Screen-printed Ion Selective Electrodes for Soil Ion Detection

by

Ron Rosenberg

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Masters of Science in Mechanical Engineering

at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

Rural Indian farmers lack an available, affordable, usable, and actionable means to
diagnose soil health, which is a prerequisite for judicious application of fertilizer. Although government labs and mobile kits are available, these fail to meet the aforementioned qualities; as a result fewer than 5% of rural Indian farmers have ever performed a soil test. This thesis details the design and characterization of a point-of-use soil testing device, comprising a set of disposable ion-selective electrode (ISE) strips and a handheld electrochemical reader, which together transduce soil analyte concentrations into a numeric input for a mobile-phone based fertilizer recommendation engine. As a proof-of-concept, potassium (K+) selective electrodes are studied, because K+ is essential to plant growth and reproduction. The strips employ a simple two electrode system, wherein carbon nanotube and silver chloride inks are the electrode contacts, plasticizer-free butyl acrylate ion selective membranes are located on the working electrodes, and sodium-chloride doped polyvinyl butyral membranes provide stable reference potentials. The electrodes were fabricated by a combined screen printing and drop casting process, and the protocol, extraction solution, and reference potential stability were tuned to maximize ISE performance and repeatability. Using a mathematical model and supporting experiments, we verified that hydrogen selectivity determines the detection limit, and furthermore, that scientists can tune the ionophore-ionic site ratio to minimize this effect. Using the final electrode fabrication process, a set of 20 full ISE devices in the presence of 0.02M SrCl₂ extraction solution were shown to have sub-uM detection limits and near-Nernstian average sensitivity (61 mV/decade). When compared to ICP data for a set of 30 soil samples using the final reader, the sensors demonstrated a 0.898 correlation factor. Workshops in India were conducted to determine user needs and corresponding product attributes, as well as a "usability index" for the system assessed across farmer demographics. The favorable system performance proves that solid-state ISEs are a promising technology for soil diagnostics in resource-constrained environments.

Thesis Supervisor: Anastasios John Hart
Title: Associate Professor
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Chapter 1

Introduction

1.1 The State of Indian Agriculture

1.1.1 Overview

Agriculture is the backbone of the Indian economy, accounting for 14% of the country’s GDP, and approximately 50% of the total employment in the country. Yet, while the Indian economy has experienced impressive GDP growth, with an overall growth rate of 6.2% in 2011-2012, the growth in agriculture was a low 3.6% in the same period, and fell by a significant margin in 2013 to just 1.8% (Figure 1-1). This decelerating trend in agricultural growth and contribution to GDP is a worrying phenomenon for a country that represents roughly 2.4% of the world’s area, but supports 17% of its population.

As a result, the situation for rural Indian farmers continues to worsen. The average landholding size has decreased to 1.15 hectares due to high birth rates and generational land redistribution, making it less feasible for farmers to leverage positive economies of scale. In fact, small holdings farmers in India whose land holdings are less than 2 hectares constitute approximately 80% of all Indian farmers.

Rural wages have also been particularly stagnant over the last three fiscal years, reaching a low of 3.8% in 2015, lower than the 4.1% increase in consumer price index that year - indicating a contraction in purchasing power. The extent of the struggle
of the rural Indian farmer can be seen not only in the resultant mass migration from rural to urban population centers, but also in the recent surge in farmer suicides, with 12,360 farmer suicides registered in 2014.

Looking to the future, the picture becomes more worrisome. With a burgeoning population expected to increase to 1.75 billion people by 2050 - a 44% increase from India’s current population - and only 12.9% of arable land left to be cultivated, if current agricultural productivity remains the same, India will not even be able to sustain its own population. When taking into account a projected increase in per capita food consumption as per capita GDP continues to rise, India will likely face this crisis sooner rather than later. Together, these findings highlight the pressing need to improve agricultural productivity so as to increase the quality of life of rural small holding farmers, strengthen the agricultural sector of the Indian economy, and ensure India’s food security for the future.

1.1.2 The State of Indian Soil Health

The "Green Revolution" in the 1960’s and 70’s in India led to a proliferation of modern agricultural methods, allowing India to go from being a food importer to a food exporter. Rural wages and crop yields also rose greatly over this time period.
Figure 1-2: India’s average crop yields of major crops are far below global averages, with the exception of wheat.

With the exception of milk and wheat production, Indian agricultural yields remain very low compared to world averages (Figure 1-2), despite growing government subsidies for fertilizer and electricity. The primary contributors to poor efficiency in India’s agriculture sector can be most accurately categorized as follows:

1. Low mechanization

2. Poor disease and pest management

3. Climate change and drought

4. Storage and transportation losses

5. Insufficient irrigation

6. Poor soil health

For the purpose of this thesis, we will focus on the latter.

Soil health can be quantified by the relative macronutrient and micronutrient concentrations in soil. Macronutrients refer to the nitrate, phosphate, and potassium
(i.e. N, P, K) ion concentrations in soil. The pH of the soil is another key indicator of soil health, often measured along with macronutrient concentrations. Micronutrients refer to nutrients at lower concentrations - specifically, calcium, boron, zinc, copper, iron and more.

The current state of Indian soil health is poor. Skewed values of macro and micronutrients are ubiquitous, water quality is declining, and organic carbon content has also diminished, leading to an overall decline in soil health. Government interventions to improve food production such as fertilizer subsidies and financing schemes have had the unintended consequence of incentivizing the imbalanced use of fertilizers. The result is that while the ideal NPK fertilizer consumption ratio is 4:2:1, the actual NPK use ratio varies widely across India. Specifically, Indian farmers tend to overuse urea as it is highly subsidized compared to other macronutrient fertilizers. On average, farmers apply twice the urea recommended, and in some northern states, farmers apply closer to 10-15 times more than the requirement.

From a farmer's perspective, this problem is doubly compounded; as it is not only an unnecessary increase in capital expenditure, but is also a detriment to their soil health. From a macroscopic perspective, overuse leads to poor crop yields for India as a whole, in addition to the contamination of downstream groundwater sources, which can cause deleterious public health effects resulting from water eutrophication.

1.1.3 The Need for Soil Health Information

Providing accurate information about a farmer's soil chemistry could curtail the negative effects of improper fertilizer use. We posit that if more farmers were able to test their soil effectively and receive actionable advisory, they would be better able to make informed fertilization and irrigation decisions, thereby increasing their productivity and profitability.
Benchmarking Current Solutions

For comparing different available soil testing methodologies, we provide a framework for assessing an ideal soil testing solution. We define that such a solution must fulfill the following attributes:

- **Availability:** the solution must be available to the farmer, ideally at the point-of-use, without the need for excessive travel.

- **Affordability:** the solution must be easily affordable for an individual farmer or a small group of farmers.

- **Usability:** the solution must be easily used and intuited without prior knowledge of soil chemistry fundamentals.

- **Actionability:** the solution must provide actionable feedback to the user in terms of quantifiable steps towards soil health improvement.

Soil testing in India currently takes place either in government labs, mobile soil-testing units, or by the use of field kits.\(^\text{13}\) Government sanctioned farmer extension service centers, called Krishi Vigyan Kendras (KVKs) are mandated to have an active soil testing facility on site, where farmers can drop off soil samples and receive a report on their soil chemistry. Most often these soil tests are available at a subsidized cost (typically 50-400 Indian Rupees (INR) or 1-6 US Dollars (USD)), based on data from surveys. The problem with the KVK system however, is four-fold:

- Farmers have to travel long distances to reach a soil lab, thereby sacrificing a day’s worth of labor and/or wages.

- The time delay between sample collection and receipt of the soil report, often more than weeks or months after the planting season, renders the report useless.

- The widespread inefficiency and mismanagement often leads to missing or incomplete soil reports.
• There are 514 government soil testing laboratories in India with a capacity of about 6.5 million samples per annum, which falls far short of the need. At only **1 KVK per 216,000 operational holdings**, the shortage of staff to accommodate demand and upkeep an efficient soil lab testing facility is an enormous constraint.

Thus, while KVKs are affordable to rural small holdings farmers, they fail in terms of poor availability and minimal actionability.

To circumvent the issue of distance, some KVKs have the additional service of a mobile soil testing lab, wherein soil diagnostic lab equipment is packed on a bus or car and travels to the villages themselves. While this theoretically alleviates problems specifically related to distance and response rate, these advantages are only available when such mobile labs are sanctioned. Given their relatively low rate of penetration, many farmers do not see the benefits of such mobile soil testing labs. Some private companies have tried to provide the service on their own, but according to analysts at the TATA trusts, these types of enterprises suffer from high expenses and low return on investments.

A third option for the farmers are field kits. Field kits are available to farmers in India for approximately 35,000 INR ($500 USD), and include a set of extraction solutions, beakers, and colorimetric reactive dyes. With respect to cost, even though such kits can perform up to 100-1000 soil tests, such a solution is far beyond the purchasing power of rural small holdings farmers, who make on average 270 INR per day ($4 USD). Instead, these soil testing kits are often used by those with greater individual or aggregate purchasing power, such as field agents hired by large scale contractors, farmer cooperatives, academic institutions, and agricultural NGOs.

Even if a farmer could afford such a solution, these kits involve multi-step chemical extraction procedures and assays, which often require prior chemistry intuition to successfully receive an accurate result. As such, while the colorimetric soil testing kits are more readily available to farmers, they fail in their affordability and usability.

Figure 1-3 summarizes the shortcomings of the three solutions on the market, using the framework of actionability, usability, affordability, and availability:
Understanding soil chemistry, and therefore treating the soil with the correct type and amount of fertilizers, is a key step towards improving crop yields while protecting soil health. This research aims to address this challenge of poor soil health and information by creating a novel low cost soil-testing sensor to measure soil nutrient concentrations, which works in conjunction with a robust information feedback system to provide farmers with timely actionable information about their soil. The ultimate goal is to empower the farmer with information about his soil and crops, so that he can make informed fertilization and irrigation decisions to improve crop yields.

1.1.4 Thesis Overview

The remainder of this thesis is outlined as follows: Chapter 2 will discuss the process of gathering user needs and interpreting those into solution agnostic product attributes and technical constraints. Chapter 3 will give an overview of the rationale for pursuing ion selective electrodes, the theory of their operation, and the prior art. Chapter 4 will discuss (i) a theoretical model which predicts ISE performance for a single analyte based off critical parameters within the ISM, and (ii) a model of how much error in the potential measurement corresponds to error in binned soil analyte prediction (i.e. "Low", "Medium", "High"). Chapter 5 will highlight the methods pursued in
manufacturing the ISEs as well as the design of the low cost potentiostatic voltmeter used to tranduce voltage readings from the ISEs into chemical concentrations of soil analytes. Chapter 6 will include the results and discussion of experimental exploration of the RE and WEs. Chapter 7 will show the methodology and results behind a usability study with 64 farmers in India, performed in July 2016. Finally, concluding remarks and potential future work will be discussed in Chapter 8.
Chapter 2

Problem Finding

The following section details the range of field research methodologies used on the ground in India to uncover customer needs. We define our target consumer as the following: the progressive, rural, small-holdings farmer. Such a target consumer desires information on his or her soil health, is accepting and open to new agricultural practices, has the financial means to independently purchase a soil diagnostic kit, and can leverage their status as influencers to disseminate new technologies.

A number of interactive activities were designed to elicit specific product and system related design inputs from the user. Further detailed information was garnered from group and individual level interviews. At each stage, specific lessons emerged which are emphasized in the descriptive text, and distilled into a "product contract", which describes how each takeaway translates into product attributes relevant to the design of the device and system. The chapter concludes with a synthesis of these various analyses that develops into the specific research question targeted in this thesis. This section is co-authored by Soumya Braganza, Tata Fellow in Technology and Public Policy, and fellow researcher on this project.

The figure below depicts the design flow described in this section, which includes the translation of data from user inputs into design requirements that ultimately guide the design of the sensor and recommendation system.
2.1 Stakeholder Interviews

Interviews were conducted with a range of stakeholders in the soil health value chain. We selected a diversity of users in order to inform our design practices for the technology as well as the accompanying recommendation system, such that the final product meets the diversity of user requirements.

2.1.1 Farmers

The small holder Indian farmer was our primary and most important stakeholder for this research, as he/she would be the ultimate beneficiary. We conducted approximately 130 interviews with farmers in villages in North Karnataka and Uttarakhand. Different geographic locations were selected to accommodate differing views on problems related to agriculture that characterizes different agro-ecological zones across India. Interviews were designed with the following principles in mind, in accordance with the human centric approach to design:

- **Location**: Interviews were conducted either at the farmer’s house or field, to establish a comfortable and non-threatening atmosphere. This encouraged open and honest answers.

- **Environment**: We avoided overwhelming participants by outnumbering them.
Each research team member was given a clear and specific role to perform prior, such as interviewer, note-taker, translator, photographer, etc.

- **Preparation:** Questions were prepared beforehand, and modified based on the first set of interviews conducted in a region, such that they were reflective of user needs and concerns in that region. The interview format started with simpler more direct fact-based questions, followed by more complex or opinion based questions later on. Questions were designed to understand general problems that farmers face, perceptions towards soil testing, the value chain that makes soil testing equipment, service, and training available to farmers, and the value chain that makes soil health related recommendations actionable to farmers.

