finally being transmitted to the Raspberry Pi via the SPI protocol. This ADC has 10-bit precision and operates off a
+5V supply, and utilizes a +5V reference signal. The conversion time of the ADC is up to ten cycles. Given that the software samples the SPI clock at a speed of 500,000 Hz, the conversion time is at most $2.0 \times 10^{-5}$ seconds. The accuracy of this ADC is measured by a unit called the least-significant bit (LSB); in the case of the MCP3008, an error of one LSB is $1/1024$ of the full signal range, or about 0.1%. This translates to an error of 0.284 ppm. The software running on the Raspberry Pi does the ppm comparisons, and if needed, calculates the amount of volume to deliver back to the reservoir. This volume is converted to steps (Equation 4.1), which then is transmitted to the stepper motor drivers via the I2C protocol. The stepper motor moves the prescribed amount of steps, and delivers the needed volume into the tank.

Major components, IC’s, connectors, drivers, the power supply, and headers are shown the Table 4.3 below. Other components such as capacitors and resistors are shown in the Appendix.
<table>
<thead>
<tr>
<th>Description</th>
<th>Part Number</th>
<th>Source</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNC Jacks</td>
<td>227161-3</td>
<td>Jameco</td>
<td>4</td>
</tr>
<tr>
<td>Instrumentation Amplifier (INA116P)</td>
<td>INA116P-ND</td>
<td>Digikey</td>
<td>4</td>
</tr>
<tr>
<td>Quad opamp (TL074)</td>
<td>TL074-BCN</td>
<td>Digikey</td>
<td>1</td>
</tr>
<tr>
<td>Molex Connector</td>
<td>11297</td>
<td>Sparkfun</td>
<td>2</td>
</tr>
<tr>
<td>ADC (MCP3008, 10bit)</td>
<td>MCP3008-FP-ND</td>
<td>Digikey</td>
<td>1</td>
</tr>
<tr>
<td>Raspberry Pi header</td>
<td>11490</td>
<td>Sparkfun</td>
<td>1</td>
</tr>
<tr>
<td>Step Motor Female Header</td>
<td>1017</td>
<td>Pololu</td>
<td>10</td>
</tr>
<tr>
<td>Step Motor Connection (header)</td>
<td>8231</td>
<td>Sparkfun</td>
<td>5</td>
</tr>
<tr>
<td>Step Motor (housing)</td>
<td>8097</td>
<td>Sparkfun</td>
<td>5</td>
</tr>
<tr>
<td>Step motor crimp pins</td>
<td>8100</td>
<td>Sparkfun</td>
<td>1</td>
</tr>
<tr>
<td>Optical interrupt (housing)</td>
<td>8096</td>
<td>Sparkfun</td>
<td>5</td>
</tr>
<tr>
<td>Optical interrupt (header)</td>
<td>8232</td>
<td>Sparkfun</td>
<td>5</td>
</tr>
<tr>
<td>Schmitt-Trigger (74HC04)</td>
<td>SN74HC04N</td>
<td>Digikey</td>
<td>1</td>
</tr>
<tr>
<td>MCP23017</td>
<td>MCP23017-QFN</td>
<td>Digikey</td>
<td>3</td>
</tr>
<tr>
<td>Stepper Motor Driver (DRV8825)</td>
<td>2133</td>
<td>Pololu</td>
<td>5</td>
</tr>
<tr>
<td>5V Reference (LT1021)</td>
<td>LT1021-BCN-8-PBF-ND</td>
<td>Digikey</td>
<td>1</td>
</tr>
<tr>
<td>Power Supply (+5V, +15V, GND, -5V)</td>
<td>MAP80-4003</td>
<td>Power-One</td>
<td>1</td>
</tr>
</tbody>
</table>
Schematics for this circuit board are shown in the Appendix. A photo of the final assembled control board is shown in Figure 4.4:

![Assembled circuit board](image)

**Figure 4.4: Assembled circuit board. BNC connectors in the foreground attach to ISE's.**

Power to the circuit is provided by a switched-mode power supply operating at +15V, +5V, and -5V. The +15V is given to the stepper motor drivers as well as the +5V reference chip. The +5V and -5V are given to the instrumentation amplifiers. Lastly, +5V only is given to the operational amplifier, the ADC, and the Schmitt trigger. To provide contamination of the analog signal, ground planes are separated very cleanly. Three distinct ground planes exist on this board, with motor ground, digital ground, and analog ground all kept separate, and tied together only at a single point at the power supply. If the grounds are not kept separate, interference from the other
power sources can leak through into the analog section, which contaminates the signal leading to the instrumentation amplifiers.

4.4 The Sensors

Epoxy bodied, potentiometric, ion-selective electrodes are utilized featuring double junctions for long-term monitoring. Unique to this electrode choice is the fact the outer membrane is user replaceable. This should serve to extend the overall lifespan of the sensor. Calibration solutions are made with serial dilutions of known standards are also important in order to give the sensor a proper calibration. Sensors utilized in this project include those described in Table 4.4:
Calibration of the sensors is mostly automated. The user dips each electrode into two solutions, a 1000ppm calibration standard, and a serial dilution of the 1000ppm standard. Thus, each voltage reading is correlated with a known ppm reading. A log transformation of ppm is performed, and plotted against the voltage data, a linear slope results. The calibration script produces a slope, and a y-intercept that describe the characteristics of the electrode response. With this calibration, the software on the Raspberry Pi can convert the electrode voltage, into a corresponding concentration.
4.5 The Control System

The Raspberry Pi communicates with the ADC via SPI, and to the stepper motors via I2C. The incoming data stream from the sensors is converted to a concentration given in ppm. The sensors are sampled with a user defined time limit. The recommended sampling time is 15 minutes to ensure total reservoir uniformity following injection.

There are two setpoints, a high setpoint, and a low setpoint. Once the low setpoint is crossed the Raspberry Pi calculates the necessary volume to add to return the concentration back to the high setpoint, calculates the amount of steps, and sends the signal to the stepper motor. To calculate the necessary volume to add, the following equation is used:

\[ C_1 V_1 + C_2 V_2 = C_3 V_3 \quad (4.4) \]

The only assumption here being that the volume in the reservoir does not change with nutrient depletion. This is possible using a float valve to add in water to compensate for water usage. \( C_1 \) describes the concentration in the reservoir; \( V_1 \) describes the volume in the reservoir. \( C_2 \) is the stock solution concentration, and \( V_2 \) is the amount of volume to inject. Lastly, the \( C_3 \) term describes the grower setpoint concentration, while \( V_3 \) describes the final volume. This is given by \( (V_1 + V_2) \). To determine the injection volume, the Control System solves for the \( V_2 \) term. The nitrate stock solution is provided by a three molar solution of ammonium nitrate.
The height of the cylinder corresponds to the distance that needs to be traveled, and this distance can be converted to a set of finite steps. With the syringe utilized (2.54cm diameter), the injection volume per step is 20.024 microliters per step. The full range of the 55mL would be covered by 2714 steps.

Once the stepper motor receives the signal via I2C, it rotates that amount of steps, which drives the linear syringe injector. Upon reaching the end of bottom, the linear syringe injector backs up until reaching the optical end stop. This stop is placed such that each syringe holds approximately 55mL’s of solution. Another method of doing this is simply counting the steps. As stepper motors do not lose steps unless an error occurs, it is possible to back up 2714 steps once the bottom is reached. The system detects reaching the body as each injection decrements from the counter. Although capabilities of the optical end switch are on the circuit board, the current iteration of the control system code (found in the Appendix) utilizes step counting in order to know when the bottom of the syringe is reached.

4.6 Validation

Prior to the measurement of the amplified electrode response, it is necessary to ensure that each amplifier is functioning correctly. To test proper performance of each amplifier, a 9V battery device was created with a 1MΩhm impedance, and output for four voltages. The schematic for this device is found in the Appendix. A switch changes
the output voltage by changing the strength of the resistors in parallel. These resistors form a voltage divider with the 9V source, and allows the output to be varied. The raw output of this battery device is 0.141V, 0.0257V, 0.0451V, and 0.0184V.

Initial validation is in a controlled setting with a reservoir simulated by a five-gallon bucket. For initial testing purposes, three ion sensors will be utilized, NO$_3^-$, K$^+$, and Ca$^{2+}$. The correction for the pH will be done manually. The nutrient concentration in this bucket is similar to that of found in a true nutrient reservoir. The control system gathers the initial data, and once three data points are collected, the user moves the sensors to a depleted nutrient solution bucket. The depleted nutrient reservoir simulates levels found at the growers low setpoint. Once the system detects that the values are below the low setpoint, the injection system corrects for the deficiency by injecting a high value stock solution, and returns the system back to the grower high setpoint.

However, ultimate validation of the system involves testing the injection system in a dynamic setting. A crop will be grown in a hydroponic system, and slowly deplete the nutrients over the course of the week. The injection system will attempt to correct for this dynamic depletion by detecting once nutrient concentration falls below the low setpoint, and like the initial bucket testing, will inject a stock nutrient concentration to return the reservoir over the high setpoint. After a certain recirculation period, the
system will sample the reservoir again. The water level is topped off each day with fresh water to ensure that the volume stays constant over the course of the grow period.