The following list is an example of a subset of questions from interviews conducted in north Karnataka in January 2015, that specifically relate to soil testing and fertilization:

1. Do you test your soil? When and why did you first start, how often do you test, and describe the process followed?

2. Do you value soil testing? Do you think it is a good thing to do, even if you do not do it?

3. If you do not soil test, why not?

4. Do others in your community test their soil? What is their perception?

5. What is difficult about soil testing? What do you like about current soil testing practices?

6. How much would you currently have to pay for a soil test? How far would have to travel?

7. How would you make soil testing different?

8. How do you get your information about soil best practices such as irrigation, fertilization, sowing, and tilling?

9. Do you fertilize your soil? Where do you get it from? How much do you pay? What kind or brand of fertilizer you use?
Figure 2.2: (Left) Interview with farmers in Hubli region, Karnataka, (Right) Interview with farmers in Dehradun region, Uttarakhand.

- **Observation:** An observation protocol was put in place prior to starting the interviews, which included specific directives for note takers to write down observations on body language as well as actual responses. Translators were prepared beforehand to convey direct quotes from farmers rather than paraphrased versions of answers, so that valuable user opinions would not be lost in translation.

A number of interesting lessons emerged from interview data. It became quickly clear that farmers in different regions in India face very different agriculture-related problems, and therefore prioritize concerns about soil differently. South Indian farmers in the plains region listed water scarcity and access to power for irrigation as their two main concerns, while North Indian farmers in Uttarakhand had an entirely different set of concerns - i.e., the prevalence of pests and spoilage of farm products due to poor access to transportation.

**Takeaway:** Soil health is of varying priority for different types of farmers, based on their location, access to commodities, and socio-economic status.

Less than 5% of farmers interviewed had ever performed or attempted to perform a soil test. Of those that did collect a soil sample and mail it to the nearest KVK, we did not come across a single person that received a soil health report in return. For this reason among others, the level of trust in the government process was seen to be low, and farmers revealed that they would much rather test their own soil if they
were able to rather than send a sample out for testing.

Our takeaway from these results was two-fold. First, this emphasized the importance of the point-of-use aspect of the device, as well as the need for the accompanying recommendation system to generate results immediately, and effectively close the loop right at the farmer's land.

**Takeaway:** *The point-of-use aspect of the device and system is a key value add.*

Second, this highlighted the importance of having a trusted brand name associated with any technological intervention in this space, which was already characterized by poor response-times and low levels of user trust. Going forward, it would likely be favorable to approach commercialization through a partnership with a trusted private or non-governmental institution in India, such as the Deshpande Foundation or the Himmothan Society that we worked with.

**Takeaway:** *Brand value is important to our end user, so associating with a trusted entity is critical to the success of our system.*

While most farmers reported that government representatives did not frequently visit their villages to offer support, some mentioned they personally traveled to district offices to obtain information about fertilizers and subsidies from them. Poor access to fertilizers and subsidies was a common problem highlighted. Data from interviews corroborated policy findings that the delivery of subsidies is a political process fraught with corruption, resulting in subsidies not reaching those who need it the most. Farmers with wealth and political connections were reported to be the ones to whom subsidies, seeds, and other inputs were made the most available. The demand for bribes from fertilizer distributors was also reported to be a common occurrence. Distributors were reported to falsely limit supply when demand for fertilizers increased (when it rained for example), supplying farmers who could pay the highest bribes, those with political connections, as well as those who required larger quantities at a time. A consideration of access to inputs was therefore an additional concern
that would directly affect the success of an intervention in this space.

Interview data also revealed that farmers gain awareness of how to improve soil fertility from liberal and/or best-performing farmers in their area. Sharing of information such as best-practices and rules of thumb within villages were found to be highly characteristic of farming communities in both the north and south of India. Families also tended to work together on their plots of land, and neighbors helped each other out with labor-intensive processes such as weeding and harvesting. The close knit nature of the majority of farming communities we observed was a clear indication that a successful technological intervention would need to take into account the importance of social networks in agricultural communities.

**Takeaway:** A good system design will incorporate a means for farmers to work with each other, as this reflects their natural social dynamic.

Many farmers who were interviewed revealed that while they had a good perception of the utility of soil testing in general, they did not know much about the specifics - the procedure for soil sampling, the meaning of nutrient names such as nitrogen and potassium (they were more familiar with fertilizer names such as urea), and the specific consequences of over and under fertilizing. This was true of both male and female farmers, however males tended to be more interested in learning and acquiring such information, if they thought that it would in general be beneficial to the productivity and growth of their farms. This was corroborated by the independent revelation of gender norms within agricultural families. According to the majority of candidates interviewed, women tended to be responsible for day to day field tasks such as weeding, planting, and ploughing, while men spent less of their time actually in the field and more time managing larger level operations such as purchasing inputs (seeds, fertilizers, etc.) and selling produce. Soil testing, therefore, was likely to be a male-focused problem area.

**Takeaway:** Target consumers are most likely males, as soil testing is a male-dominated area.
2.1.2 Krishi Vigyan Kendras (KVKs)

KVKs are front-line agricultural extension centers financed by the Indian Council of Agricultural Research (ICAR). Among other functions, KVKs are mandated to organize and conduct training courses and educational programs for farmers in their region, demonstrate the latest agricultural technologies to farmers as well as extension workers, and perform analyses of soil samples sent to them from farmers. KVKs in each district are equipped with fully functional laboratories to perform in-depth analyses of soil, measuring macro nutrient concentrations, micro nutrient concentrations, electrical conductivity, moisture content, and organic carbon content of soil samples. A total of 642 KVKs are operational in the country, which is equivalent to 1 lab for every 216,000 operational holdings. This under-capacity for soil testing is partly to blame for the low fraction of farmers who test their soil. Additionally, the performance and success of KVKs varies widely depending on location, management, and business model, and have recently come under great scrutiny.

We visited labs and interviewed scientists at a total of three KVKs across India - two in the state of Karnataka, and one in Uttarakhand. Only one of those appeared to be functioning at full capacity, and provided us with a view of what a KVK that embodied the true spirit of the mandate given to them could achieve. This KVK was very well maintained, and appeared to be managed in a transparent manner. A number of farmer training programs were in session when we visited, and there
appeared to be good participation from farmers as well as staff. We also observed a
number of test plots in which various hybrid seeds were being tested for performance
in arid conditions. Part of the funding for this particular center was from the govern-
ment, with the day to day management being outsourced to a private company. This
public-private partnership model appears to be a very successful one for KVKs in
general, ensuring a base level of competition and accountability, while retaining the
benefit of government funding, standardization of procedure, and outreach. A num-
ber of important takeaways emerged from interviews with a range of stakeholders in
this progressive KVK, and these are listed below:

1. The process of behavioral change in agricultural communities takes approx-
imately 3 years. New technological solutions should start with liberal farmers,
make use of demonstrations as a tool to encourage adoption, and involve several
follow up visits to the field.

2. Incorporating a field for "suggested crops" could be very helpful as part of
recommendation system for farmers.

3. Other pressing concerns such as weather, water availability, and geography often
trumps soil health, therefore reducing the urgency for awareness building in this
space. It is therefore important to lower the economic and social barriers
to adoption as much as possible if a solution in this field is to be successful.

4. Government subsidies on urea are a likely cause of over-fertilization and im-
balanced NPK ratios, which is a difficult problem to address. This is just one
of the geopolitical and economic factors that come into play; technological
solutions need to leverage these factors or find ways to circumvent them.

5. Organic fertilizer recommendations would be valuable for farmers, or per-
haps a combination of organic and inorganic, depending on the appropriateness
to a specific region.
**Takeaway:** Behavioral change in communities takes approximately 3 years, suggested crops would be useful to provide to farmers as well as organic fertilizer recommendations.

Our observations in the other more poorly maintained KVK labs indicated that in general, soil labs were understaffed, disorganized, and inefficient. We observed over-reporting of monthly test numbers, which we struggled to corroborate given the scenario observed in the lab. While two samples are not enough to draw broad conclusion, our interactions helped us appreciate why farmers strongly advocated for an alternative solution to the problem of poor soil health.

### 2.1.3 Corporate Farming Entities

Corporate farming entities are a common phenomenon in India. These aggregators are most frequently seen where there is a market for high value and high volume commodities such as sugar, wheat, and rice. Specific employment terms vary across companies, but in general, farmers are hired on contract to grow a particular crop (such as sugar cane) on their land during certain times of the year, and to sell 100% of their produce to the aggregator (the sugar mill) at a fixed price. The sugar mill acts as an assured source of income for the farmer, as well as a source of information on best practices for crop growth. This aggregator model was of interest since it represented a common alignment of incentives towards improving soil health and productivity, and therefore presented a potentially efficient platform for outreach to farmers.

We visited and interviewed stakeholders at Godavari Biorefineries Ltd. (Figure 2-4), a global agribusiness and bio-energy corporation in Karnataka. The company is one of the largest producers of sugar in the world, the leading manufacturer of sugar in India. They produce sugar, ethanol, bio-fertilizer, and power, which are all products generated from the raw material sugar cane. In Karnataka, Godavari engages with over 30,000 farmers in the area. Interviews with scientists at the sugar mill revealed that while traditionally there has been a lot of focus on seed quality and hybrid plant variety, in recent years they have also leveraged the tools of information
and communications technology and the Global Positioning System to record the land holdings, some agricultural practices, and soil testing results of each farm. The sugar mill performs in house R and D of new high yielding varieties of sugar cane, which they test on the numerous plots of land acquired close to their campus specifically for testing. However, they rely on subsidizing farmers for testing their soil via the government labs. The situation highlights that such a corporate farming entity could potentially benefit from a point-of-use soil testing solution by reducing dependency on government laboratories, performing timely testing, and providing soil related recommendations via their internal extension network.

**Takeaway:** Corporate farming entities are another potential target user, as crowdsourcing point-of-use soil testing on their contracted farms would be efficient and economical.
2.1.4 Research Institutions

There are a large number of agricultural research facilities in India, both government and private that conduct huge volumes of research and produce numerous publications on a variety of topics of use to farmers - crop varieties, seed varieties, agricultural techniques, pest and disease, etc. Our extensive interactions with farmers in both Hubli and Dehradun regions of India revealed that in general, although such large volumes of useful information exist from credible and reliable scientific sources, farmers often rely on rules of thumb and traditional agriculture practices passed on to them from their forefathers. Even those farmers that expressed interest in modern practices and techniques were frequently unaware of where to access information that would be beneficial to them. The following is a synthesis of findings from interviews with a range of private and government research institutions.

Indian Agricultural Research Institute (IARI)

IARI is a national multi-disciplinary research institution in India that is over 100 years old. They perform research in the areas of Agriculture, Cattle Breeding, Chemistry, Economic Botany, Mycology, and Bacteriology.

IARI has developed a mobile soil testing unit that was in large part, an inspiration for our solution. While the unit, which costs approximately $600, is far more cost effective than a full scale laboratory, it is not cheap enough to be affordable by a single farmer, or even a group of farmers. The device is small enough that it can be transported directly to a farmer’s location, which goes a long way in addressing the issue of time delays between sending a sample for testing and receiving a recommendation report. The device comes with a range of chemical reagents for testing a range of nutrients, as well as an inbuilt shaker necessary for the chemical process. The disadvantages of the mobile unit lie in the need for a qualified technician to operate it, the long wait time for a result (about 40 minutes), and the minimalism of the recommendations generated. Our discussion with various researchers at IARI was therefore focused on the most important aspects of a potentially new solution
in this area that would improve on the mobile soil testing kit that they had created. Their experience corroborated our findings that the point-of-use aspect of the system was critical to generating trust and therefore adoption of the solution. Additionally, interviewees were in favor of a solution that would be affordable enough and easy to use for a farmer on his own, if such a thing were feasible.

**International Plant Nutrient Institute (IPNI)**

IPNI is a global non-profit organization that runs initiatives and manages programs to address growing global needs for food, fuel, fiber, and feed. Their mission is to "develop and promote scientific information about the responsible management of plant nutrition for the benefit of the human family."¹⁶

IPNI works with state and national agricultural universities and international organizations to increase the productivity and profitability of farms while minimizing environmental impact. IPNI has developed a proprietary software called Nutrient Expert intended to help farmers make informed fertilization decisions on the basis of plant symptoms. This is an interesting complementary product to our proposed solution that bypasses the need for a soil test and performs only symptom-based diagnostics. Their software product is currently used by ITC eChoupal and Tata Consultancy Services mKrishi, which are both large scale CSR initiatives to assist rural Indian farmers with soil-health related decisions. Additionally, they have developed a system for sending text messages to farmers that are populated with generalized state level recommendations. This is accompanied by a call center setup where farmers can call in and get information about different types of fertilizers and how to use them. This setup describes a promising route for commercialization of a low cost point-of-use soil testing sensor with an accompanying recommendation system, as this addresses a currently unfilled niche within this system, while complementing their business model instead of competing with it.

Another important lesson from IPNI is the consideration of farmer typology when generating strategies to address nutrient management in farms. An IPNI study on typology revealed that the use of fertilizers and other inputs used by farmers, is
strongly influenced by the resource endowment of a farmer, as well as a combination of other socio-economic determinants. Therefore, categorizing farmers on the basis of various socio-economic parameters allows for the design of realistic and effective intervention strategies.

**Takeaway:** A typology based approach to categorizing farmers will allow for the design of an effective and successful technological intervention.