The growers high setpoint is far below the initial reservoir concentration. Due to temporal depletion of nutrients, and the plant depleting both nitrate and potassium quickly, maintaining the initial reservoir concentration would result in nitrate or potassium toxicity due to the over addition of nutrients. Thus, the grower high setpoint is maintained at 75 ppm for nitrate, 45 ppm for potassium, and 50 ppm for calcium. The plant is allowed to naturally deplete these nutrients until the grower low setpoint. In the bucket, experiment, the low setpoint was chosen to be 20 ppm for nitrate, 25 ppm for potassium, and 20 ppm for calcium. In the dynamic experiment, the low setpoint was chosen to be 10 ppm for nitrate, 10 ppm for potassium, and 15 ppm for calcium.

An oscilloscope is used to verify the integrity of incoming signal, and ensure that the signal is free from outside influences. Without proper grounding, external frequencies may leak into the analog signal, which renders the electrodes prone to external interferences. The response of the electrode is verified for both the raw reading, and post amplified readings. The raw electrode readings are verified by an oscilloscope, while the amplified values are read from the output of the ADC.
The assembled control system is found in the below Figure 4.5:

![Control System Image](image)

**Figure 4.5:** Fully assembled control system. Each stepper motor corresponds to a strong stock solution concentration. A hose links the stock solution with the nutrient reservoir. The grey box holds the control circuitry as well as the Raspberry Pi controller.

### 4.7 The Test Bed

To test the performance of the control system on a dynamically depleted reservoir, the injection system was tested in an Ein-Gedi system. A heat resistant lettuce cultivar (Adriana, green butterhead) was placed into this recirculating hydroponic system. This cultivar has a about a four week maturing period. This system is the General
Hydroponics, AeroFlo2-60 site. Lettuce was started in plugs, and when roots began to poke out (about two weeks), the lettuce was transplanted into the netpots. Clay hydroton rocks were placed into coco-coir netpot liners. The plug was placed on top of the rocks, and the gaps filled in also by hydroton rocks. Water level was adjusted in each trough such that the stream was just below each netpot. The table below (Table 4.5) shows the weekly nutrient strength, and total PPM of the reservoir.

<table>
<thead>
<tr>
<th>Week</th>
<th>FloraGro</th>
<th>FloraMicro</th>
<th>FloraBloom</th>
<th>Total PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2 tsp/gal</td>
<td>1/2 tsp/gal</td>
<td>1/2 tsp/gal</td>
<td>194</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>387</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>508</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>628</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>779</td>
</tr>
</tbody>
</table>

The pH range is maintained manually between 5.5–6.5 throughout the entire course of the grow.
CHAPTER 5: RESULTS

To test this system, only nitrate, potassium, and calcium are selected to ensure proper system response. Calibrations were done in the fertilizer test solution, as competing ions change the overall response of the sensor. The strength of this fertilizer solution are serial dilutions made from one mL each of Flora Micro, Grow, and Bloom dissolved in 500mL of tap water. The specific PPM for each ion can be found using the General Hydroponic PPM calculator designed for the Flora Series. Calibrations in pure ionic solutions are different than that of calibrations in fertilizer solution, so only fertilizer calibrations are shown. Comparison of nitrate voltage at 10ppm in pure ionic solution versus nitrate voltage in fertilizer solution at 10ppm yields approximately a 1.5V difference. Raw voltage data for the three electrodes in fertilizer are shown in the figures below (Figure 5.1, 5.2, and 5.3). All are measured with an oscilloscope. Due to each electrode having input impedance of approximately 2 MΩ (discussed at length further in this chapter), the 1 MΩ impedance of the oscilloscope introduces an error of approximately 33% as the probe forms a voltage divider with the electrode itself. The response of each electrode follows modified equation 3.2 where $E$ is the electrode voltage, $E^\ominus$ is the y-intercept, $c$ is the slope where $c = RT/zF$, and the ion
concentration is given by [X]. The \( c \) term reduces to 0.05916V at room temperature, and when the natural log is converted into a common log.

\[
E_{\text{cell}} = E_{\text{cell}}^\oplus - \frac{0.05916V}{z} \log [X] \quad (5.1)
\]

The sign of the slope term \( c \) is influenced by the \( z \) variable, the number of moles of electrons transferred in the half-cell reaction. This value is determined by the charge of the ion to be measured. Slope of the nitrate and potassium ion are equal, but opposite in charge as both ions carry only a single unit charge. The slope of the calcium ion is half that of the potassium ion, but still positive, as the calcium ion carries two units of charge, and the ion is positively charged.

![Response of Nitrate Electrode](image)

**Figure 5.1**: Raw voltage data for the nitrate ion. Voltage is plotted against log ppm. An extended calibration solution is used to probe the entirety of the response.
A similar response is shown for the potassium ion. The slope goes the opposite way as nitrate due to potassium carrying a positive charge, and nitrate carrying a negative charge.

![Response of Potassium Electrode](image)

**Figure 5.2**: Raw voltage data for the potassium ion. Voltage is plotted against log ppm. An extended calibration solution is used to probe the entirety of the response.

The response of the calcium electrode matches that of the potassium electrode, and similarly, shows a positive slope response. Calcium is positively charged, similar to potassium, which is why the slope response is similar. At lower ppm’s, the log-linear relationship of the calcium breaks down, and data below 15 ppm is untrustworthy. This is confirmed by the amplified response curve, which shows that calcium has an approximately correct slope above the 15 ppm limit. Thus, calcium measurements above 15 ppm are still trustworthy, but measurements below 15 ppm are to be regarded with suspicion.
Figure 5.3: Raw voltage data for the calcium ion. Voltage is plotted against log ppm. An extended calibration solution is used to probe the entirety of the response. The calcium response starts breaking down at approximately the equivalent to 15ppm, and no longer has a log linear response.

Raw measurement voltages, although showing linear responses for nitrate, and potassium, as well as linear responses for calcium in a defined range, do not agree with the Nernst equation slopes. One reason for this could be the fact that the oscilloscope probe is both voltage, and current limited. The effect changes from one to another as the voltage increases. However, with the low raw voltages recorded, the slope could be influenced. With a high impedance amplifier however, the current limit no longer plays a role, and the correct slope should be recorded there.

The following data is the performance of each amplification channel using the battery device described in Chapter 4.6. Nitrate occupies channel 0, potassium channel 1, and calcium channel 2. Expected voltage is calculated by dividing the amplified voltage by

\[
y = 0.0081x - 0.0452 \\
R^2 = 0.5929
\]
voltage, with the expected gain of 16.15x. The tables below (Table 5.1, 5.2, and 5.3) show the amplifier performance of each channel.

**Table 5.1: Amplifier performance of the INA116P for channel 0**

<table>
<thead>
<tr>
<th>Switch Status</th>
<th>Raw (V)</th>
<th>Amplified (V)</th>
<th>Calculated Gain</th>
<th>Expected Voltage</th>
<th>Percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Both off</td>
<td>0.141</td>
<td>2.37</td>
<td>16.8</td>
<td>0.146</td>
<td>0.0374</td>
</tr>
<tr>
<td>1 on</td>
<td>0.0257</td>
<td>0.444</td>
<td>17.3</td>
<td>0.0275</td>
<td>0.0668</td>
</tr>
<tr>
<td>2 on</td>
<td>0.0451</td>
<td>0.758</td>
<td>16.8</td>
<td>0.0469</td>
<td>0.0386</td>
</tr>
<tr>
<td>Both on</td>
<td>0.0184</td>
<td>0.323</td>
<td>17.5</td>
<td>0.0200</td>
<td>0.0788</td>
</tr>
</tbody>
</table>

**Table 5.2: Amplifier performance of the INA116P for channel 1**

<table>
<thead>
<tr>
<th>Switch Status</th>
<th>Raw (V)</th>
<th>Amplified (V)</th>
<th>Calculated Gain</th>
<th>Expected Voltage</th>
<th>Percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Both off</td>
<td>0.141</td>
<td>2.39</td>
<td>16.9</td>
<td>0.148</td>
<td>0.0472</td>
</tr>
<tr>
<td>1 on</td>
<td>0.0257</td>
<td>0.455</td>
<td>17.7</td>
<td>0.0281</td>
<td>0.0869</td>
</tr>
<tr>
<td>2 on</td>
<td>0.0451</td>
<td>0.767</td>
<td>17.0</td>
<td>0.0475</td>
<td>0.0508</td>
</tr>
<tr>
<td>Both on</td>
<td>0.0184</td>
<td>0.332</td>
<td>18.0</td>
<td>0.0206</td>
<td>0.106</td>
</tr>
</tbody>
</table>

**Table 5.3: Amplifier performance of the INA116P for channel 2**

<table>
<thead>
<tr>
<th>Switch Status</th>
<th>Raw (V)</th>
<th>Amplified (V)</th>
<th>Calculated Gain</th>
<th>Expected Voltage</th>
<th>Percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Both off</td>
<td>0.141</td>
<td>2.37</td>
<td>16.8</td>
<td>0.147</td>
<td>0.0402</td>
</tr>
<tr>
<td>1 on</td>
<td>0.0257</td>
<td>0.451</td>
<td>17.6</td>
<td>0.0279</td>
<td>0.0801</td>
</tr>
<tr>
<td>2 on</td>
<td>0.0451</td>
<td>0.755</td>
<td>16.7</td>
<td>0.0467</td>
<td>0.0352</td>
</tr>
<tr>
<td>Both on</td>
<td>0.0184</td>
<td>0.330</td>
<td>17.9</td>
<td>0.0204</td>
<td>0.0991</td>
</tr>
</tbody>
</table>

The response of each amplifier channel shows that higher input voltages shows lower percentage error. The percentage error of the channels ranges from 3.5% (channel 2, switch 2 on) to 10.6% (channel 1, both on). In order for easier analysis of the voltage signal, each input voltage to the channels is amplified before processing by the
Raspberry Pi. Impedance of each electrode was measured by adding a resistor between the input pins, and varying the strength of this resistor. With several resistors, it is possible to correlate the resistor strength, with the measured voltage. This has the effect of forming a voltage divider with the inherent impedance of the electrode. Thus, the measured voltage of each electrode is given by the following formula:

\[
V_{\text{measured}} = V_{\text{output}} \cdot g \cdot \frac{R_x}{(R_x+Z)} \quad (5.2)
\]

Where \(V_{\text{measured}}\) is the measured voltage post-amplification, \(V_{\text{output}}\) is the theoretical potential of the electrode as described in equation 5.1, \(g\) is the amplification of the INA116P, \(R_x\) is the resistor that is varied, and \(Z\) is the inherent impedance of the electrode. The unknowns of this equation are \(V_{\text{output}}\) and the impedance of the electrode \(Z\). It is possible to solve for both the combined \(g \cdot V_{\text{output}}\) term and the unknown impedance \(Z\) by utilizing a nonlinear regression model. These two variables act like the regression coefficients. Once the best fit curve line for the nonlinear regression is found, these coefficients can then be related to the theoretical potential of the electrode, and the impedance of the electrode. The below figure 5.4 shows the response of measured voltage against resistor size for the nitrate electrode:
Figure 5.4: Measured voltage plotted against the size of the resistor between the electrode inputs into the amplifier. Measured voltage goes up as impedance is increased, but once the resistor crosses the electrode impedance, the voltage increase levels off. The impedance $Z$ is 1.7MOhm

The regression line of the nitrate response yields the impedance $Z$, which is shown to be 1.7 MOhms. Similar graphs are shown below in Figure 5.5 and 5.6 for potassium and calcium respectively, with the same approach a nonlinear fit to solve for combined term $g^*V_o$ and the impedance, $Z$. 

\[ V_{\text{meas}} = 1.78192 \times \left( \frac{R_x}{1.65505 + R_x} \right) \]
Figure 5.5: Measured voltage plotted against the size of the resistor between the electrode inputs into the amplifier. Measured voltage goes up as impedance is increased, but once the resistor crosses the electrode impedance, the voltage increase levels off. The impedance is 2.1 MOhm.
Figure 5.6: Measured voltage plotted against the size of the resistor between the electrode inputs into the amplifier. Measured voltage goes up as impedance is increased, but once the resistor crosses the electrode impedance, the voltage increase levels off. The impedance is 1.9Mohm.

The input impedance of the amplifier used is $10^{15}$ (89). This is significantly different from the measured impedances of the electrodes. Thus, the measurement error from the amplification is minimal, as the input impedance of the amplifier is several orders of magnitude higher than that of the electrodes. The figures below show the post-amplification voltages of nitrate (figure 5.7), potassium (figure 5.8), and calcium (figure 5.9) correlated with log ppm.
Figure 5.7: Amplified nitrate response. Nitrate is attached to the channel 0 amplifier, and undergoes an amplification of 16.15x. A four point calibration solution is utilized to create this curve. A high $R^2$ value indicates the response of the curve is log-linear.

The raw data for the above nitrate curve is shown below table 5.4:

Table 5.4: Raw data for the amplified nitrate electrode.

<table>
<thead>
<tr>
<th>Nitrate</th>
<th>LOG PPM</th>
<th>Amplified Voltage (V)</th>
<th>Raw Voltage (V)</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>132</td>
<td>2.12</td>
<td>1.79</td>
<td>0.111</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>1.81</td>
<td>2.04</td>
<td>0.127</td>
<td>-0.0501</td>
</tr>
<tr>
<td>13.2</td>
<td>1.12</td>
<td>2.63</td>
<td>0.163</td>
<td>-0.0521</td>
</tr>
<tr>
<td>1.32</td>
<td>0.121</td>
<td>3.13</td>
<td>0.194</td>
<td>-0.0309</td>
</tr>
</tbody>
</table>

The slope of this electrode between 132 and 13.2 ppm is within the manufacturer specification of 51-59mV per order of magnitude from 100-10 ppm. The slope between
13.2 and 1.32 is lower, as electrode response changes drastically once lower concentration regimes are probed. For more accurate calibration curves, values below 10ppm should not be included in the calibration curve. If it is required to probe below 10ppm, separate calibration standards and curves should be made for a more accurate response.

Figure 5.8: Amplified potassium response. Potassium is attached to the channel 1 amplifier, and undergoes an amplification of 16.15x. A four point calibration solution is utilized to create this curve. A high $R^2$ value indicates the response of the curve is log-linear.

The raw data for the above potassium electrode is shown in table 5.5:
Table 5.5: Raw data for the amplified potassium electrode

<table>
<thead>
<tr>
<th>Potassium PPM</th>
<th>LOG PPM</th>
<th>Amplified Voltage (V)</th>
<th>Raw Voltage (V)</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>2.28</td>
<td>0.645</td>
<td>0.0399</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>1.98</td>
<td>0.924</td>
<td>0.0572</td>
<td>0.0573</td>
</tr>
<tr>
<td>19</td>
<td>1.28</td>
<td>1.51</td>
<td>0.0935</td>
<td>0.0536</td>
</tr>
<tr>
<td>1.9</td>
<td>0.279</td>
<td>2.04</td>
<td>0.126</td>
<td>0.0327</td>
</tr>
</tbody>
</table>

The slope between 95 and 19 ppm follows manufacturer specifications of between 51-59 mV between 100 and 10 ppm. From 19 to 1.9 ppm, the slope changes drastically as the electrode probes low concentration values. Thus, to probe low concentrations below 100 ppm, new sets of calibration values are needed. For more accurate calibration results for concentrations above 10 ppm, concentration values below 10 ppm should not be included. The direction of the slope is reversed from the raw values due to the ADC only having a positive supply. Thus, the inputs for the potassium electrode are reversed in order for output of the voltage to be positive.
Figure 5.9: Amplified calcium response. Calcium is attached to the channel 2 amplifier, and undergoes an amplification of 16.15x. A four-point calibration solution is utilized to create this curve. Similar to the raw voltage response of calcium, below 10 ppm, the response of the calcium electrode is reversed.

Table 5.6 shows the raw data for the amplified calcium electrode:

<table>
<thead>
<tr>
<th>Calcium PPM</th>
<th>LOG PPM</th>
<th>Amplified Voltage (V)</th>
<th>Raw Voltage (V)</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>2.01</td>
<td>0.435</td>
<td>0.0269</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>1.71</td>
<td>0.582</td>
<td>0.0360</td>
<td>0.0302</td>
</tr>
<tr>
<td>10.2</td>
<td>1.01</td>
<td>0.752</td>
<td>0.0466</td>
<td>0.0197</td>
</tr>
<tr>
<td>1.02</td>
<td>0.00860</td>
<td>0.650</td>
<td>0.0403</td>
<td>0.00635</td>
</tr>
</tbody>
</table>

Slope requirements from the manufacturer between 100 and 10 ppm are at 24-29mV; though the slope is out of range, the electrode response between 102 and 10.2 ppm is still linear. As with the raw data measurements, the electrode response below 10ppm is poor. The curve is mirrored as the inputs leading to the amplifiers were reversed in order to measure only a positive signal for the ADC conversion. Due to the poor
response at the bottom of the measurement range, a more detailed calibration is shown in figure 5.10 and was created with multiple calibration solutions between 102 and 10.2 ppm.

![Calcium Response (Amplified)](image)

**Figure 5.10**: Electrode response of the calcium electrode in calibration solutions ranging from 102 ppm to 10.2 ppm. Response of the calcium electrode below 10ppm was demonstrated to be poor in both the raw voltage measurement, as well as the amplified measurement. Thus, to probe a more accurate response of the calcium electrode, only the ppm range between 100 and 10 is considered.