**Indian Council of Agricultural Research (ICAR)**

The Indian Council of Agricultural Research is an autonomous organization under the Department of Agricultural Research and Education (DARE) of the Government of India’s Ministry of Agriculture and Farmers Welfare. There are over 100 ICAR institutes and 71 agricultural universities spread across the country, making it one of the largest national agricultural systems in the world. ICAR’s mandate is to coordinate, guide and manage research and education in agriculture in India. The following information is from an interview with scientists at the ICAR Soil Conservation Center near Dehradun, Uttarakhand. Scientists at ICAR that we interviewed were in strong agreement that the wealth of information available with state agricultural universities was a great resource for the generation of recommendations. They further agreed that the biggest challenge impeding a successful soil testing technology was a lack of knowledge among farmers regarding the proper techniques for soil collection and fertilizer management. Although the management of KVKs fall under the mandate of ICAR, interviewees’ impression of KVK soil labs in India was poor, as was their impression of mobile soil testing systems that exist in the market without customized recommendations. They also offered additional suggestions for expansion of a testing solution to materials such as manure and cow dung, which are increasingly gaining popularity as fertilization materials, as the demand for organic produce rises.
MS Swaminathan Research Foundation (MSSRF)

MSSRF is a non-profit trust foundation that aims to "accelerate [the] use of modern science for agricultural and rural development for development and dissemination of technology to improve lives and livelihoods of tribal and rural communities". The foundation runs a number of programs that explore ways of adopting science and technology to address practical problems faced by rural populations in agriculture, food and nutrition. The following information is from an interview with Dr. Ajay Parida, Executive Director of MSSRF. The interviewee listed the following five factors as the biggest challenges in agriculture today: Uncertainty in rainfall patterns, post-harvest losses, a need for food processing technologies, a lack of mechanization, and the migration of youth away from farming. He further emphasized that these problems do not exist in isolation, rather they interact and compound in intensity. For instance, the migration of youth away from agriculture has resulted in a dearth of farm labor resources, thereby increasing the need for mechanization in agriculture. He highlighted information dissemination as a key way to sustain interest in the field of agriculture, citing the Indian Meteorological Department’s initiative to disseminate weather alerts via text message as a positive success. Additionally, he mentioned that farmers tend to share information between themselves, and that members of farming communities tended to be highly inter-dependent and social.

2.2 Interactive Workshops

A series of design workshops were conducted to further engage directly with the end user in an interactive, group setting. These workshops were conducted in January and August of 2015, with the help and coordination of the Deshpande Foundation and The Himmothan Society.
2.2.1 Workshop Design Principles

In planning the execution of the workshop, the following design principles were taken into account:

Tone

The tone of the workshop first and foremost had to be respectful and amicable in order to facilitate open and honest discussion. For all workshops, a local leader within the NGO was deemed the workshop coordinator given their previous rapport with the community, ability to speak the local dialect, and understanding of local culture, tradition, gender roles, and social norms. This coordinator was responsible for all explanations of the activities, encouraging positive group morale, and ensuring that everyone was engaged.

At the start of each workshop, locally sourced popular music was playing in the room as the users walked in to immediately create a positive atmosphere. In order to create a sense of community and break down social barriers, icebreakers were subsequently conducted, wherein all workshop participants and coordinators shared their favorite food or Bollywood movie.

Finally, whenever possible, it was made clear that the mission of the workshop was to help them become better farmers. By reminding the participants of the mission and creating a positive and cordial tone, we were able to extract farmers’ honest feedback.

Group Size

For this research activity in particular, it was essential that we chose an appropriate number of participants. Too large a group could become chaotic, loud, and a logistical challenge. Too small a group could become too narrow in scope. Through practice sessions, it was determined that the best ratio of participants to workshop coordinators was 5:1, such that each coordinator could be in charge of a group of five, along with the help of a translator.
In addition to group size, we made it an intentional effort to plan productive groups. Prior to each workshop, we communicated with the local NGO of interest to incorporate users across different demographic spectra - across age, gender, landholdings, educational background, and family size. We also asked the NGO to invite users that represented both "extremes and mainstreams" so as to learn from extreme behaviors that challenge the status quo of smallholdings farming.

Establishing a shared reference frame

In order to extract accurate information from all workshop activities, it was essential that all participants share the same reference frame. Such a reference frame included not only the details of the activity of interest - i.e. whether it was group or individual work, how much time the activity would last, etc - but also what knowledge would be required in order to perform an activity. If, for example, the activity required users to draw on previous knowledge of other analogous agricultural devices, the workshop coordinators or translators would ensure that all users were familiar with such a device and could articulate in their own words what they were envisioning. If there was a word or phrase that was confusing to the participants, the workshop was designed with frequent call and response checkpoints to ensure that all users were on the same reference frame. By avoiding assumptions of previous knowledge and maintaining frequent feedback mechanisms between the users and the workshop coordinators, we were able to encourage empowered participation.

Making ideas visible and tangible

From initial farmer interactions, it became clear that they did not respond well to hypothetical scenarios, but rather preferred concrete examples and questions. With this feedback in mind, we designed workshop activities to target a specific critical question of interest. In the case of questions that did try to engage more hypothetical scenarios ("what would your ideal soil diagnostic device be?"), we encouraged farmers to draw on concrete examples or experiences within their own lives to better perform the activities ("what is your favorite agricultural device that you own and why?").
Being cognizant of social and cultural norms:

As outsiders, it was essential for us to try to be proactive in addressing social and cultural norms. On our end, this manifested itself in many ways. We dressed accordingly. We addressed those older than us with a respectful suffix, "ji". We thanked participants in a traditional fashion with our hands clasped together. It was anticipated that we would not fully be able to learn all the social norms, but by studying them, asking our NGO partners, and being cognizant of them on the ground, we were able to assimilate as best as possible.

The importance of these social and cultural norms was further amplified in the rural agricultural communities from which participants came. In these communities, social hierarchy is very much built upon demographic traits such as age, gender, landholdings, literacy, and education level. Thus, in order to achieve a successful workshop, we tried to be proactive in foreseeing such issues by encouraging self-selection of groups rather than pre-selection of groups before demographic data had been collected. In addition, it was made very clear to the main workshop coordinator encourage all voices to be taken into account, and that no voice should overpower another.

2.2.2 Workshop Activities

With the above principles as the fundamental guideline, workshop activities were designed with the goal of understanding not only the users’ main pain points and needs, but also to gauge feedback on prototype designs. Through these workshops, the user’s voice was incorporated throughout, feeding an iterative process of ideation, modeling, and user testing. These activities were designed and executed in coordination with Soumya Braganza and Jasmine Florentine, Masters student in Mechanical Engineering and Product Design.
Workshops (Round 1)

The first set of workshops, which took place in January of 2015 in Hubli, Karnataka were focused on gauging the pain points of current soil testing methodologies, determining the main user needs, and distilling those needs into the required product attributes for a new soil testing system.

Workshops consisted of several interactive activities conducted over a four-hour period. Over the course of three separate workshops, variations of specific activities were introduced to simultaneously study the effect of different activity executions on the quality of feedback received. Each workshop was organized into six different exercises, further described below.

The order of the exercises was intentional. At the onset of the workshop, we wanted to prepare the group with more casual discussions that users would find easy to speak about. The casual, communal nature of this section of the workshop was intended to establish a shared sense of purpose across participants and coordinators alike.

The most important exercises were at the latter end of the workshop, at a time when users would feel not only most comfortable with us, but also have enough contextual knowledge and discussion to provide the highest quality feedback. In addition to importance, the chronology of the workshop also matched that of the soil testing process itself - thereby allowing users to maintain a shared analogy with respect to their own soil testing experiences.

- **Introductions and Project Purpose:**

At the start of the workshop, we introduced ourselves and gave a short review of the project and workshop. Intentionally, the project overview remained vague so as not to limit the scope conversation.

The workshop was specifically attributed to the MIT Tata Center as well as the Desphande Foundation, so as to separate the workshop from ourselves, and make the participants less likely to avoid critical feedback. Finally, the mission of the workshop was emphasized to be beneficial for the participants, that the
only right answer is an honest answer, and that ultimately we were there to learn from them and not the other way around. In this way, the notion of hierarchy was minimized.

Following the project purpose discussion, everyone shared their respective ice-breakers - specifically what their name was, what crop they grow, and what their favorite Bollywood movie was. Ice breakers helped lighten the mood and make participants more comfortable.

• Pain points:

The first activity was devoted to helping getting participants in a mindset conducive to discussing soil testing and brainstorming solutions. In an open-discussion format, participants first were asked to share the difficulties they face in general as farmers, and second, to ask them to narrow down those problems with respect to soil health. As farmers were speaking of their pain points, translators and workshop coordinators were recording audio and taking down notes to ensure that these pain points could be converted into user needs for later stages in the design process. In addition to concerns about soil health, the following is a summary of the main pain points identified:

1. **Water**: Regardless of soil health or fertilizer purchased, plants cannot grow without adequate water. The majority of crops in the region require irrigation (rice, sugarcane, chilly, groundnut) but water pumps and systems are power intensive and expensive. Thus, users must rely on rain-fed irrigation of their crops. Rainfall is unpredictable, and since droughts have intensified over the last decade, users find it difficult to navigate risk given the unpredictability of climate patterns.

2. **Lower yields over time**: Across the board, farmers reported crop yields worsening over the past few years, however no specific causal factors were identified.

3. **Labor**: The unavailability of labor in agriculture was a frequently cited
issue, partly due to the migration of youth in agriculture to cities for work. The majority of farmers interviewed mentioned labor intensive tasks such as sowing and harvesting as a problem.

4. **Fragmented landholdings:** Over time, the average size of land holdings in India has been falling, due to fragmentation as land owners divide up their properties between their children. Fragmentation raises issues such as difficulty in scaling up production techniques, and difficulty managing land fragments in locations far from each other.

**Takeaway:** While soil health remained a serious pain point for farmers, issues related to water and drought were most concerning to them.

- **Product Attribute Exercise:** The product attribute exercise was the first structured element of the workshop. We conducted this exercise in three different iterations for different workshops but the goal was the same: to have users identify a hierarchy of product attributes such as accuracy and cost.

Given that soil diagnostic technologies were not fully available or used by the participants, we first asked users to think about their favorite products in their homes or on their farm, share aloud why the valued it, and correspondingly, what attribute they found most valuable. While it was known that product attributes vary across products, we were most interested with participants' rationale as to what they value in products and why. Three variations of this exercise are described below:

1. **Product Attribute Cards:**

   This exercise involved users ranking a set of pre-made pictographic cards (Figure 2-5) designed by Jasmine Florentine, depicting specific product attributes. The visual aspect of these cards was made so as to accommodate for illiteracy amongst participants as well as leverage visual imagery to reinforce the meaning of the attribute to the users. For the exercises,
participants were split up into groups of five and each given a set of five cards - depicting attributes such as cost, durability, reusability, time required, and labor intensiveness. Participants had five minutes to review the cards and ask the translators any questions they had about any of the card meanings or ambiguities. Then, in iterations of 30 seconds, the users were asked to get rid of the card they least cared about and put it in a bin in the center of the group. Translators and coordinators collected the bins after each round and ranked the cards 5-1 respectively by round, with 5 signifying least desirable attribute. The 30 second time period was intentional so as to ensure users acted on intuition and gut feel rather than logical cognitive processes.

Figure 2-6 shows the resulting product attribute rankings of farmers from the first round of workshops. A higher average ranking implies a lower
value for that attribute. The data shows that users value product attributes like durability and reusability of a product, and are willing to trade off cost for these attributes. This finding was somewhat unexpected, given that the common approach to designing for resource-poor communities involves minimizing cost as the primary concern. The important lesson from this finding was to not underestimate user's expectations, and therefore avoid designing an inappropriate solution that would compromise quality for cost.

**Takeaway:** Users are willing to trade off cost for product attributes related specifically to longevity, durability, and reliability.

2. **Product Attribute List:** In this exercise, the attributes were written on the board in English and in Kannada (Figure 2-7) with their respective definitions. The moderator discussed each of the definitions one by one so as to reinforce a shared reference frame. Similarly, groups were divided up into five participants and users were to rank each attribute of either "low," "medium," or "high importance" and describe to the translator their rationale.

3. **Product Attribute Tradeoffs:** This iteration was designed to gauge
the types of tradeoffs participants make when purchasing an agricultural product. Tradeoff pairs such as a cost versus durability and accuracy versus simplicity were introduced in the context of a hypothetical situation: i.e. you are choosing between two tractors, a more expensive one with a brand you trust or a less expensive one of a knockoff brand: which do you chose and why? Translators then relayed the information of the preferred attribute and rationale to the note takers in each group, who marked the preferred attribute a 1 and the other a 0.

• Soil Collection Methods: The purpose of this exercise was to take the users through the chronology of the soil testing process, starting from soil collection. Three types of prototypes were prepared, and three methods of presentation were executed for the three respective workshops, described below:

1. Storyboards: A series of images were prepared depicting the user steps of the soil collection process. The images were projected onto a large screen in the center of the room, and the moderator walked through the storyboard one by one, explaining the step, and opening up the room for group discussion.

2. Coordinator roleplay with prototypes: The moderator and the main workshop coordinators roleplayed the soil collection process with foam, cardboard, and paper props (Figure 2-8). The moderator described each point of the soil collection process, and paused afterwards for a group discussion.

3. Participant roleplay with prototypes: Participants themselves role-played with the props outdoors. For example, for the method that involved digging a hole in the ground, a participant volunteer actually dug a hole out in the garden with a shovel provided. In this way, the users were able to viscerally engage and experience a mock version of the soil collection process, and therefore be able to comment on their feelings and pain points more effectively.
Figure 2-8: (Left) Storyboards depicting soil collection methods, (Right) Farmers participating in role play exercise with outdoor props.

The overwhelming consensus among farmers was that soil collection was not a difficult process at all. This came as a surprise to us, given that the task of digging 15 holes is labor intensive and difficult. However, given the laborious nature of their day to day work, farmers were able to quite easily do this, indicating that the soil sample collection part of the cycle was not of great concern.