The raw data and the concentrations of the calibration solutions used is shown in the below table:

**Table 5.7: Raw data for the amplified calcium electrode between 102 and 10.2 ppm**

<table>
<thead>
<tr>
<th>Calcium PPM</th>
<th>LOG PPM</th>
<th>Amplified Voltage (V)</th>
<th>Raw Voltage (V)</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>2.01</td>
<td>0.391</td>
<td>0.0242</td>
<td></td>
</tr>
<tr>
<td>76.5</td>
<td>1.88</td>
<td>0.440</td>
<td>0.0272</td>
<td>0.0242</td>
</tr>
<tr>
<td>51</td>
<td>1.71</td>
<td>0.493</td>
<td>0.0306</td>
<td>0.0189</td>
</tr>
<tr>
<td>25.5</td>
<td>1.41</td>
<td>0.601</td>
<td>0.0372</td>
<td>0.0221</td>
</tr>
<tr>
<td>10.2</td>
<td>1.01</td>
<td>0.684</td>
<td>0.0423</td>
<td>0.0129</td>
</tr>
</tbody>
</table>
Response of the calcium electrode between 102 and 10.2 is very linear, though the slope is below manufacturer specification. Despite this, it is still possible to make measurements with this electrode due to the very good linear response. It is also visible from the slopes that between 25.5 and 10.2, the response is beginning to flatten out. As can be seen from the previous figures of the calcium electrodes, the slope below 10.2 ppm is very poor. Thus, the functional minimum of the calcium electrode is approximately 15ppm.

The effect of temperature of the amplifier on electrode response was also probed. Measurements were taken with an infrared thermometer with an accuracy of ±2%. An electric hairdryer was used to heat up the amplifier, while temperature data was logged in conjunction with voltage. Figure 5.11 below shows the effect of temperature on the channel 0 amplifier. Although tests were not done for the channel 1 or 2 amplifier, the amplifier performance is the same as can be seen from tables 10, 11, and 12, and thus it is expected that the other two amplifier will show similar responses to increasing temperature.
Figure 5.11: Response of the INA116P amplifier to changing temperature. Nominal amplification is 16.15x. Heat was applied through a hairdryer, and measured by a infrared thermometer with ±2% error.

Voltage response of the electrode increases with increasing temperature, but over the range of the entire temperature response, the voltage response changes from only 0.02V, which translates to a difference of approximately 6ppm.

Prior to testing the injection system in a dynamic system, the injection system was tested in a five-gallon bucket to ensure that the stepper motors and overall algorithm were working. Each electrode was placed into a stock solution, consisting of 2 mL of FloraBloom, FloraGro, and FloraMicro dissolved into one liter of tap water. This yields a guaranteed analysis of 132ppm nitrate, 190 ppm potassium, and 102 ppm calcium. Following this immersion in this solution for three minutes to collect a baseline, each electrode is then immersed into a depleted nutrient solution, made by forming a 10% dilution with the stock solution. Correction was done by the stepper
motor injection back to above the grower setpoint. Potassium and calcium are injected first, in which a delay of one and half minutes is introduced. This is because the potassium stock solution also contains nitrate, and this delay is needed for the nitrate sensor to properly detect the nitrate added to the solution. Once the grower high setpoint is reached, injection stops and the system is considered to have reached its target. Calculation of injection volume is based on equation 4.4. The below figure shows correction for the nitrate ion:

![Nitrate Bucket Correction](image)

**Figure 5.12: Correction of the nitrate ion in a fixed volume.** Initial setpoint of nitrate was 128 PPM in the stock solution bucket. The depleted solution bucket was calculated to be approximately 17 ppm. Grower high setpoint was set to be 75, while the low setpoint was set to be 20. Injection of potassium added in nitrate as well, and initially raised nitrate levels to 45, before the dedicated nitrate injection took place. Once the grower high setpoint was reached, injection concluded. Stock solution for the nitrate ion is a 3M solution of ammonium nitrate.
Nitrate bucket correction showed that it took roughly 30 minutes to reach its final setpoint. The length of time was due to the placement of the syringe. The syringe holder was askew from the linear axis of the injector. This meant that each injection actually puts fewer ions into the solution than the calculated amount. Each subsequent injection calculation pushed the ppm closer to the grower high setpoint, but since none of the injections were full, the nitrate response exhibited an exponential decay model. This was fixed prior to dynamic injection by realigning the syringe holder to be in the same linear axis as the injector. The correction for potassium is shown below:

![Potassium Bucket Correction](image)

**Figure 5.13:** Correction of the potassium ion in a fixed volume. Initial bucket was calculated to be 187ppm in the stock solution. The depleted solution bucket was calculated to be 24ppm. Grower high setpoint was set to be 45 ppm, while the low setpoint was set to be 10ppm. Stock solution for the potassium ion is a 1.75M solution of potassium nitrate. Due to injection of potassium also adding nitrate, potassium injection is first, followed by a nitrate. Once the high grower setpoint is reached, injection is concluded. Potassium injection occurred at $t=395$ seconds.
The potassium injection did not show the exponential decay characteristics of the nitrate injection due to proper alignment of the syringe holder. The injection only occurred once at \( t=395 \) seconds, and this one injection was all that was needed to return the concentration to the grower high setpoint. Correction for the calcium ion is shown in the figure below:

![Calcium Bucket Correction](image)

**Figure 5.14:** Correction of the calcium ion in a fixed volume. Initial calcium concentration in the stock solution bucket was calculated to be 101 ppm. Once the electrode was placed in the depleted solution bucket, the calculated concentration was 14 ppm. Grower high setpoint was set to be 50 ppm, while grower low setpoint was set at 10 ppm. Stock solution for the calcium ion was a 0.06M solution of monobasic calcium phosphate. This solution is low molarity due to the low solubility of calcium phosphate in water. Calcium injection follows potassium injection and occurred at \( t=395 \) seconds.

Calcium injection takes place directly following potassium injection, and occurred also at \( t=395 \) seconds after the sensors were immersed into the depleted solution. In all subsequent injections, the stock solution was replaced to calcium nitrate due to the
increased solubility of the salt versus calcium phosphate. The higher solubility allows for
stronger stock solutions to be made, which in turn reduces the number of steps required
for the stepper motor to return the setpoint back to the grower high point.

Following successful injection in a controlled bucket, the sensors were placed into
a dynamic system for 24 hour logging to test the response of the sensors in a dynamic
system. Data logging from this dynamic system occurred in the week 2 nutrient solution
strength as found in table 4.4. The results of this dynamic logging experiment are shown
in Figure 5.15:

![Data Logging of Three Sensors in Hydroponic Solutions](image)

**Figure 5.15:** Logging of three sensors immersed into a hydroponic solution over a 24
hour period. Only data is logged, and no injection is taking place. Data is logged
every 15 minutes.

There is significant variation in this data over the 24 hours, especially during the night
hours. Another logging experiment was setup with sensors immersed into a stock
solution, and concentration was logged for a period of 18 hours. Stock solution logging is shown in Figure 5.16 below:

![Data Logging of Three Sensors in a Stock Solution](image)

**Figure 5.16**: Logging of three sensors immersed into a hydroponic stock solution over a 20 hour period. Only data is being logged, no plants are in the system. Data is logged every 15 minutes.

Similar to the dynamic logging, drift is present in all the electrodes. There is a significant increase in potassium concentration in a single fifteen minute period. Attempted efforts at dynamic control yield poor results as well. Due to drift of the sensors, accurate ppm of the reservoirs is not able to be taken. Two representative days are shown in the figures below. Figure 5.17 shows the calculated ppm of the reservoir on Day 5, while Figure 5.18 below shows the attempted monitoring and correction of the system on day 6.
Figure 5.17: Control system attempting nutrient control on Day 5. Data is sampled every 15 minutes. No grower setpoints were exceeded, and no injection took place. Total logging occurred over a 24 hour period.

Figure 5.18: Control system attempting nutrient control on Day 6. Data is sampled every 15 minutes. Calcium exceeded the grower low setpoint of 15 ppm. However, similar to Figure 3.7, this was due to electrode fluctuation. Attempted correction placed over 55 mL’s of a 2M Ca(NO$_3$)$_2$ into the reservoir, without any response from the calcium electrode. This is evident from the nitrate spike, but even that is inaccurate, as there is significant fluctuation during the night periods.
CHAPTER 6: DISCUSSION

6.1 Electrode Calibration Methods

All calibrations of electrode solution were carried out in serial dilutions of the measurement solution. The presence of competing ions changes the impedance of the solution, and the final voltage. Thus, a calibration curve calculated with an electrode in a pure solution with distilled water will yield incorrect concentrations of approximately 100ppm when used in a solution with high amounts of competing ions such as fertilizer solution. This large error makes it imperative for all calibrations to take place in a fertilizer solution. Typically, a calibration solution is calculated from a three point solution formed with a full-strength solution, a 10% dilution, and a 1% dilution. However, due to the changing of the electrode slope at low ppm’s, if the 1% solution is below the 10ppm limit, a different calibration solution is used. In these cases, a 50% solution will be substituted for the 1% calibration solution. In still other cases, especially in low fertilizer level cases immediately following transplant, even a 10% dilution may cause the relevant ions to be lower than the 10ppm limit. For these special instances, a two-point calibration solution is used with the full strength solution, and either a 75% dilution or a 50% dilution. Three point calibrations are needed to verify
the linear response of the electrode for testing purposes, but once the electrode has been
caracterized, it is possible to use a two point calibration solution in field testing to
streamline the calibration process.

The changing slope indicates that the response of the electrode over its entire
measurement range is in fact nonlinear. The calibration is performed in order to get a
piecewise linear approximation, of an otherwise nonlinear electrode response. Between
certain ppm ranges, this piecewise approximation serves as a very good estimate of the
electrodes slope response. However, in still other low ppm ranges, this linear
approximation does not fully capture the nonlinearity of electrode response.

When calibrating in a dynamic reservoir, it is necessary to keep the electrode
stirring at all times. Recirculation ensures that water is constantly moving, and
calibration needs to reflect that as well since electrode voltage in a moving solution
changes the recorded voltage. The difference is approximately 10 ppm or so, but
nonetheless, keeping the electrode stationary will lead to an incorrect calibration curve.
In addition, singular calibration an electrode in its own solution will yield a different
result versus all electrodes calibrated together in the same solution of approximately
hundreds of ppm. The fertilizer solution is highly conductive of charge, and when
electrodes are calibrated together, the conductive fertilizer source essentially acts like a
resistor, and connects the electrodes together.
Thus, for accurate results in calibration, all electrodes must be calibrated in the same nutrient solution, as well as with constant movement to simulate the conditions in the reservoir. Moreover, temperature of the calibration solution should be considered as well. Though the amplifier is resistant to temperature changes, the electrodes are less robust against swings in temperature. An increase of 1° C changes the raw voltage by 1%, which translates to roughly a 10ppm difference per every degree Celsius difference. Thus, it is imperative that calibration solutions be kept at the same temperature, or close to the same temperature as the measurement solution.

**Stock Solutions**

To minimize the amount of steps needed for injection, high concentration stock solutions are utilized. The potassium stock solution is a 1.75M solution of potassium nitrate, while the nitrate solution is a 3M solution of ammonium nitrate. The calcium stock solution used in the bucket experiment was a 0.06M solution of calcium phosphate; however, this has been changed to calcium nitrate. The initial choice of calcium phosphate was to avoid co-injection of nitrate with calcium injection. However, the low solubility of calcium phosphate means it is possible to make a much stronger calcium nitrate solution, than calcium phosphate solution. In all dynamic logging experiments, a 2M solution of calcium nitrate is used. Due to potassium and calcium both injecting nitrate into the system, the nitrate injection is staggered. This means
that the control system first samples the potassium and calcium ions, and if injection is needed, the stepper motors are driven. After 15 minutes in order for complete reservoir mixing, the nitrate ion is sampled, and if still out of range, the control system drives the stepper motor for ammonium nitrate. In this manner, over injection of nitrate is avoided, as both injection of potassium and calcium adds nitrate into the system. The time delay between the potassium/calcium injection and the nitrate injection is user selectable. Fifteen minutes was selected in this case, due to the size of the 40 gallon reservoir, and ensuring complete homogeneity of the nutrient solution post injection. Theoretically the pump used in this system is capable of moving 1268 gallons per hour through a one inch pipe. However, the forcing of the nutrient solution through extremely narrow channels and aeroponic sprayers significantly decreases the fluid moved per hour. In addition, the slope percentage of each gully influences the volume of water being returned to the central reservoir. Due to these variables, the gap between the potassium/calcium injection and the nitrate injection must be calculated empirically. A container was placed below a return gully, and in 30 seconds, approximately filled up to 800 mL’s. There are six return gullies in the system, which translates to approximately 2.3 gallons being returned to the central reservoir in a minute. Over the course of 15 minutes, a total of 38 gallons of fluid are recirculated back to the central reservoir. This indicates that following potassium/calcium injection
approximately 15 minutes are needed to fully homogenize the reservoir, before nitrate sampling can take place. Through this delay, the nitrate added by the potassium and calcium stock solutions can be allowed to fully disperse throughout the system, before an accurate measurement can be taken by the nitrate sensor.

**Bucket Experiment**

Control system performance in the bucket performed quickly in regards to the potassium and calcium electrodes. It is plainly visible that nitrate concentration rose in conjunction with potassium injection, as the stock solution for potassium is $\text{KNO}_3$. Like the dynamic system, potassium and calcium injection occurs together, while the delay for nitrate injection was set to one and half minutes. Homogenizing of the bucket solution following injection was done manually by agitating the bucket solution following injection so the ions can fully homogenize. Calculation of stock solution injection volume was based on equation 4.4, and total injection steps was calculated by equation 4.1. Response of the control system when presented with a depleted solution indicated that the control system functions correctly and returns the solution to the grower setpoint. Realigning the syringe holder with the injector solved the extended injection time of the nitrate ion. The askew angle of the syringe on the system meant that the injection steps of the system were translated to both a vertical, and horizontal component. This introduced an error between the calculated injection volume, and the
actual injection volume. To fix this error, the syringe holder was realigned with the axis of the injection system.

Accurate results in this experiment were due to the relative concentrations of the stock solution, and the depleted bucket are the same. The calibration curves of the electrodes for the bucket were made from a stock solution diluted to two other solutions. The first was solution was 50%, while the second was a 10% dilution of a stock solution. The depleted solution bucket was approximately a 13% dilution of the stock solution; thus, response of the electrodes in that solution exhibited proper characteristics.

**Dynamic Logging**

In Figure 5.15, significant fluctuations of the ppm can be seen. Part of this can be attributed to the temperature difference between the reservoir during the daytime and nighttime periods. A water chiller was installed into the reservoir in order to lower the daytime temperatures in order for higher amounts of dissolved oxygen to be available to the plants. However, during nighttime periods, the water chiller remains running, which serves the purpose of cooling the solution as much as possible in anticipation of the day. However, the electrodes have a temperature dependence of 1% error per 1°C difference in temperature. The difference between daytime, and nighttime temperature is about 25°C (100°F vs 75°F), or about 14°C. For example, using the
nitrate ion, the high ppm from Figure 5.15 is approximately 260 ppm, which is 1.23V. The starting voltage is 1.55V, which is 120 ppm. Since the amplification from the instrumentation amplifier is 16.15, the raw voltage for these concentrations is 76 mV and 96 mV respectively, only a 20 mV difference. A 14% error at 96mV is 13 mV, and when converted into ppm, is a substantial difference of 100ppm.

**Static Logging**

Logging in the static solution for 20 hours showed significant electrode drift. Logging this solution in a beaker, and without a water chiller minimized drift due to temperature. While the drift for nitrate and calcium were lessened as compared to Figure 3.7, the drift is substantial. The potassium electrode showed a marked increase between 7:12PM and 7:27PM. The reason for this sharp jump is not known. Nonetheless, the electrode response for all three electrodes showed significant drift over the 20 hours.

**Dynamic Control**

Attempted hydroponic control on Day 5 of the 2nd week nutrient solution (Figure 5.17) showed a similar result to that Figure 5.15. Though the control system was active, no nutrient injection occurred due to no setpoints being crossed. However, during the nighttime hours, the ppm showed significant drift, possibly due to temperature. In this case, however, the ppm returned back to similar starting points in the morning, where
presumably the temperature was similar to the calibration solutions temperature. However, the fluctuations of the calculated ppm render meaningful control impossible, as it is impossible to trust the electrode responses.

Figure 5.18 shows another attempted hydroponic control on Day 6 of the 2\textsuperscript{nd} week nutrient solution concentration. However, in this case, the calcium response showed similar response to Figure 5.15 during the nighttime period, where the voltage drops, and the calculated ppm drops as well. However, in this case, the calculated ppm of the calcium ion dropped below the grower setpoint, and injection occurred. The system attempted to return the calcium concentration back to the grower setpoint, but the response of the calcium electrode did not shift. This caused the system to continue to inject more stock solution into the reservoir, with no response from the calcium electrode. This injection can be seen in the spike of the nitrate ion. This lack of response in the calcium electrode could be attributed to poor lifespan of the calcium electrode. It could also be attributed to interference from the potassium ion. Another research group reported no significant correlation of the calcium electrode as compared with the gold standard spectroscopy method when measuring concentration of the calcium ion. This was attributed to “lower sensitivity and poor selectivity for Ca in the mixed hydroponic nutrient solution as compared to results obtained in a pure Ca solution.” Furthermore,
“the performance of the Ca electrode was not satisfactory for use in hydroponic solution due to its low sensitivity.” (90)

Problems with continuous monitoring of both nitrate and potassium ions are hindered by other factors including biofilm accumulation caused by the presence of organic materials in hydroponic solutions, which may contribute to the signal drift (91). Another issue could be due to differential depletion of ions by the plant system, which causes the relative concentrations of ions in the analyte solution to differ from the relative ion concentration in calibration solution. Ion-selective electrodes are not truly specific to any single ion, but respond to a variety of interfering ions. To overcome these interference issues, multivariate calibration models may be needed, which allow cross responses from primary and interfering ions to be decoupled. This method involves nonlinear optimization by use of the Nicolsky-Eisenman equation, which is an extension of the Nernst equation:

\[
E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{z_F} \ln \left[ a_i + \sum_j \left( k_{ij} a_j^{z_i/z_j} \right) \right] \quad (6.1)
\]

Where \( E_{\text{cell}} \) is the measured voltage, \( E_{\text{cell}}^\ominus \) is the standard potential, \( z \) is the charge of the ion, \( F \) the Faraday constant, \( a_i \) the activity of the ion of interest, \( a_j \) the activity of the interfering ions, and \( k_{ij} \) the selectivity coefficient. This equation was used in conjunction with an array of 24 calibration solutions, each containing varying relative amounts of three of the measurement ions (92). Another group attempting
simultaneous analysis of soil macronutrients by four ion-selective corroborates these findings. This group utilized what they termed a baseline-correction method, which was also based on the Nicolsky-Eisenmann equation, and 64 calibration solutions (93). Using this calibration technique, they were able to determine interfering effects of ions on each ion-selective electrode, and calculate a relevant calibration equation.