**Takeaway:** Soil collection method was not a concern, given the laborious nature of farmer’s day-to-day work. However, quality control may remain an issue, therefore an educational informational card on proper soil collection techniques should be distributed along with the device.

- **Soil Test Cards:**

For this exercise, we created a variety of looks-like paper prototypes that demonstrated different colorimetric techniques of soil detection and presentation of the result. Given that a colorimetric based approach was the most likely form of transduction mechanism at this stage of the project, we specifically wanted to focus on whether users found this solution intuitive to use. The paper mockups
Figure 2-9: Female participants working together to decode colorimetric sensor prototypes.
created showed colorimetric readouts of N, P, K, and pH values in the form of blocks, circles, and distance-based 'lines', shown in Figure 2-9. Participants were divided into subgroups of five and asked to decode a series of fake readouts, depicting different concentrations of soil nutrients. After evaluating the soil nutrient concentrations, participants were asked to evaluate the difficulty of decoding it before moving to the next card. Workshop coordinators observed users as they worked with each other to decode the card, and compared their qualitative observations of user difficulty with those reported.

35% of participants reported that they preferred the sensor with maximum colored area (four quadrants colored for each nutrient), since it was easier to read. The remaining sensor mockups received about equal rankings for preference. Notably, there was some level of ambiguity in reading and interpreting color based results, and participants within a group often disagreed about color-matching.

*Takeaway:* Although error rate and self-reported ease were satisfactory; qualitatively, users found colorimetric methods to be ambiguous, subjective, ambient light-dependent, and requiring extra instruction.

- **Open Discussion and Close:** The final part of the workshop consisted of an open discussion as to what activities they found particularly engaging or useful, and what suggestions they had for future workshop iterations. It also consisted of demographic data collection for which we used to match to individual qualitative and quantitative results from the workshop. Lessons from this discussion were applied to subsequent workshops in order to improve the quality of interaction.

**Workshops Round 2**

The second set of workshops occurred in August of 2015 and took place in two locations: Hubli, Karnataka and Dehradun, Uttarakhand. In expanding to a second
Figure 2-10: (Right top) Paper mockups of colorimetric soil testing sensors, (Right bottom) Soil card to interpret color-based sensor reading (Left) Soil card to interpret distance-based sensor reading.
locations, we hoped to garner a greater diversity of user feedback and determine whether our soil diagnostic system would be appropriate for different types of agricultural communities.

The main purpose of these workshops were to generate user feedback on a set of ion selective electrode based user experience dummy prototypes, and to determine the preferred input and output communication mechanisms for the recommendation system. These mechanisms refer respectively to the method in which users send their soil diagnostic result to a central database and subsequently the method in which they receive their soil fertilizer recommendation result.

A total of four workshops were conducted, each approximately 3 hours long. The introductions, discussion of pain points, and conclusions in this workshop were the same as previously described, with the central activities varying. These are described below.

- **Demonstrative Video:** Prior to the workshops, we created a short two-minute demo video (Screenshot of video shown in Figure 2-11) highlighting the various steps of the user experience. This video started at a stage after which the user had a composite soil sample from the farm, and subsequently highlighted (i) adding an extractant solution to release anions from the soil (ii) dipping the ion selective electrode strips into the aqueous soil solution (iii) waiting for the sensor to calibrate (iv) interpreting the soil diagnostic result from the reader (v) reading the crop code from the back of the device and (vi) creating alphanumeric codes representing the respective N, P, K, pH values and crop type of the user, to be used as an input to the recommendation system later on. The moderator allowed users to watch the video on their own once, and then played the video again, pausing at each step in the process to explain and open it up to group discussion. The video primed users for the next exercise, in which users interacted with a 'works-like' prototype of the device.

- **Product Demo** A set of paper-based prototypes were created with an Arduino microcontroller system acting as the ion selective electrode strips and reader re-
Figure 2-11: A screen shot of the product demo video shown to the farmers in the beginning of the Design Workshops, Round 2. Users received a works like prototype of a paper based reader with an arduino microcontroller, a spoon, an aliquot of dried and seived soil, extraction solution, and a mixing cup from which to take the measurement.
spectively. Prototypes were created to simulate a fake test result that mimicked the actual functionality of the sensor. In each workshop, the soil testing process was demonstrated to users using a fake soil sample, and fake extractant solution. Users were instructed to provide feedback to translators and note takers on their perception of ease of each step. User feedback included comments on the size of the device, location and structure of information printed on the device (N, P, K, pH), and brightness of LED display, all of which directly fed into design specifications for the device.

• **Input/Output Mechanisms Roleplay:** Once users had the chance to interact with the dummy works-like prototype, they each had a precoded alphanumeric code representing their respective N, P, K, pH values and crop type. Using that alphanumeric code as an input, we role-played three different methods for sending that information to the central database: via postal service, text, and
through a website. The role play involved acting out the specific interaction method under discussion (such as looking at the alphanumeric code, and texting it out to a number) accompanied by a verbal description of each method by the translator. After each role play, the moderator facilitated a group discussion on what users found appealing or difficult. At the end of the exercise, users ranked their favorite input method in decreasing order of preference.

The same activity was repeated for the soil fertilizer recommendation output. We role-played three methods: postal service, voice message received on the phone, and an interactive web based GUI. Feedback and rankings were similarly collected for the output mechanism. Results of this exercise are shown in Figure 2-13, in which a lower ranking is indicative of a higher preference for that mode. Based on the role play and verbal description of the interaction mechanism, users expressed a preference for the text message as an input mechanism, and the voice recording as the preferred format in which to receive a recommendation from the system. In general, older farmers preferred text based recommendations that they could read at leisure later, while the younger demographic was more comfortable with using text messages.

- **Interpreation Exercise:** In order to determine the relative efficacy of text or voice as a mode for relaying soil fertilizer recommendations, this activity asked
participants to either read a text-based recommendation or listen to a voice-based recorded version. A group discussion followed, asking users specific information about the soil recommendation they had just read or heard, such as "What was your Nitrate concentration?", and "How much urea should you apply on your farm?". In general, farmers were seen to perform better at interpreting written recommendations, as opposed to being able to follow voice-based instructions. Notably, although many users ranked a high preference for the voice recording mechanism in the previous exercise, the majority of them changed their mind after experiencing the voice recording first hand.

**Takeaway:** Farmers found it much easier to comprehend recommendations provided to them in text form, as opposed to hearing detailed instructions delivered to them in a voice recording. This is in contrast to preferences expressed without a demonstration.
Cost Threshold Exercise: In the final exercise, users specified a cost threshold for the system. By this stage in the workshop, users were able to envision the whole system including the core technology and recommendation system, and were therefore able to gauge the value of such a soil diagnostic solution in their lives. Given that the technology consisted of disposable diagnostic ion selective electrode strips and a fixed reader, we asked users to independently price their value for each component. On a scale of 1-1000 Indian Rupees, users circled where they felt each respective component should be priced. In order to generate as realistic a price point as possible, we emphasized that there was no right or wrong answer to this question. Further, participants were informed that this exercise was voluntary, and that they need not specify a price if they were not comfortable doing so. On average, users specified a cost threshold of approximately 500-600 INR for the fixed cost of the reader, with a variable cost of 15-60 INR for each sensor strip.

**Takeaway:** Users specified a cost threshold of approximately 500-600 INR for the fixed cost of the reader, with a variable cost of 15-60 INR for each sensor strip.

Product Contract

This section is a distillation of lessons from the interviews and workshops previously described into specific attributes of the product and system. These attributes, summarized in Figure 2-15, directly translate into design guidelines for the product and system, which determine the research direction and ultimate system design.
<table>
<thead>
<tr>
<th>Use case:</th>
<th>Rural small landholding farmers with adequate access to water resources and fertilizer distributors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Use case:</strong></td>
<td>Twice a year before planting in the Kharif and Rabi seasons, users take a composite soil sample representative of their farm, perform a soil test, and receive a customized soil fertilizer recommendation.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Product Contract</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>User data</strong></td>
<td><strong>User need</strong></td>
</tr>
<tr>
<td>&quot;Accuracy is the most important aspect of a quality soil test&quot;</td>
<td>Can accurately measure macronutrients and pH in soil</td>
</tr>
<tr>
<td>&quot;The current system is too slow, if I were able to get a result on my own fairly easily, I would do it&quot;</td>
<td>Can perform test on their own</td>
</tr>
<tr>
<td>&quot;I had to travel 50km to the local KVK and I never got a soil test result back&quot;</td>
<td>Can be used on the farm</td>
</tr>
<tr>
<td>&quot;We need more information about how much fertilizer to use, what crops to grow, and how to use inputs effectively&quot;</td>
<td>Can provide actionable feedback to improve soil health</td>
</tr>
<tr>
<td>&quot;If the task takes me too much time I will not care anymore&quot;</td>
<td>Can provide soil test results quickly</td>
</tr>
<tr>
<td>&quot;I don't trust anyone but myself, and so I want to do the test myself&quot;</td>
<td>Can be used by an individual farmer</td>
</tr>
<tr>
<td>&quot;I don’t mind paying if it’s good quality&quot;</td>
<td>Can easily be afforded</td>
</tr>
<tr>
<td>&quot;I can afford to buy this only once so longevity is important&quot;</td>
<td>Can last a long period of time over multiple uses</td>
</tr>
<tr>
<td>&quot;We are used to spending many hours a day working in the field&quot;</td>
<td>Can provide result with minimal physical activity</td>
</tr>
</tbody>
</table>

Figure 2-15: Product contract describing attributes that determine technical and system design constraints.
Chapter 3

Sensor Selection and Design

Chapter 2 culminated in a solution agnostic framework (i.e. the product contract), mapping user needs to desired product attributes and ultimately, technical constraints. With the product contract constraints in mind, the first step in the technological development process was brainstorming many (many) ideas, and then downs-selecting those into the most fitting. By deferring a final technology direction until after preliminary fieldwork was complete, we were able to achieve a "market driven" solution rather than one resulting from "technology push".

Ultimately, ion selective electrodes were proposed as the most appropriate solution. In addition to an overview of the brainstorming phase, this section reviews ion selective electrodes in terms of their fundamental operation, prior art, and potential use for multi-analyte soil analyses.

3.1 Brainstorming

The resulting list gives a brief overview of some of the ideas brainstormed throughout the first phase of the project. Notably, at this stage, we deferred judgement as to whether or not the idea would ultimately be technically feasible, but rather sought to explore the solution space laterally, undeterred. In this way, seemingly outlandish ideas remained in consideration so as to provide inspiration for future technical directions.
Figure 3-1: A dye-based microfluidic device for HIV detection.\textsuperscript{19}

Figure 3-2: An SEM image of the Morpho Didius butterfly wing. Structural color arises from the interaction of light with the alternating layers of differing refractive index on the scales.

1. **Colorimetric dyes**: Inspired by Whitesides et al.,\textsuperscript{19} such a solution encompassed filter paper doped with dyes which change color upon interaction with an analyte.

2. **Photonic stacks**: Inspired by the structural color of a butterfly wing, this solution consisted of nanostructured surfaces which change color in accordance to a change in the refractive index of the surrounding solution.

3. **Plasmonic nanorods**: This idea built off the photonic stack idea, but leveraged additional amplification due to plasmon resonance of metal nanorod forests.
4. **Chemically-modified substrates**: Inspired by the pattern of a dried droplet of coffee (Figure 3-4), this approach consisted of a chemically modified surface controlling the position of the solution front of a drying aqueous soil droplet. Specific activated regions would be responsible for different analytes of interest. After a soil droplet would dry it would create a unique "fingerprint" of the chemical makeup of the soil - later be transduced via optical analysis.

5. **Enzymatic flow assays**: Inspired by the ELISA method and pregnancy strips, such a solution entailed analytes from the sample attaching to a surface immobilized with enzymes specific to the analyte of interest. Then, a further specific antibody is applied over the surface so it can bind to the antigen. This antibody is linked to an enzyme, and, in the final step, a substance containing the enzyme’s substrate is added. The subsequent reaction produces a detectable signal, most commonly a color change in the substrate.

6. **Fluorescent bacterial substrates**: Inspired by the glow in the dark plants inoculated with fluorescent bacteria responsive to environmental changes, this solution includes bacterial colonies on a filter paper substrate which exhibit chemi-luminescence in the presence of particular analytes of interest.

7. **Origami electrophoresis**: This direction was inspired by a publication on a
low voltage origami electrophoresis device. The devices uses multiple, thin filter paper layers as the porous electrophoretic medium (Figure 3-5). A low voltage battery supplies the electric field which separates out fluorescently-labeled analytes introduced via a slip layer in middle layers of the device.

8. Ion selective electrodes: This solution involves an ion-selective membrane that generates a potential proportional to the logarithm of the chemical activity of the analyte of interest.

3.2 Downselection

The downselection process was driven by a socio-technical analysis consisting of what made most sense for the user, as well as what was most feasible from a technical perspective. The product contract was used as a guideline throughout, in combination with back of the envelope calculations and experiments exploring feasibility.

According to fieldwork in India, the success of colorimetric methods (dyes, photonics, plasmonics) required ensuring that the subjectivity of color perception does not impede accurate understanding of the result. In this way, we sought to see if
there would be a microfluidic based approach to pre-amplify the analytes to further increase optical range of color seen by the user. We also investigated an approach in which a color space would represent a value, i.e. a ternary combination of colors could perhaps expand the optical range for a range of analyte concentrations.

In the end, however, all three colorimetric solutions were abandoned. Colorimetric dyes were the first to go due to the exponential increase in complexity of the user experience as more analytes (N, P, K, pH, etc) were involved. Given that each analyte required a different assay with different extraction solutions, dyes, and incubation times - it became increasingly difficult to imagine an device which could parallelize chemical assays without vastly increasing the number of steps in the user process. Furthermore, stability and toxicity of the dyes posed additional risks that made us conclude this approach was not ideal.

Plasmonic, photonic solutions, and enzymatic assays were the next to be omitted. The main issue with these approaches was the lack of specific binding agents that could selectively bind the analytes of interest. While these binding agents are widely available for larger, biological macromolecules (i.e. glucose, lactose, proteins), there were few antibodies or enzymes that showed particular selective affinity to soil ions (potassium, calcium, etc). Stability and lifetime of such substrates (enzymatic activity is highly temperature dependent, for example) posed an additional concern.
For photonic structures, a preliminary back of the envelope demonstrated that in the case of a binding event, without pre-amplification of the analyte concentrations, the change in color would be barely perceptible by the human eye. A snapshot of the calculation is found below. It uses the fundamental theory of the refractive index of mixtures for compounds a and b ($\eta_a$ and $\eta_b$), at a specific concentrations ($\phi$ and $(1 - \phi)$, respectively). The resultant color ($\lambda$) arising from a multilayer stack of varying two different refractive indices ($\eta_1$ and $\eta_2$) and thicknesses ($d_1$ and $d_2$) with light coming in at an angle ($\theta$) is approximated:

$$\eta_{eff}^2 = \phi \eta_a^2 + (1 - \phi) \eta_b^2$$  \hspace{1cm} (3.1)$$
$$m \lambda = 2 \left( d_1 \sqrt{\eta_1^2 - \eta_b^2 \sin^2(\theta)} + 2 \left( d_2 \sqrt{\eta_2^2 - \eta_b^2 \sin^2(\theta)} \right) \right)$$  \hspace{1cm} (3.2)$$
$$\lambda \approx \eta \ast d$$  \hspace{1cm} (3.3)$$
$$\eta_{eff} \approx \sqrt{\phi}$$  \hspace{1cm} (3.4)$$
$$\frac{\partial \lambda}{\partial \eta_{eff}} = \frac{d}{2 \ast \sqrt{\phi}}$$  \hspace{1cm} (3.5)$$
$$\Delta \lambda = \frac{d}{2 \ast \sqrt{\Delta \phi}} \ast \Delta \phi$$  \hspace{1cm} (3.6)$$

As demonstrated in the Figure 3-6, the minimal perceptible color change of a human eye is about 10nm. With this in mind, the final equation in the calculation can be calculated for the color change associated a nitrate solution in water with 200nm stack spacing. For a 10nm shift, the change in nitrate concentration would have be over 200ppm, which is too much for a range of nitrate concentrations in soil typical of sub-1000 ppm. And furthermore, there would be an angle-dependence of the photonic stack’s color, which would serve to confuse the user. Thus the only way this approach would be viable would be through the use of a colorimeter at an angle normal to the substrate surface, perhaps adorned to a users’ phone or iPhone, but this would increase cost significantly.

The additional sensitivity attributed to surface plasmon resonance of plasmonic structures offered a potential fix to the aforementioned hurdle with photonic stacks.
Figure 3-6: Pairs of colors at 10nm shifts with respect to one another. Notably, given our eyes' decreased sensitivities at the extrema of the visible light spectrum, even 10nm shifts would not suffice.

But as mentioned prior, the lack of available binding agents, along with the costliness of the light source and detector for plasmonic systems, made this approach not viable.

Next to go was origami electrophoresis. While it was exciting that such an approach seemed to only need a 9V battery, some binder clips, and filter paper, the lack of fluorescing binding agents specific to the soil analytes of interest made this approach difficult to achieve. Furthermore, such a solution would require the use of some iteration of a fluorometer, increasing cost and decreasing the ease of use of the user experience. Of course, with the advent of selective binding agents and a low-cost fluorometer easily retrofitted to a user's mobile phone, this approach could be possible, but difficult nonetheless.

Finally, the bacterial approach was concluded to not only be out of the scope of our technical abilities, but also technically challenging due to the temperature, pH, light, and humidity sensitivity of the bacterial colonies. For these reasons, this approach was abandoned.

In the end, it was determined that ion selective electrodes would not only be the most fitting solution from a user standpoint (i.e. affordability and usability) but also from a technical standpoint. The main challenges for ion selective electrodes are minimizing cost of the reader responsible of transducing voltages across the ion selective membranes into chemical concentrations and reducing the number of steps in the user experience (i.e. soil sampling, ion extraction, filtration, calibration, etc). Of the ideas found feasible, a tradeoff chart comparing relative cost and ease of use is represented in Figure 3-7.
Figure 3-7: Cost and usability tradeoffs of some of the brainstormed ideas, excluding those found infeasible and including benchmarked current solutions - colorimetric kits and government sanctioned soil labs. Relative attractiveness of a solution can be found increasing diagonally from bottom left to top right. Ion selective electrodes were chosen in the end due to their technical feasibility, ease of use, and relatively low cost.
3.3 Ion Selective Electrode Review

Ion selective electrodes (ISEs) are one of the most common electrochemical sensors for physiological analysis, manufacturing process control, and - as it pertains to low cost soil diagnostics - environmental analysis. According to Bühlmann et al, one billion tests are taken annually with ISEs, making them a preferred testing methodology for trace ion detection. In typical configurations, the ISE is constructed such that the sensing layer lies between an internal filling solution with constant ion activity and a sample solution for which the ion activity is unknown. These are called "symmetric" ISEs. Although symmetric ISEs are the main standard, they suffer from high costs, temperature sensitivity, evaporation of the inner filling solution, and oversized physical footprints. It is necessary, therefore, to replace the state of the art with miniaturized all solid-state ISEs. Among the various types of such ISEs, this literature review focuses attention mainly on neutral ionophore-based all solid state ISEs.

Much of the work with respect to ionophore-based transduction is dedicated to achieving lower and lower detection limits, especially useful for trace analysis in the micro to nano-molar range. For the purpose of this review, we will cover (i) the fundamental theory, anatomy, and characteristics of two dimensional, neutral ionophore based ISEs, (ii) the history of their discovery and development, (iii) common constructions and manufacturing techniques, (iv) new developments with respect to lowering the detection limit and improving selectivity, as well as (v) recent developments with respect to ISEs for soil analysis.

Not to be overlooked, however, is the importance of a stable reference electrode (RE) to accompany the working electrode (WE) part of the ISE. As this review pertains mostly to potentiometric ISEs, in order to accurately measure the potential of such a WE, the RE must remain at a constant voltage - irrespective of temperature, chemical environment, or mechanical stresses. Thus, in addition to the analysis of working electrode ISEs, a short review a planar all solid state REs is provided.
3.3.1 Construction

Prior to discussing the underlying response mechanism, it is helpful to highlight the typical construction of an ISE and the purpose of each component.

First, there is the ion selective membrane (ISM). While ISEs based on solid crystalline, glassy carbon, glass, ceramic, or liquid membranes are common, the archetypical sensing layer of ISEs is comprised of a polymer matrix with an organic backbone. Particularly important to this component is a minimized glass transition temperature, such that the polymer membrane remains sufficiently fluid at room temperature - permitting high ionic conductivity and free diffusion of active membrane components. The most widely employed polymer matrix material is poly vinyl chloride (PVC), because it offers low cost, thermal, chemical, and mechanical stability, as well as amenability to plasticization for sufficient glass transition temperatures. Beyond PVC matrices, silicone rubbers, and polystyrenes have also been used. Most often these polymers are prepared by dissolution in an organic solvent such as tetrahydrofuran (THF), and then solution casting on a solid support.

Due to typically high glass transition temperatures of the aforementioned polymers, they require a large weight percent addition of plasticizer. With required plasticizer-to-polymer weight ratios around 2:1, the membrane essentially becomes a viscous liquid comprised of vesicles of plasticizer and polymer phases, with all the active membrane components dissolved in the plasticizer phase. While this achieves the desired glass transition temperature below room temperature, these kinds of sensing layers suffer from non-ideal performances due to plasticizer leakage - which leads to degraded potentiometric stability and poor detection limits.

Recently, though, membranes based on acrylate and methacrylate derivatives have been suggested as "plasticizer-free" alternatives. Such plasticizer free alternatives also offer the advantage of ultraviolet photocurability, leading to increased manufacturability and minimized solidification times with respect to solvent-cast polymer membranes.

One of the most important membrane components of ionophore-based ISEs is the
Aqueous sample

<table>
<thead>
<tr>
<th>Ion Selective Membrane (ISM)</th>
<th>(PVC, Polyurethane, Poly-butyl-acrylate, etc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transducer</td>
<td>(CNT, conductive polymer, etc)</td>
</tr>
<tr>
<td>Solid Support</td>
<td>(Ag, Pt)</td>
</tr>
<tr>
<td>Conductor</td>
<td>(CNT, Ag, Cu, Al, Pt, etc)</td>
</tr>
</tbody>
</table>

To Potentiostat

Figure 3-8: Construction overview of typical ISEs, including all optional components. Form top to bottom: (i) the ISM establishes a phase boundary potential with the aqueous phase due to charge separation between the primary analyte and its counter ion in solution (ii) the transducer layer undergoes an electrochemical reaction at the specified potential to produce an electron flux (iii) the solid contact stabilizes the potential in the transducer layer and provides extra hydrophobicity to avoid water layer formation and finally (iv) the conductor conducts electrons to the potentiostat for a final reading. Note: it is possible to have functional ISEs without the transducer or solid support layers.
Figure 3-9: (Left) The neutral ionophore, valinomycin, which selectively complexes with potassium (K+) and (Right) Potassium tetrakis 4-chlorophenyl borate, a typical salt exchanger used in ISE membranes. It is comprised of a hydrophobic aromatic tetrakis salt complexed with a hydrophilic potassium ion.

The final component inside the sensing layer is a lipophilic salt. The purpose of this component is to increase the ionic conductivity of the membrane, maintain charge neutrality, and most importantly maintain permselectivity - that is, either cations or anions can diffuse into the membrane without co-extraction of the respective counterion. Tetradecyl ammonium salts are typically used for cationic sensors, while for anionic sensors, tetraphenylborate salts are chosen.

Given that sensor performance is highly sensitive to the specific ratio of ionophore to ionic sites, it is important to identify the optimal ionophore/salt ratio for a specific
ion-ionophore stoichiometry. In practice a series of membranes with different ionic concentrations can be tested for optimal performance.

### 3.3.2 Response Mechanism

#### The Phase Boundary Potential

Potentiometric ISEs sense the analyte of interest via a changed potential with respect to a constant reference electrode potential. ISE responses toward an analyte are typically defined under the condition of thermodynamic equilibrium at the sample/membrane interface, as well as the condition of no net ionic flux. Above their detection limit, their responses can be described by the Nernst equation:

$$E = E_0 + \frac{RT}{z_i F} \ln a_i$$

(3.7)

Where $E$ is the measured potential, $E_0$ is a constant potential, $R$ is the universal gas constant, $T$ is the absolute temperature, $F$ is the Faraday constant, $z_i$ is the charge on ion I, and $a_i$ is the activity of ion I.

Nernst formalism defines a linear relationship between the logarithm of the analyte activity and the potential at the organic/aqueous phase boundary. Thus, for a given ISE, a calibration curve can be generated by plotting the logarithm of the ion activity versus the measured potential. Since the potential is actually dependent on the activity rather than the concentration, Debye-Hückel theory is applied to convert between the two values to accommodate for reduced activities at higher ionic strength sample solutions. The Debye-Hückel equation is as follows:

$$\ln a_i = -A * z_i^2 * \sqrt{I}$$

(3.8)

Where $A$ is a constant that depends on temperature (i.e. $1.172 \text{ mol}^{-1/2} \text{kg}^{1/2}$ at $25^\circ C$ for water), and $I$ is the ionic strength of the sample solution.
As described by Nernst theory, the slope of the response curve at 25 Celsius should be 59.2/z mV/decade, where z is the valency of the ion of interest. So how does the Nernstian response come about?

In order to highlight this response mechanism in more detail, let us consider the formalism provided by Bühlmann et al.22 In this formalism, there exists an interface between a hydrophobic "organic" phase (i.e. the ion selective membrane) and an aqueous phase (i.e the sample). Upon addition of a lipophilic salt and the establishment of thermodynamic equilibrium - i.e. minimizing electrochemical potential gradients - between the two phases, the salt, comprised of the cation (C+) and anion (A-) diffuses into both phases. By Gauss’ law, bulk electroneutrality must be maintained, and therefore there will be equal concentrations of C+/A- in both the organic and aqueous phases.22

Due to the salt’s lipophilicity, it desires to be in the organic phase more than the aqueous phase. But as said before, the concentrations of the dissociated C+/A- in each phase must equal each other (electroneutrality condition).22 Only right at the boundary do the local concentrations of C+/A- differ. Given differing solvation energies in the organic phase (in this case, let’s presume that of C+ is lower), there will be an excess of A- in the double layer of the organic phase and an excess of C+ in the aqueous phase. The ratio of the concentration of A- and C+ within the double layer is given by the partition coefficient, which is dependent on the ratio of the respective energies of solvation of the two ions into the organic phase. The local charge separation at the interface between the two phases gives rise to the all important phase boundary potential (PBP) (Figure 3-7).