Lack of repeatability for measurement ions could be attributed to lack of a buffer solution in the hydroponic solution. The buffer solution keeps the ionic strength of analyte solution constant in light of other interfering ions. Without a buffer, the ISE’s respond to ionic activity, which require the use of other analysis methods to calculate the ionic activity in order to directly relate the electrode response to the concentration. Addition of a Tris buffer would be necessary to obtain accurate estimates of NO₃ and K concentrations in mixed hydroponic solutions (90).

Other issues with instable ppms are caused directly by the testing apparatus itself. The electrode sensors are refillable, and thus, have a fillport hole in which the internal solutions are added. In lab conditions, typically two days are needed prior to refilling of the electrode. However, in the NFT system, no filling is needed at all. This can be attributed to the nutrient solution leaking into the electrode body through the fill hole, and contaminating the inner fill solution. This also causes drift in measured voltage, and impacts repeatability of the concentration readings.
CHAPTER 7: CONCLUSION

Through this type of control system, individual ions are sampled and processed by a centralized control system. Calibrations in fertilizer solution ensure that accurate ionic concentrations of the reservoir solution are known at all times. A grower can set a high setpoint for injection, as well as a low setpoint to activate the injection. Stepper motors add a high strength ionic solution when reservoir concentration is out of bounds to return ionic concentration back to grower setpoint. Consistent maintenance of the reservoir concentration ensures that nutrient deficiencies of major ions will not occur. This form of control system can be utilized on all recirculating reservoir modalities.

7.1 Control System Implementations

Ebb and Flow

Control system and sensor implementation onto ebb and flow designs would focus the control system in the underlying reservoir. Nutrient absorption after each flood and drain event would quickly change nutrient concentrations. This is especially true if ebb and flow is being applied to multiple grow beds. After the first one or two floorings, the first planting beds would essentially deplete certain mobile elements such as nitrate. Reinjection of nutrients prior to flooding secondary beds, would allow for optimal
nutrient use from each growing bed.

**Top-feed Drip**

Automated ion control would target the severely depleted runoff from the containers. The central reservoir that the runoff returns too would be interrogated and automated injection would occur once reservoir levels fell below predefined levels. In this method, a method that has traditionally not lent itself to recirculation would be able to do so now. The advantages of top-feed drip, is that its water use efficiency is very high when combined with an appropriate substrate. With automated ion control, the water use efficiency would rise to even higher levels as runoff is recaptured.

**Nutrient-Film Technique - NFT**

Automated ion-injection approaches to NFT should target the main reservoir that each gully empties into. Nutrient depletion would take place continuously over time as the stream is constantly running. Any nutrient injection should take into consideration the flow rate. This influences how quickly the reservoir is turned over. If taking measurements from this reservoir, misgauging the turnover rate could lead to incorrect measurements, as the reservoir has not reached steady-state.

**Recirculating Deep-Water Culture – rDWC**

Automated ion-control for rDWC systems should target the central reservoir, which feeds the control bucket. This reservoir holds the greatest volume of water, and would
be the optimal place to sample. Sensors placed into the main reservoir could easily receive the best representative indication of system status in terms of ion ppm and pH. As the control bucket is also connected to this reservoir via a pump; nutrient depletion by each plant would reflect itself in this reservoir. Commercially available systems that utilize this form of method include several models by Current Culture, General Hydroponics - Waterfarm, and Titan - Flo N Gro.

**Aeroponics**

Despite these downsides with aeroponics, it still remains an important tool in a grower’s arsenal. Most importantly, as a recirculating modality, nutrient depletion will be inevitable. The main spot of implementation of any automated control system would be reservoir the emitter’s are drawing from. The liquid that drips down from the roots will be collected back into this same reservoir. Thus, any nutrient depletion would manifest itself here. Aeroponic systems available on the market commonly are cloning systems, and a popular implementation of the technique is E-Z Clone. Cloning is possibly the largest commercial application of pure aeroponics thus far.

**Deep-Flow Technique**

An automated control system would monitor and keep ion set points from dropping too low. Any control should target the central reservoir that the troughs are emptying into. This holds the greatest volume of water and will likely be representative of the system
as a whole. This form of technique is widely used in industry for lettuce rafts. Grow tables with drainage channels are supplied by a number of hydroponic suppliers, including Botanicare.

**Hybrid-Techniques**

Sensor implementations onto the Ein-Gedi technique should focus on the main central reservoir. Each trough empties into this reservoir, so nutrient depletion from all the plants combined will be seen most readily here. In NFT environments slope, and thus slope rate is the important variable in terms of reservoir turnover time. In the Ein-Gedi technique, the independent variable is the pump size. Since fluids are being forced into a water line, head pressure of this pump is very important. The emitter rate is not dependent on the slope of the trough, but rather on the size and power of the pump. A stronger pump will cycle more water, and thus decreases the reservoir turnover rate. The speed of turnover should be considered in an automated sensor implementation.

**7.2 Future Work**

To minimize the effect of electrode drift, as well as lifespan issues of the membrane, a device needs to be developed that removes the electrodes from the constant immersion environment it currently is in. This includes only periodic sampling of the analyte solution, followed by rinsing of the electrode tips to prevent biofilm buildup. In addition, this separate system needs to contain a temperature sensor, and a means to
hold the temperature of measurement solution constant. These two improvements would maximize lifespan of each electrode, minimize electrode drift, and decrease sensitivity changes of the electrode.

In addition to the development of a physical device that can minimize external effects on the electrodes, there also needs to be improvement in the calibration methods. Current calibration methods can yield a linear curve from a known calibration solution, but only because relative amounts of each ion remain the same after serial dilution. This curve cannot be extrapolated into samples of varying relative nutrients, and yields incorrect results. Development of a new calibration curve needs to take into consideration dozens of calibration solutions, each with differing relative ion concentrations. This equation must take into account non-linear affects due to ionic activity as described into the Nicolsky-Eisenmann equation. Statistical modeling is needed to elucidate specific coefficients of the new calibration equation.

Future work could also focus on wireless capabilities. This includes interfacing programmable, Xbee chips to the Raspberry Pi and acquisition system. In this scheme, an Xbee chip is placed on the acquisition board where it interfaces with the sensors via SPI and the stepper motor drivers via I2C. The Raspberry Pi controller would have another programmable Xbee chip, and the communication between the acquisition board and the Raspberry Pi would be wireless. This would enable a grower to control
multiple automated injection units with a single Raspberry Pi controller. In a true greenhouse environment, there are multiple reservoirs. The ability to interface several acquisition boards to a single controller would give the grower a significantly more control.
BIBLIOGRAPHY


**APPENDIX**

Small Components required for acquisition board.

### Small Components Required for Acquisition Board

Yellow is Sheet 1. Green is Sheet 2. Red is Sheet 3. See asterisks for repeat parts.

<table>
<thead>
<tr>
<th>Component Description</th>
<th>Part Number</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gain resistor (15K) (pack of 10) (1206)</td>
<td><a href="http://www.digikey.com/product-detail/en/CRCW120615K0DHEAP/541-15KBADKR-ND/3594003">Link</a></td>
<td>4x</td>
<td>0.55</td>
</tr>
<tr>
<td>INAMP Bypass caps (0.1uf) (0805)**</td>
<td><a href="http://www.digikey.com/product-detail/en/CL21F104ZBCNNNC/1276-1007-1ND/3889093">Link</a></td>
<td>4x</td>
<td>0.10</td>
</tr>
<tr>
<td>TL074 Bypass caps **</td>
<td><a href="http://www.digikey.com/product-detail/en/CL21F104ZBCNNNC/1276-1007-1ND/3889093">Link</a></td>
<td>2x</td>
<td>0.10</td>
</tr>
<tr>
<td>MCP3008 Bypass caps **</td>
<td><a href="http://www.digikey.com/product-detail/en/CL21F104ZBCNNNC/1276-1007-1ND/3889093">Link</a></td>
<td>1x</td>
<td>0.10</td>
</tr>
<tr>
<td>Resistors for filter circuit (pack of 10) (1206)</td>
<td><a href="http://www.digikey.com/product-detail/en/CRCW12062M61FKEA/541-2.61MFCT-ND/1182147">Link</a></td>
<td>8x</td>
<td>0.10</td>
</tr>
<tr>
<td>Capacitors for filter circuit (high precision) (0805)</td>
<td><a href="http://www.digikey.com/product-detail/en/C0805C104J4RACTU/399-11163-1ND/4357875">Link</a></td>
<td>8x</td>
<td>0.50</td>
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<td>Bypass caps for Shmitt-Trigger **</td>
<td><a href="http://www.digikey.com/product-detail/en/CL21F104ZBCNNNC/1276-1007-1ND/3889093">Link</a></td>
<td>6x</td>
<td>0.10</td>
</tr>
<tr>
<td>Bypass caps for MCP23017 **</td>
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<td>3x</td>
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<td>Component Description</td>
<td>Reference URL</td>
<td>Quantity</td>
<td>Price</td>
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<td>---------------------------------------</td>
<td>-------------------------------------------------------------------------------</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>Bypass caps for +5V polygon (10uF) (PTH)***</td>
<td><a href="http://www.digikey.com/product-detail/en/SK100M100ST/338-1700-ND/1627386">http://www.digikey.com/product-detail/en/SK100M100ST/338-1700-ND/1627386</a></td>
<td>1x</td>
<td>0.32</td>
</tr>
<tr>
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<td><a href="http://www.digikey.com/product-detail/en/UMK212F105ZG-T/587-1308-1-ND/931085">http://www.digikey.com/product-detail/en/UMK212F105ZG-T/587-1308-1-ND/931085</a></td>
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<tr>
<td>Bypass cap for +15V (1uF) (0805)*****</td>
<td><a href="http://www.digikey.com/product-detail/en/UMK212F105ZG-T/587-1308-1-ND/931085">http://www.digikey.com/product-detail/en/UMK212F105ZG-T/587-1308-1-ND/931085</a></td>
<td>1x</td>
<td>0.11</td>
</tr>
<tr>
<td>Bypass cap for LT1021**</td>
<td><a href="http://www.digikey.com/product-detail/en/CL21F104ZBCNNNC/1276-1007-1-ND/3889093">http://www.digikey.com/product-detail/en/CL21F104ZBCNNNC/1276-1007-1-ND/3889093</a></td>
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<td>1x</td>
<td>0.32</td>
</tr>
<tr>
<td>Bypass cap for -5V (10uf) (PTH)***</td>
<td><a href="http://www.digikey.com/product-detail/en/SK100M100ST/338-1700-ND/1627386">http://www.digikey.com/product-detail/en/SK100M100ST/338-1700-ND/1627386</a></td>
<td>1x</td>
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<td>Bypass cap for -5V (1uF) (0805)*****</td>
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<td>1x</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Schematics used in Battery Testing System:
Schematics used in Control System:
Sheet 1:
Sheet 2:
Control System Code:

Main.c:

```c
#include "calibration.h"
#include "global.h"
#include "sample.h"
#include "io.h"
#include <stdio.h>
#include <string.h>
#include <sys/time.h>
#include <signal.h>

#define NITRATE 0
#define POTASSIUM 1

void sample_routine(int signum);

char save_file[10];
float ppm[3];
int rotate;

int main(int argc, const char* argv[]) {
    struct sigaction sa;
    struct itimerval timer;
    int interval=60;
    if (argc == 2)
        strcpy(save_file, argv[1]);
    else if (argc == 3)
    {
        strcpy(save_file, argv[1]);
        if(sscanf(argv[2],"t=%d",&interval) == EOF)
        {
            printf("Wrong parameter\n");
            exit(0);
        }
        else
            printf("interval = %d\n",interval);
    }
    else
        strcpy(save_file, "data.txt");
    if(ReadCaliFile("sensor.cal") == -1)
    {
        printf("Can't find calibration file.\n");
        exit(0);
    }
    else
```
```c
{   printf("Total volume: %f\n", totalVolume);
    printf("Nitrate: %d %f %f %f %f %f\n", Sensors[0].num, Sensors[0].c.intercept, Sensors[0].c.slop, Sensors[0].user_PPM, Sensors[0].Stock_PPM, Sensors[0].user_low);
    printf("Potassium: %d %f %f %f %f %f\n", Sensors[1].num, Sensors[1].c.intercept, Sensors[1].c.slop, Sensors[1].user_PPM, Sensors[1].Stock_PPM, Sensors[1].user_low);

    IOInit();
    if (InitADC() == -1)
    {
        printf("Can't open ADC.\n");
    }
    else
    {
        printf("create data file\n");
        rotate = POTASSIUM;
        /* Install timer_handler as the signal handler for SIGVTALRM. */
        memset (&sa, 0, sizeof (sa));
        sa.sa_handler = &sample_routine;
        sigaction (SIGALRM, &sa, NULL);
        /* Configure the timer to expire after 300 seconds... */
        timer.it_value.tv_sec = interval;
        timer.it_value.tv_usec = 0;
        /* ... and every 300 seconds after that. */
        timer.it_interval.tv_sec = interval;
        timer.it_interval.tv_usec = 0;
        /* Start a virtual timer. It counts down whenever this process is executing. */
        setitimer (ITIMER_REAL, &timer, NULL);
    }
}

while (1);
return 0;
}

void sample_routine(int signum)
{
    char date[100];
    struct tm *info;
    float addVolume;
```
int addStep;
int i;
FILE *fd;
fd = fopen(save_file,"a");
switch (rotate)
{
    case NITRATE:
        GetSample(0,10);
        printf("Nitrate = %f ppm\n",Sensors[0].currentPPM);
        if(Sensors[0].currentPPM<Sensors[0].user_low)
        {
            //calculate the volume need to eject.
            //printf("before inject, %f, %f, %f, %f\n",
            Sensors[0].user_PPM, Sensors[0].currentPPM, Sensors[0].Stock_PPM, totalVolume);
            addVolume = (Sensors[0].user_PPM - Sensors[0].currentPPM)*totalVolume/MOLE_CONST_NION/Sensors[0].Stock_PPM;
            printf("Inject nitrate: %.9fmL\n",addVolume);
            // steps to rotate
            addStep = (int)(addVolume/VOLUME_RESOLUTION);
            printf("inject steps: %d\n", addStep);
            if (Sensors[0].leftStep - addStep < 0)
            { //if the left step is smaller than the step need to rotate
                MotorStep(CLOCKWISE, 0, TOTAL_STEP-Sensors[0].leftStep, 10); //first refill stock solu$
                MotorStep(ANTICLOCKWISE, 0, addStep, 10); //then eject
                Sensors[0].leftStep = TOTAL_STEP;
            }
            else
                MotorStep(ANTICLOCKWISE, Sensors[0].channel, addStep, 10); //eject
                Sensors[0].leftStep = Sensors[0].leftStep - addStep;
        }
        rotate = POTASSIUM;
        break;
    case POTASSIUM:
        GetSample(1,10);
        GetSample(2,10);
        printf("Potassium = %f ppm\n",Sensors[1].currentPPM);
        printf("Calcium = %f ppm\n",Sensors[2].currentPPM);
        if(Sensors[1].currentPPM<Sensors[1].user_low)
        {

//calculate the volume need to eject.
printf("Inject potassium: %.9fmL\n", addVolume);
// steps to rotate
addStep = (int)(addVolume/VOLUME_RESOLUTION);
printf("injection steps: %d\n", addStep);
if (Sensors[1].leftStep - addStep < 0)
//if the left step is smaller than the step need to rotate
{
    MotorStep(CLOCKWISE, 1, TOTAL_STEP-Sensors[1].leftStep, 10); //first refill stock solu$
    MotorStep(ANTICLOCKWISE, 1, addStep, 10); //then eject
    Sensors[1].leftStep = TOTAL_STEP;
}
else
    MotorStep(ANTICLOCKWISE, Sensors[1].channel, addStep, 10); //eject
    Sensors[1].leftStep = Sensors[1].leftStep - addStep;
}
if(Sensors[2].currentPPM<Sensors[2].user_low)
{
    //calculate the volume need to eject.
printf("Inject Calcium: %.9fmL\n", addVolume);
// steps to rotate
addStep = (int)(addVolume/VOLUME_RESOLUTION);
printf("injection steps: %d\n", addStep);
if (Sensors[2].leftStep - addStep < 0)
//if the left step is smaller than the step need to rotate
{
    MotorStep(CLOCKWISE, 1, TOTAL_STEP-Sensors[2].leftStep, 10); //first refill stock solu$
    MotorStep(ANTICLOCKWISE, 1, addStep, 10); //then eject
    Sensors[2].leftStep = TOTAL_STEP;
}
else
    MotorStep(ANTICLOCKWISE,
Sensors[2].channel, addStep, 10); // eject
        }
        rotate = NITRATE;
        break;
        default:
        break;
    }
    GetSample(0,10);
    GetSample(1,10);
    info = localtime(&Sensors[0].t);
    strftime(date, sizeof(date), "%D %H:%M:%S", info);
    fprintf(fd, "%s
V:
%f
%f
%f
PPM:
%f
%f
%f
%f
", date, Sensors[0].currentVoltage, Sensors[1].currentVoltage, Sensors[2].currentVoltage, Sensors[3].currentVoltage,
Sensors[0].currentPPM, Sensors[1].currentPPM, Sensors[2].currentPPM, Sensors[3].currentPPM);
    printf("%s
V:
%f
%f
%f
PPM:
%f
%f
%f
%f
", date, Sensors[0].currentVoltage, Sensors[1].currentVoltage, Sensors[2].currentVoltage, Sensors[3].currentVoltage,
Sensors[0].currentPPM, Sensors[1].currentPPM, Sensors[2].currentPPM, Sensors[3].currentPPM);
    fclose(fd);
}

Global.c:

#include "global.h"

int numberofsensors;
struSensor Sensors[10];
float totalVolume;
#include "io.h"

const int motor_pin_num[MOTOR_NUM][5] =
{{100,101,102,103,200},{104,105,106,107,201},
 {108,109,110,111,202},{124,125,126,127,204},{120,121,122,123,203}};

void IOInit()
{
    int i;
    wiringPiSetup();
mcp23017Setup (MCP1_PIN_BASE, MCP1_I2C_ADDR);
mcp23017Setup (MCP2_PIN_BASE, MCP2_I2C_ADDR);
mcp23017Setup (MCP3_PIN_BASE, MCP3_I2C_ADDR);
    for(i=0; i<MOTOR_NUM; i++)
    {
        pinMode(motor_pin_num[i][MOTOR_DIR], OUTPUT);
        pinMode(motor_pin_num[i][MOTOR_STEP], OUTPUT);
        pinMode(motor_pin_num[i][MOTOR_RST], OUTPUT);
        pinMode(motor_pin_num[i][MOTOR_FLT], INPUT);
        pinMode(motor_pin_num[i][MOTOR_HOME], INPUT);

        pullUpDnControl(motor_pin_num[i][MOTOR_FLT], PUD_UP);
        pullUpDnControl(motor_pin_num[i][MOTOR_HOME], PUD_UP);
        digitalWrite(motor_pin_num[i][MOTOR_RST], HIGH);
    }
}

int MotorStep(int dir, int motor, int steps, int t)
{
    int i;
    int flag;
    flag = steps;
    digitalWrite(motor_pin_num[motor][MOTOR_DIR], dir);
    for (i=0; i<steps; i++)
    {
        if (digitalRead(motor_pin_num[motor][MOTOR_FLT]) == LOW)
        {
            flag = -1;
            break;
        }
        if (digitalRead(motor_pin_num[motor][MOTOR_HOME]) == LOW)
        {
            flag = i;
            break;
        }
        digitalWrite(motor_pin_num[motor][MOTOR_STEP], HIGH);
        delay(t);
        digitalWrite(motor_pin_num[motor][MOTOR_STEP], LOW);
delay(t);
}
return flag;
}

void MotorCycle(int dir, int motor, int cycle, int s) {
}

void MotorReset(int motor) {
    digitalWrite(motor_pin_num[motor][MOTOR_RST], LOW);
    delay(10);
    digitalWrite(motor_pin_num[motor][MOTOR_RST], HIGH);
}

int MotorHome(int motor) {
    int i, flag;
    flag = 1;
    for (i=0; i<1000; i++) {
        if (digitalRead(motor_pin_num[motor][MOTOR_FLT]) == LOW) {
            flag = -1;
            break;
        }
        if (digitalRead(motor_pin_num[motor][MOTOR_HOME]) == LOW) break;
        digitalWrite(motor_pin_num[motor][MOTOR_STEP], HIGH);
        delay(100);
        digitalWrite(motor_pin_num[motor][MOTOR_STEP], LOW);
        delay(100);
    }
    return flag;
}

Calibration.c

#include "calibration.h"

/*
int FindCaliFile(char *name) {
    DIR *d;
    struct dirent *dir;
    int find = -1;
    d = opendir(".");
    if (d)
{ while ((dir = readdir(d)) != NULL) 
{ 
    printf("%s
", dir->d_name);
    if (strstr(dir->d_name, "cal") != NULL) 
    { 
        strcpy(name, dir->d_name)
        find = 0;
        break;
    } 
} 
closedir(d); 
} 
return find; 
}*/

int ReadCaliFile(char* filename) 
{ 
    FILE *fd;
    char line[100];
    int sensor_num, total;
    float intercept, slop, setting, ppm, setting_low;
    fd = fopen(filename, "r");
    if (fd == NULL) 
    { 
        printf("Can't find calibration file\n");
        return -1;
    } 
    else 
    { 
        if(fgets(line, 100, fd) != NULL) 
        { 
            if (sscanf(line, "%d", &total) == EOF) 
            return -1;
            printf("total=%d\n",total);
        } 
        if(fgets(line, 100, fd) != NULL) 
        { 
            if(sscanf(line, "%f", &totalVolume) == EOF) 
            return -1;
        } 
        while(fgets(line, 100, fd) != NULL) 
        { 
            if(line[0] == '#') //comment line, ignor it 
            continue;
            else 
            { 
                if (sscanf(line, "%d\t%f\t%f\t%f\t%f\t%f", &sensor_num, &slop, &intercept, &ppm, &setting, &setting_low) != EOF) 
                { 

//printf("%s", line);
//printf("%d\n", sensor_num);
Sensors[sensor_num].c.intercept = intercept;
Sensors[sensor_num].c.slop = slop;
Sensors[sensor_num].num = sensor_num;
Sensors[sensor_num].channel = sensor_num;
Sensors[sensor_num].leftStep = TOTAL_STEP;
Sensors[sensor_num].user_PPM = setting;
Sensors[sensor_num].Stock_PPM = ppm;
Sensors[sensor_num].user_low = setting_low;
total--;
}
if (total == 0)
    break;
}
if (total!=0)
    return -1;
else
    return 0;
}

Sample.c:

#include "sample.h"
#include "global.h"
#include <math.h>

int InitADC()
{
    pinMode(SPI_CS, OUTPUT);
    digitalWrite(0, HIGH);
    if (wiringPiSPIsetup(SPI_CHANNEL, SPI_SPEED)==-1)
        return -1;
    else
        return 1;
}

float GetVoltage(int sensor_num)
{
    unsigned int vol;
    unsigned char data_buffer[3]={0,0,0};
    data_buffer[0]=0x01;
    data_buffer[1] = (Sensors[sensor_num].channel|0x08)<<4;
    digitalWrite(0, LOW); //set CS to low, start ADC
    wiringPiSPIDataRW(SPI_CHANNEL,data_buffer, 3); //start conversion and get result
vol = data_buffer[1]&0x03;
vol = (vol<<8)+data_buffer[2];
digitalWrite(0, HIGH);
return vol*ADC_REF/ADC_RES;  //return voltage
}

void GetPPM(int sensor_num)
{
    Sensors[sensor_num].currentPPM = powf(10,
    (Sensors[sensor_num].currentVoltage -
    Sensors[sensor_num].c.intercept)/Sensors[sensor_num].c.slop);
}

void GetSample(int sensor_num, int times)
{
    int i;
    float sum=0;
    for (i=0;i<times;i++)
    {
        sum=sum+GetVoltage(sensor_num);
    }
    Sensors[sensor_num].currentVoltage=sum/times;
    GetPPM(sensor_num);
    Sensors[sensor_num].t = time(NULL);
}

Typedef.h:

#ifndef _TYPEDEF_H
#define _TYPEDEF_H 1

#include <sys/time.h>

#define TOTAL_STEP 2714
#define VOLUME_RESOLUTION 0.020  //20uL per step
#define MOLE_CONST_NION 62.0049 // g/mol
#define MOLE_CONST_PION 39.0983 // g/mol
#define MOLE_CONST_CION 40.078 // g/mol
//Define calibration information structure
typedef struct {
    float intercept;
    float slop;
} Cali;

typedef struct {
    int num;
    int channel;
}
Cali c;
    float currentVoltage;
    float currentPPM;
    int leftStep;
    float Stock_PPM;
    float user_PPM;
    float user_low;
    time_t t;
}struSensor;
#endif

Sample.h:

#ifndef _SAMPLE_H
#define _SAMPLE_H

#include "typedef.h"
#include <stdio.h>
#include <time.h>
#include <wiringPiSPI.h>
#include <wiringPi.h>

#define SPI_CHANNEL 0
#define SPI_SPEED 500000
#define SPI_CS 1
#define ADC_REF 5.0
#define ADC_RES 1023.0

int InitADC();
float GetVoltage(int sensor_num);
void GetPPM(int sensor_num);
void GetSample(int sensor_num, int times);

#endif

IO.h:

#ifndef _IO_H
#define _IO_H

#include <wiringPi.h>
#include <mcp23017.h>

#define MCP1_PIN_BASE 100
#define MCP2_PIN_BASE 120
#define MCP3_PIN_BASE 200

152
#define MCP1_I2C_ADDR 0x20
#define MCP2_I2C_ADDR 0x21
#define MCP3_I2C_ADDR 0x23

#define MOTOR_NUM 5
#define CLOCKWISE 0
#define ANTICLOCKWISE 1

#define MOTOR_DIR 0
#define MOTOR_STEP 1
#define MOTOR_RST 2
#define MOTOR_FLT 3
#define MOTOR_HOME 4

void IOInit();
int MotorStep(int dir, int motor, int steps, int t);
void MotorCycle(int dir, int motor, int cycle, int s);
void MotorReset(int motor);
int MotorHome(int motor);
#endif

Global.h:

#ifndef _GLOBAL_H
#define _GLOBAL_H

#include "typedef.h"

extern int numberofsensors;
extern struSensor Sensors[10];
extern float totalVolume;
#endif
Calibration.h:

```c
#ifndef _CALIBRATION_H
#define _CALIBRATION_H

#include "typedef.h"
#include <stdio.h>
#include <stdlib.h>
#include <dirent.h>
#include <string.h>
#include "global.h"

//int FindCaliFile(char *name);
int ReadCaliFile(char* filename);

#endif
```