The PBP for the two phases containing a single-salt is therefore independent of the salt concentration22 (neglecting the scenario wherein high concentrations increase ionic shielding and reduce activity coefficients). To demonstrate this, let’s review the generalized PBP:
Figure 3-10: Schematic depicting the equilibrium distribution of a lipophilic salt comprised of hydrophilic cation (C+) and lipophilic anion (A-). The phase boundary potential arises at the interface between the aqueous and organic phases where there is charge separation of C+/A- due to the different energies of solvation of the respective ions in each phase.

\[
E_{PB} = E_{PB,i}^0 + \frac{RT}{z_iF} \ln \frac{a_{i,\text{aqueous}}}{a_{i,\text{organic}}} 
\]

(3.9)

Where \(E_{PB,i}^0\) is a constant depending on the energies of solvation of the ion in each phase,

The partition coefficient dictates a constant ratio of the concentration of the ions in the aqueous and organic phases. Thus, any addition of salt into the system may increase the respective values of \(a_{i,\text{aqueous}}\) or \(a_{i,\text{organic}}\) but the ratio between the two will remain the same, and therefore the PBP remains constant.\(^{22}\)

The Addition of Ionophores

But what if \(a_{i,\text{organic}}\) is constant, and \(a_{i,\text{aqueous}}\) is variable? The above equation reduces to:
In this case, the phase boundary potential would be logarithmically proportional to the activity of the ion of interest. This is characterized by the idealized "Nernstian" response mentioned previously in this section, with a slope of 59.2 mV/decade for monovalent cations, like potassium at room temperature. To have a perfectly Nernstian response, therefore, the activity of the primary ion in the bulk organic phase is constant and sample independent. Any sample dependence will yield non-Nernstian behavior.

With this in mind, let's add a neutral, potassium-selective ionophore, valinomycin (hereon named "L"), into the organic phase. When immersed in an aqueous solution of potassium chloride, there will be some - albeit small - KCl that diffuses into the membrane upon reaching thermodynamic equilibrium. Most of the potassium that does diffuse into the membrane complexes with valinomycin, that is, LK+. It is possible to write an equilibrium chemical reaction describing the formation of the LK+ complex:

\[
LK^+ \rightleftharpoons K^+_{\text{(organic)}} + L_{\text{(organic)}}
\]  

(3.11)

The concentration of free potassium uncomplexed with valinomycin in the hydrophobic phase can be calculated using the equilibrium constant of complexation, \( \kappa_{eq} \):

\[
\kappa_{eq} = \frac{[LK^+]}{[L][K^+]} \quad (3.12)
\]

\[
[K^+] = \frac{[LK^+]}{[L]\kappa_{eq}} \quad (3.13)
\]
By LeChatlier's principle, an increase in aqueous potassium increases the free potassium concentration in the organic phase, which in turn increases the complex concentration and decreases the free ionophore concentration. By equation 3.11, this means that the concentration of free potassium in the membrane varies with the concentration of aqueous potassium (that is, of course, until valinomycin is fully saturated with potassium ions in the membrane). Thus, while the ionophore facilitates the selective diffusion of potassium into the membrane phase, we still cannot achieve a Nernstian response purely by the addition of ionophore.\textsuperscript{22}

The Addition of Ionic Sites

In order to adequately achieve sample independence, one must add ionic sites in the form of a lipophilic ion, opposite in sign with respect to the primary ion of interest. For potassium, therefore, such a salt can be tetrakis 4-chlorophenyl borate. Due to the electroneutrality condition, the concentration of free and bound potassium in the organic phase must equal the sum of all anions in the organic phase - including anionic impurities in the polymer backbone. Assuming that the tetrakis anion is the only one
present in the organic phase, and that there is no leaching of the salt into the aqueous phase, this maintains that the concentration of potassium in the organic phase will be sample independent, "pinned" at the tetrakis anion concentration. A Nernstian response, therefore, will result.

Another benefit of the salt as mentioned previously is Donnan exclusion of the counterion in the aqueous phase. By having a lipophilic anion in the bulk, this increases electrostatic repulsion of any anions, and thereby prevents coextraction of the counterion from the organic phase into the aqueous phase. Such coextraction would result in sub-Nernstian behavior.

Notably, the concentration of ionic sites must be low enough so as to maintain a substantial concentration of free, unbound ionophore. Typically, molar ratios of ionophore to ionic sites should remain above 2:1 so as to ensure that upon equilibration with the aqueous, there remains more than half of the ionophore sites free. At ratios below this point, it is expected that the membrane performance will approach ionophore-free case containing only ionic sites.

The Typical ISE Measurement

A typical ISE response curve is found in Figure 3-12:

Beyond slope, another important parameter is the lower detection limit of ISEs. The IUPAC definition of the detection limit is the activity at which extrapolations of the two distinct linear segments of the potentiometric response cross.\textsuperscript{39} For measurements close to the detection limit, there exists an increased concentration of primary ions at the surface boundary layer due to transmembrane fluxes of primary ion from the membrane into the aqueous phase.\textsuperscript{40,41} The primary ions diffuse from either together with their counterions or in counter diffusion with an interfering ion from the sample.\textsuperscript{42}

While most ISEs have a limit of detection around 1uM, sub-nM detection limits have been realized by minimizing these trans-membrane fluxes of primary ion into the sample solution.\textsuperscript{43} For solid state ISEs, this can be done by anchoring the ionophore along the membrane backbone,\textsuperscript{44} conditioning with a low concentration of analyte
ions, or minimizing the ionophore-salt ratio to avoid the excessively high primary ion activities within the membrane. Notably, though, the salt concentration cannot be too low, as this would compromise the permselectivity of the membrane.

Of course, there is no such thing as a perfectly selective ionophore. Thus, ion selective electrode scientists quantify selectivity of ion selective membranes by measuring the potential of the ISE via the fixed interference method, matched potential method, or separate solution method. For brevity, the differences between the three methods will not be explained. Regardless of the method, however, the parameter of merit with respect to selectivity of the ISE is determined via the Nickolskii equation:

\[
E_{\text{measured}} = E^\circ_{PB,i} + \frac{RT}{z_i F} \ln (a_{i,\text{aqueous}} + k_{i,j} a_j^{z_j})
\]  

(3.14)

Where \(k_{i,j}\) is the selectivity coefficient of an interfering ion, \(z_i\) and \(z_j\). Notably, for negligibly small selectivity coefficients the Nickolskii equation reduces to the Nernst equation. Typically, selectivity is dictated by the respective energy of solvation of

Figure 3-12: A typical potassium ion selective electrode response. In this case, they achieve a Nernstian slope of 59 mV/decade and a limit of detection of \(10^{-6.6}\) M.
interfering ions due to non-negligible binding interactions with the ionophore chosen.

**Operating Principle of Reference Electrodes**

Although intense research effort has focused on the development and characterization of working electrode ISEs, the reference electrode remains an equally vital part of electrochemical sensors.

While conventional reference electrodes in a laboratory setting come in a variety of formulations - from standard hydrogen electrodes (SHEs) to mercury-based calomel electrodes - the most widely used reference electrode is the silver-silver chloride (Ag/AgCl) reference electrode. The reason for their widespread popularity is due to their low cost, temperature stability, simple setup, and amenability to a variety of sample solutions and solvents.

The Ag/AgCl reference electrode works as a redox couple with the silver chloride (AgCl) salt undergoing a reduction reaction in the presence of chloride ion. Given that the electrochemical potential associated with this reaction is linearly proportional to the logarithm of the chloride ion activity by a similar Nernst formalism, the potential of such reference electrodes can remain constant in the presence of a saturated chloride-containing electrolyte solution.

To understand this more in detail, the overall reaction at the Ag/AgCl electrode is presented below:

\[
\text{AgCl}_s + e^- \rightleftharpoons \text{AgCl}_s + \text{Cl}^-
\]  

(3.15)

Much like the phase boundary potential, the Nernst potential dictates the potential of the Ag/AgCl electrode as a function of the concentration of chloride ion in the surrounding electrolyte solution:

\[
EMF = E^0 + \frac{RT}{z_i F} \ln a_{cl}
\]  

(3.16)
For a saturated (3M KCl) solution, the potential of the Ag/AgCl electrode is +197 mV higher than the SHE potential (a universal reference system). Saturated KCl is typically used so as to minimize the electrode impedance, as well as to minimize the sensitivity of the electrode to any contaminant species often found in concentrations orders of magnitude lower.

To further enhance the stability of the electrode, typically a porous glass frit is added at the bottom of the reference electrode to minimize the rate of diffusive flux of electrolyte into the sample solution. The capillary pressure within the frit counteracts the diffusive flux of ions down their chemical potential gradient into the sample.

### 3.3.3 Prior art

**ISE Designs Throughout History**

It has been a half century since the first all-solid state ISE was proposed by Hirata and Date in 1970.46 In this paper, the two researchers coated a platinum wire with a plastic membrane that specifically complexed copper ions. This construction would later be described as the "coated wire" approach - one where an electronically conducting contact is coated with an ion sensing layer. Cattral et al followed up on this work with the first use of an ionophore doped ISE membrane for calcium ion detection - considered the first archetype of ionophore based solid state ISEs.47

One major drawback of the coated wire ISE construction was the thermodynamically ill-defined interface resulting from the absence of a redox couple between the electronically conducting wire and ionically conducting membrane. Since no charged species can transfer between the metal contact and the sensing layer, the potentiometric mechanism therefore relied solely on capacitance changes.27 Unfortunately, this could lead to unstable potential measurements due to any capacitive interferences in the system (i.e human touch).

Furthermore, as reported in 2000 by Pretsch et al, 48 these types of ISEs had the additional problem of an unintentional water layer film formed at the interface of the sensing membrane and the electrode support. Such a water film lead to a
constant drift in the potential, associated with diffusion of the primary analyte into the water reservoir between the membrane and the electrode. They also lead to sensitivity to ionic strength, unattractive detection limits, and delamination of the sensing membrane from the electrode support.\textsuperscript{49} 

In order to circumvent the aforementioned problems, the idea of a "transducer layer" was introduced. Such a layer requires the use of an redox-active material showing both electronic and ionic conduction as well as super hydrophobicity to avoid water layer formation.\textsuperscript{45} In addition, ideal transducer layers also offer the advantages of high interfacial contact area for increased capacitance.\textsuperscript{45} 

The first ion-to-electron transducers suggested were conjugated polymers such as polyaniline, polypyrrole, and PEDOT-PSS.\textsuperscript{50} The introduction of conjugated polymers as transducer layers increased potential stability and reduced detection limits. But while conducting polymers offer the advantages of high redox capacitance, low cost, and ease of processing, they suffer in terms of their light sensitivity and insufficient hydrophobicity. New directions in solid state ISEs have focused on incorporating high specific area carbonaceous materials - as well as nanoporous and nanostructured noble metals (i.e. gold and silver) - which have shown to offer both excellent high redox capacitance and superhydrophobicity.\textsuperscript{45} The Rius-Ruiz group, for example, has successfully used octadecylamine-functionalized single walled carbon nanotubes (SWCNTs) as a transducer layer for potentiometric strip cells based for potassium measurements.\textsuperscript{51} 

Typically, the transducer layer is constructed above the electrode material or solid contact. With the use of an additional noble metal solid contact - such as gold or platinum - sub micromolar limits of detection have been realized even for the common potassium ISE.\textsuperscript{52} Recently, however, Michalska et al.\textsuperscript{53} reported a simplified design wherein a carbon-nanotube doped PVC layer served the dual purpose of the electrical contact and ion-to-electron transducer simultaneously. In a subsequent paper they also suggested PEDOT as such an option, dubbing them "all plastic" disposable ISEs.\textsuperscript{54} Notably, limits of detection were worse than the solid contact approach, but the advantage of reduced cost and ease of manufacturing is a significant achievement.
Lowering the Detection Limit

In terms of the detection limit, most of the prevailing literature has identified the main problem leading to non-ideal detection limits as leaching of the analyte into the aqueous phase. Because ISEs respond to phase boundary conditions, even a small leakage of membrane components will greatly affect the surface concentration of analyte. And since a properly conditioned membranes often contain approximately 10mM of analyte sites, it is ever more likely for leakage to occur at concentrations significantly below 0.1 mM. As such, for symmetric ISEs it has been shown that by reducing the analyte concentration of the inner filling solution, detection limits can be improved to approximately 1uM for K+ sensors and even 1pM for Ag+ sensors. While for solid state ISEs this approach is not relevant, the same principle of minimizing trans-membrane fluxes is one plausible theory for the detection limit. For example, it has been shown that acrylate membranes have relatively better detection limits than conventional PVC ISEs because of their lower ion diffusivities. Sutter et al demonstrated this with a methyl-methacrylate decyl-methacrylate (MMA-DMA) based sensing membrane with a poly(3-octyliophene) transducer, showing a $5 \times 10^{-10}$ M detection limit for Pb+, the lowest reported detection limit reported so far for all solid state ISEs.

Another theory related to the origin of the detection limit suggests that the detection limit arises due to interfering ion in solution competing for ionophore complexation. In this case, the detection limit $a_{DL}$ is related to the selectivity coefficient and the interfering ion activity, $a_j$ as follows:

$$a_{DL} = K_{ij}^{pot} \times a_j$$

Another way to reduce the detection limit has been through optimizing the conditioning protocol of the sensing membrane. Typically, after deposition of the sensing layer on top of the electrode support, the membrane is conditioned in a mM bath of primary ion so as to reduce counterion impurities already present in the membrane.
and thereby increase the stability of the potentiometric response. But electrodes conditioned in a two step process - first in a mM bath for approximately 12-24 hours, followed by second uM bath for a similar time period - demonstrated decreased detection limits in the subnanomolar range.\textsuperscript{56-58}

Other approaches have focused on driving the flux of the primary ion in the reverse direction through the application for a galvanostatic current.\textsuperscript{59} For example, Michalska et al.\textsuperscript{60} demonstrated two orders of magnitude reduction in limit of detection by applying an anodic current to a polypyrrole film, transporting the chloride ion away from the aqueous sample and towards the conducting polymer solid support. This approach, however, is unreliable as the required anodic current is sample dependent.\textsuperscript{45}

A final approach is in varying the salt-ionophore content so as to optimize the selectivity coefficients of the membrane against the main interfering ion in solution.\textsuperscript{22} This approach is predicated on the theory that the detection limit is limited not by transmembrane fluxes perturbing the interface concentration of primary analyte, but rather non-ideal selectivities of the ISM itself.

**Novel Sensor Designs for Low-Cost Diagnostics**

There has been considerable interest in recent years around solid state ISEs as potential candidates for simple and portable point of use diagnostic devices. Solid state ISEs offer miniaturized physical footprints, and low cost due to scalable manufacturing techniques such as screen printing, spray deposition, and even inkjet printing.\textsuperscript{61} Once achieving sufficient reproducibility and scale, it is possible to achieve nearly an order of magnitude reduced price with respect to commercially available diagnostic devices on the market.

As mentioned previously, Rius et al. developed a potentiometric strip cell with a methacrylate working and reference electrode, and carbon nanotubes as the transducer layer. By using commercially available filter paper as the substrate rather than PET, the group was also able to reduce cost while maintaining commensurate performance. Similarly, the Whitesides group demonstrated a low cost potentiometric cell for potassium measurement based on wax-modified filter paper and screen printing.
Ag/AgCl inks - though this cell was characterized by sub-par limits of detection of approximately 0.1 mM K+.63

Beyond reduced cost, increased flexibility and disposability, filter papers offer the ability for microfluidic pre-modification of the sample solution prior to contact with the sensing layer. By leveraging the capillary forces of the filter paper or surface functionalization techniques, it is possible to achieve pre-concentration of samples or even removal of interfering ions, respectively. Even with all of these advantages, the challenge remains in maintaining mechanical robustness and reproducibility with filter-paper based ISEs.

In addition to the aforementioned developments, there has been a significant push in recent years towards low-cost, open source, potentiostat devices. With devices such as the D-stat and the Cheapstat,64,65 it is possible to design and manufacture potentiostats for open-circuit voltage, cyclic voltammetry, and linear sweep voltammetry electrochemical measurements at a price point of under 100 USD. With the advent of low-cost all solid state ISEs and open source potentiostats, the path to successful deployment of decentralized low cost soil diagnostics seems ever more clear.

All Solid State Reference Electrode Designs

Much like the push to move away from large-volume, liquid phase conventional working electrode ISEs, newfound research and development has focused on recreating reference electrodes in a solid state, planar form. Most commonly, the reference electrode is manufactured via a layer-by-layer (LbL) approach, wherein the sensing layer (AgCl), electrolyte layer (containing chloride ion), and junction layer are deposited in serial.

For the sensing element and electrode, the most popular manufacturing method is screen-printing of a AgCl ink on top of a conductive substrate. Screen printable AgCl ink is readily available from large manufacturers such as DuPont, and only requires a low-temperature heating step to remove the solvent from the ink. AgCl can also be produced via electrodeposition, and in one of the more creative approaches - chlorination of inkjet printed silver nanoparticles66 using household bleach.
Above the AgCl layer is the electrolyte layer. The purpose of this layer is to surround the sensing element with a saturated chloride ion concentration. The most common chloride-containing electrolyte used is aqueous potassium chloride. The potassium chloride is most often dissolved in a hydrophilic polymer (i.e. PVP, PVA) or a hydrophilic gel (acrylamide, agar). Grisel et al were able to encapsulate potassium chloride in a UV curable hydroxyl-ethyl methacrylate (HEMA) polymer, which was a promising step closer to easily manufactured planar REs.\textsuperscript{67} Uniquely, Shitanda et al forwent dissolving the potassium chloride in a polymer matrix, and instead drop casted it onto filter paper, which interacted with the AgCl layer to create a stable potential.\textsuperscript{68} This group was able to achieve sub-mV stability for over 75 hours in potassium chloride solution with such a construction.

From a manufacturing perspective, one main challenge with creating all solid state planar reference electrodes by the LbL approach is in parallelizing the process for both hydrophilic and hydrophobic electrode components. With a hydrophilic electrolyte layer laying on top of a hydrophobic AgCl sensing layer, the formation of a mechanically robust interface becomes a challenge. To overcome this challenge, chloride-containing hydrophobic ionic liquids have also been suggested.\textsuperscript{69} Bühlmann et al used 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide and got 42uV/h stability over 26 days using ionic liquids.\textsuperscript{69} A major drawback, however, is the highly toxic nature of such compounds, as well as their exorbitant costs.

Another challenge with solid state planar reference electrodes is encapsulating the electrolyte layer with an \textit{ion-insensitive polymeric junction} which maintains the concentration of the electrolyte layer constant. Nafion membranes have been used\textsuperscript{70} due to their cationic selectivity, ensuring that the chloride concentration is maintained. But this cationic selectivity also serves to generate a double layer potential at the nafion-sample interface which yields the reference junction potential sample dependent, and thereby unusable. Aliphatic polyurethane reference junctions, meanwhile, have shown extremely promising results, with potential changes of less than 2mV/decade for various chloride containing samples. Similarly, polyurethane junctions doped with 30wt\% cellulose acetate and solution casted on top of PVP-
electrolyte support have shown excellent stability in a variety of salt solutions.\textsuperscript{71}

Perhaps most promising, though, is the recent discovery of polyvinylbutyral (PVB) as a porous, sample independent junction which can be doped with chloride ion in order to serve as both the electrolyte and the junction layer simultaneously. Pioneered by Andrade et al\textsuperscript{72} and further used in an integrated in-situ sweat sensor,\textsuperscript{77} the PVB electrolyte support/polymer junction serves as a simple and robust system for an all solid state planar reference electrode.

**ISEs in the Context of Soil Analysis**

To date, significant progress has been made in realizing ISEs for many of the common soil macro and micronutrients important to plant growth. In terms of macronutrients, ISEs for nitrate ($\text{NO}_3^-$), phosphate, ($\text{PO}_4^{2-}$), and potassium ($\text{K}^+$) detection have all been realized - opening the door to parallelized, multi-analyte detection for soil samples. But in order to successfully bridge the gap between lab and field, it is necessary to consider how to actually get an accurate result from *soil*, not from deionized water solutions in lab.

A review of typical soil testing methods is presented in Figure 3-16. Broadly, typical steps involve:

1. **Soil Collection**: Collecting a composite soil sample often involves demarcating a Z over a homogenous area of farmland, and then taking 15 samples along the Z (5 on each leg of the Z), comprised each of 5 sub samples taken at 20cm depth in the soil. The soil sample is mixed thoroughly, sieved through a 2mm sieve and dried overnight.

2. **Ion Extraction**: Given the negatively charged nature of most soil colloidal particles, an extraction solution is necessary to "release" ions from the soil into an aqueous solution for further testing.

3. **Filtration**: Once the extract is produced, filtration of the solution is necessary so as to remove soil particles and provide for a homogeneous sample for subsequent analysis. Notably, this filtration step is only necessary for optical
measurements such as the ICP, but is in fact not necessary for ISE measurements as ISE measurements can be taken directly in the soil slurry.

4. Analysis: Analysis methods include ICP, flame photometry, atomic electron spectroscopy, among others - depending on the analyte desired.

For multi-analyte testing, it is beneficial to have a single extraction solution which can release all of the desired analytes into the aqueous soil solution. Such extractants are called "universal extraction solutions" (UES) and they are a necessity in terms of achieving highly parallelized, low cost, and time-efficient multi-element detection. Thus, in order to truly gauge the potential of ISEs as an appropriate technology for soil nutrient testing, not only must an appropriate universal soil extraction solution must be identified, but also the ISEs must maintain adequate selectivity and sensitivity in the presence of such an extraction solution.

Given that different soil test methods can result in vastly different results, the appropriate UES for a given region is selected based on soil characteristics and climate. In New England, for example, the two extraction solutions used are the weak acid Modified Morgan extract (0.62 N ammonium hydroxide (NH4OH) + 1.25 N acetic acid (CH3COOH)) and the strong acid Mehlich III extract (0.015 M NH4F + 0.2 M CH3COOH + 0.013 M nitric acid (HNO3) + 0.25 M ammonium nitrate ((NH4NO3) + 0.001 M ethylenediaminetetraaceticacid (EDTA)). Given the diversity of Indian top soils, it is possible that region-specific extraction solutions would need to be administered along with an ISE system for point-of-use diagnostics.

In terms of ISE performance in the presence of soil extracts, Kim et al investigated the suitability of different PVC-based ion-selective membranes for sensing soil macronutrients (NPK) and developed a multi-ISFET integrated with an automatic soil extraction system for real-time soil analysis. They further characterized the performance of the ISFETs in the presence of different extraction solutions - namely, DI water, as well as Kelowna, Bray, and Mehlich III solutions. They concluded that the ISMs were significantly affected by soil extractants - losing, for example, three orders of magnitude in the detection limit when in DI water versus Bray solution.
Figure 3-13: Soil testing procedures for a variety of soil analytes. Broadly, steps involve soil collection, ion extraction, filtration, and final analysis. Source: http://soiltest.cfans.umn.edu/.
Even with these results, they suggested the Kelowna solution as the optimal extract, allowing membranes to maintain a $10^{-4}$M detection limit. Such a detection limit would ultimately not affect the output of the recommendation, as it corresponds to the lowest values of potassium in soil anyhow.

The same group more rigorously characterized the appropriateness of the Kelowna extract for ISE analysis.\textsuperscript{75} In soil extracts, $NO_3^-$ ISEs provided concentrations similar to those obtained with standard laboratory methods, while $K^+$ ISEs and $PO_4^{2-}$ provided concentrations about 50\% and 64\% lower than standard methods, respectively. However, given that for the three types of ISEs tests, $R^2$ regression coefficients were all higher than 0.8 ($P < 0.001$) a simple calibration factor could address this issue. These results show that ISE technology paired together with the Kelowna extractant can be implemented successfully for available N, P, and K measurement.

While the Kelowna extract proved suitable for the PVC based ISM system studied by Kim et al - there is no doubt that it still had deleterious effects on ISE performance. This can be explained by the high ionic strength of the soil extracts, which combined with non-ideal selectivities of any given ISM, yield decreased detection limits and perhaps even nonlinear slopes. A better UES, therefore, would have as low ionic strength as possible while still maintaining its extraction capability.

To that end, barium, calcium, and strontium chloride salts could serve as a potential solution.\textsuperscript{73} Recently, for example, Li et al\textsuperscript{73} recently developed and characterized a 0.02M $SrCl_2$ UES. Such a UES, they concluded, correlated N, P, and K values with high significance and high extraction efficiencies. Regardless of the type of extraction solution used, though, the purpose of this section is to underscore the challenges and opportunities for ISEs to work in accord with the necessary steps in the soil analyte detection process.
Chapter 4

Modeling of Ion Selective Electrode Performance

4.1 Electrochemical Model

The intention of this model is to serve as a predictive tool to understand the electrochemical phenomenon of ion selective electrodes. It aims to quantitatively model the important parameters of an ion selective electrode, including the limit of detection and the slope of the potential with respect to sample concentration. Meaningfully, it also helps answer the question: "If the limit of detection is predicated by the pH at the interface, how does the pH change at the interface accordingly to different salt-ionophore ratios?"

The ion selective electrode architecture we will be investigating is comprised of a working electrode and a reference electrode. The working electrode includes an ion selective membrane, specific to potassium. The membrane layer includes a lipophilic salt (potassium tetrakis 4-chlorophenyl borate, KTpClB) and a neutral ionophore (valinomycin) all homogenously dispersed inside of a polymer matrix. For simplicity sake, we will only look at potassium ion selective electrodes, measured in solutions of pure potassium chloride, though future iterations will take into account impurities and selectivities of the ionophore with respect to other ions in solution.

The reference electrode for now will be considered to be an Ag/AgCl in saturated
KCl electrode. The salt bridge junction will be made out of an inert salt with similar anion and cation mobilities so as to neglect the diffusion potential generated due to charge separation across the salt bridge.

The total potential of an ion selective electrode, therefore, can be broken down into three parts, corresponding to the architecture aforementioned: (1) the phase boundary potential at the electrode-membrane interface, $\Delta \phi_{em}$, (2) the phase boundary potential at the membrane-sample phase interface, $\Delta \phi_{ms}$, and finally (3) the diffusion potential associated with the salt bridge, $\Delta \phi_d$:

$$\Delta \phi_{ISE} = \Delta \phi_{tm} + \Delta \phi_{ms} + \Delta \phi_d$$ (4.1)

The most critical part of this model concerns what is happening at the membrane/sample interface $\Delta \phi_{ms}$. Therefore, the first iteration of this model will be dedicated to answering what $\Delta \phi_{ms}$ is under increasingly few simplifying assumptions. Later stages of the model will also calculate the other parts of the system: $\Delta \phi_{tm}$ as well as $\Delta \phi_{ms}$.

### 4.1.1 Theoretical Background

In order to determine the potential at the membrane/solution interface, we invoke four main sets of equations: (1) Poisson's equation, which dictates that the Laplacian of a vector field (in this case, electric field) is zero, allowing us to solve for the potential for a given charge distribution, (2) Maxwell-Boltzmann statistics, which relates the potential in any given position in space with the charge in that position, (3) the condition of charge neutrality across the device in each phase and finally (4) chemical equilibrium of the analyte of interest in both the membrane and aqueous phase.

For a first iteration, we consider the following assumptions which allow us to have a tractable, linear relationship of potential vs. natural log of concentration:

- **Debye Huckle limit:** Our potentials are small relative to the thermal voltage, $\varphi_{thermal} = \frac{RT}{F}$. Therefore we can reduce exponentials to their respective
exponents.

- **No steric hindrance**: There is no electrostatic interaction between ions of the same charge; no shielding nor crowding at the interface. Therefore, an infinite concentration of ions of the same charge is feasible at the interface.

- **No membrane impurities**: There are no cation or anion impurities in the membrane. In the aqueous phase there is carbonate anion ($\text{HCO}_3^-$) to effectively simulate natural deviations from neutral pH due to dissolution of carbon dioxide into aqueous solutions.

- **No transmembrane fluxes**: No concentration gradients in the bulk membrane; it is fully in equilibrium. Therefore, there is no potential associated with the diffusion of the analyte of interest across the membrane and within the debye length from the membrane interface.

- **Chemical equilibrium at interface**: The potential is continuous at the interface. Note that Stark et al. measured a chemical equilibrium constant $\kappa_{eq} \approx 1 M^{-1}$ in a lipid membrane and aqueous potassium ($K^+$) in the following chemical reaction:

$Val_{mem} + K^+_{aq} \rightleftharpoons Val - K^+_{mem}$  \hspace{1cm} (4.2)

and so,

$\frac{a_{Val-K^+,mem}}{a_{Val,mem} \cdot a_{K^+,aq}} = \kappa_{eq} \approx 1 M^{-1}$  \hspace{1cm} (4.3)

### 4.1.2 Equations

With the following simplifying assumptions we can write our constitutive equations to solve for our unknowns. Note that for our system of equations we will use nondimen-
sional potentials normalized by the thermal voltage, \( \varphi^*_i = \frac{\varphi_i}{\varphi_{\text{thermal}}} \) and denote amounts of each ion in terms of the activity in the surrounding phase, \( a_{i,\text{phase}} = \gamma_{i,\text{phase}} * c_i \) where \( \gamma_{i,\text{phase}} = e^{-0.512*Z_i*\sqrt{IS_{\text{phase}}}} \) and \( IS_{\text{phase}} = \sum z_i^2 c_i \) is the ionic strength of the phase.

The unknowns we hope to solve for are:

- The potential at the interface: \( \varphi^*(0) \)
- The potential in the bulk of the membrane: \( \varphi^*(-\infty) \)
- The concentration of potassium at the membrane side of the interface: \( c_k(0^-) \)
- The concentration of the lipophilic salt anion in the membrane side of the interface: \( c_(0^-) \)
- The concentration of potassium at the sample side of the interface: \( c_k(0^+) \)
- The concentration of chloride ion at the sample side of the interface: \( c_c(0^+) \)

The knowns are:

- The permittivity of water: \( \varepsilon_{aq} = 78.4 \times \varepsilon_0 \)
- The permittivity of the plasticized membrane: \( \varepsilon_{mem} = 14 \times \varepsilon_0 \)
- The chemical equilibrium constant of ionophore (valinomycin)/potassium complexation: \( k_{eq} = 1 \)
- The reference electrode potential: \( \varphi_{+\infty} = +197mV \) (w.r.t standard hydrogen electrode (SHE))
- The concentration of the valinomycin in the bulk membrane, typically 30mM: \( c_{val}(-\infty) = 30mM \)
- The concentration of the lipophilic salt ion in the bulk membrane, typically 0.25 to 0.5 times the molar loading of ionophore: \( c_(\infty) \)
• The charges of the respective ions: \( z_i \)

• The Gas constant, temperature, Faraday constant, vacuum permittivity: \( R = 8.314 \frac{J}{\text{molK}}, T = 298K, F = 96485 \frac{A}{\text{mol}}, \epsilon_0 = 8.854 \times 10^{-12} \frac{F}{m} \)

We then set up the following equations in order to solve for our unknowns. Notably, all of the potentials are normalized by the thermal voltage and all the concentrations are normalized by ionic strength in the respective phase:

**Poisson-Boltzmann Equations**  These sets of equations relate the potential drop across a phase with the corresponding concentration differential. Thus, we can theoretically split the solution into two segments: one which extends from the membrane bulk up to the membrane-sample interface and the other which extends from the bulk sample to the membrane-sample interface.

\[
\varphi^*(0) - \varphi^*(0^{-\infty}) = \frac{-1}{z_i} \ln \frac{c_i^*(0^-)}{c_i^*(0^{-\infty})} \quad (4.4)
\]

\[
\varphi^*(0) - \varphi^*(0^{+\infty}) = \frac{-1}{z_i} \ln \frac{c_i^*(0^-)}{c_i^*(0^{+\infty})} \quad (4.5)
\]

**Chemical equilibrium across the interface**  This set of equations dictates thermodynamic equilibrium at the interface. At thermodynamic equilibrium, the electrochemical potential of the primary analyte is equal in both phases. In other words, the gradient of the electrochemical potential, \( \mu_i = \mu_i + z_i \frac{F}{\varphi} \), between potassium in the aqueous phase and unbound potassium in the membrane phase, is zero.

In order to write out the above relationship more fully, we can relate the concentration of unbound potassium in the membrane by the equilibrium constant of the reaction of potassium complexing with valinomycin in the membrane, \( k_{eq} \).
\[ \varphi^*(0) - \varphi^*(0) = 0 = \frac{-1}{z_i} \cdot [\ln(k_{eq} + \ln \frac{c_i^s(0^-)}{c_i^s(0^+)})] \]  

(4.6)

**Charge neutrality** We define charge neutrality in terms of net zero charge within the entire system. This ensures that at no point does a part of our system have a net charge, as this would be physically infeasible. Rearranging the equation for capacitance \( C = \frac{q}{\varphi} \), and solving for charge, we write:

\[ q_{aq} = \frac{\epsilon_{aq}}{\lambda_{D,aq}} \cdot (\varphi^*(0) - \varphi^*(0^+)) \]  

(4.7)

\[ q_{mem} = \frac{\epsilon_{mem}}{\lambda_{D,mem}} \cdot (-\varphi^*(0) + \varphi^*(0^{-}\infty)) \]  

(4.8)

\[ q_{aq} = -q_{mem} \]  

(4.9)

### 4.1.3 MATLAB code

Because our underlying assumptions in this phase predicate linearity, we can solve the above six equations for our six unknowns using matrix division: \( A \cdot u = B \). Our matrix A contains all of the coefficients of our unknowns, u is our unknown matrix, and finally B consists of all the knowns that correspond to each specific equation. We non-dimensionalize all of our potential values by the thermal voltage and we use activities rather than concentrations throughout.
Our matrix $A$ is therefore:

$$
\begin{pmatrix}
1.0 & -1.0 & 1.0 & 0 & 0 & 0 \\
1.0 & -1.0 & 0 & 0 & -1.0 & 0 \\
0 & 0 & -1.0 & 1.0 & 0 & 0 \\
1.0 & 0 & 0 & 1.0 & 0 & 0 \\
1.0 & 0 & 0 & 0 & 0 & -1.0 \\
\frac{e_{\text{mem}}}{\lambda_{D,\text{mem}}} - \frac{e_{\text{aq}}}{\lambda_{D,\text{aq}}} & \frac{e_{\text{mem}}}{\lambda_{D,\text{mem}}} & 0 & 0 & 0 & 0
\end{pmatrix}
$$

Where the columns 1 through 6 represent:

$$
\begin{pmatrix}
\varphi^*(0) \\
\varphi^*(-\infty) \\
\ln a_{K^+}(0-) \\
\ln a_{K^+}(0+) \\
\ln a_{R_-}(0-) \\
\ln a_{\text{Cl}^-}(0+)
\end{pmatrix}
$$

and our $B$ matrix,

$$
\begin{pmatrix}
\ln a_{K^+}(-\infty) \\
\ln a_{R_-}(-\infty) \\
\ln a_{\text{val,free}}(0-) \\
\varphi^*(\infty) + \ln a_{K^+}(\infty) \\
\varphi^*(\infty) - \ln a_{\text{Cl}^-}(\infty) \\
\frac{e_{\text{mem}}}{\lambda_{D,\text{mem}}} \ast \varphi^*(\infty)
\end{pmatrix}
$$

which is equal to,

$$
\begin{pmatrix}
-3.949 \\
3.949 \\
4.423 \\
5.438 \\
9.906 \\
58899.0
\end{pmatrix}
$$

for $C_{K^+,aq,\infty} = 0.1$ M.

4.1.4 Results

The symbolic solution for $\varphi_{-\infty}^*$ according to $A \ast u = B$ as defined above is:

$$
\varphi_{-\infty}^* = \varphi_{\infty}^* + \ln a_{\text{val,free}}(0-) + \ln a_{K^+}(-\infty) \quad (4.10)
$$

$$
\Delta \varphi_{\text{ms}} = \varphi_{\text{thermal}} \ast \ln \frac{a_{K^+}(\infty)}{a_{K^+}(-\infty)} + \ln a_{\text{val,free}}(0-) \quad (4.11)
$$
Membrane bulk ($y=-\infty$) and interfacial ($y=0$) potentials

![Graph showing potential vs. KCl concentration](image)

**Figure 4-1:** Potentials in the membrane as well as at the interface as a function of KCl concentration in the aqueous phase.

Which correctly predicts Nernstian behavior as seen in the plot of potential versus aqueous KCl concentration in Figure 4-1 ($\phi_{-\infty}$). This shows that our model agrees with existing models for ISM behavior while providing additional information at the interface, such as $\phi(0)$, which cannot be measured directly.

When we consider the potential drop across each phase, as seen in Figures 4-1 and 4-2, we can see that there is negligible potential drop within the membrane phase for $C_{K^+,aq,\infty} < 10^4$, accompanied by very little interfacial polarization within the membrane as seen in Figure 4-3.

To understand the physical reason for this, we consider the electric double layer capacitance (EDL capacitance) within each phase. As seen in Figure 4-4, for low aqueous concentrations of KCl, the aqueous phase has a lower capacitance than the membrane phase, resulting in most of the potential drop and interfacial polarization occurring within the membrane. At higher concentrations of KCl, the Debye length within the aqueous phase decreases, resulting in increased capacitance and a negative relative voltage drop. This in turn results in a greater voltage drop and degree of interfacial polarization within the membrane phase, as seen in the graphs of the
Figure 4-2: Potential drops in each phase as a function of KCl concentration in the aqueous phase.

Figure 4-3: Concentrations of lipophilic anion and potassium in the membrane at the interface as a function of KCl concentration in the aqueous phase.
Figure 4-4: Capacitances of the electric double layers in the membrane and aqueous phases as a function of KCl concentration in the aqueous phase.

potential drop (Figure 4-2) and interfacial membrane concentrations (Figure 4-3) vs KCl concentration.

We can also observe this effect by considering the profiles of potential $\phi$ and ion concentration near the interface. As seen in Figure 4-5, for $C_{K+,aq,\infty}$ of 1nM or 1uM, there is very little potential drop within the membrane ($y < 0$) and that potential drop occurs in a much smaller distance within the membrane than within the aqueous phase ($\lambda_{D,mem} << \lambda_{D,aq}$). However for $C_{K+,aq,\infty} = 1mM$ or 100mM, the Debye lengths are of similar magnitude. When we consider the profiles for ion concentration (Figure 4-6), we can similarly see that very little interfacial polarization occurs within the membrane for $C_{K+,aq,\infty} = 1uM$, whereas we can see that the behavior of ions and resulting potential changes dramatically once the capacitance of the aqueous electric double layer exceeds that of the membrane electric double layer.

Upon consideration of the calculated Debye lengths in each phase (Figure 4-7) it is immediately apparent that the calculated Debye lengths are greater than those achievable in actual water samples (up to $\approx 1mm$). In actual water samples, even those without solid ionic impurities, dissolved carbon dioxide from the atmosphere
will dissociate to form carbonate with a concentration of approximately \(2.5 \times 10^{-6}\) M. This will result in a minimum possible capacitance of the aqueous EDL and result in some potential drop and interfacial polarization with the membrane, even for very low KCl concentrations.

The first part of this commentary was mostly dedicated to characterizing the concentration and potential in the organic and aqueous phases. Focusing now on the pH at the interface, we take into consideration (as mentioned in the previous paragraph) the dissolution of carbonate, causing the pH of water at room temperature to be about 6.5 rather than 7. Dissolved carbonate ion \((HCO_3^-)\) from atmospheric carbon dioxide \((CO_2)\), is at a typical concentration of about \(2.56 \times 10^{-6}\) M.

With this new impurity we are now able to measure the pH at the interface on the aqueous side of the interface as a function of salt-ionophore ratio. For each iteration of the salt-ionophore ratio, the matrix B changes to accommodate new values of \(c_r(-\infty)\) and \(c_{val}(-\infty)\). It then solves the matrix equation and extracts out the aqueous interface potassium concentration, \(c_k(0^-)\). It is assumed, then, that the ratio of potassium at the interface and that in the aqueous bulk is equivalent for that of interfacial carbonate and bulk carbonate:

![Potential profiles](image)
Figure 4-6: Spatial profiles of ion concentrations at 1μM, 1mM and 100mM KCl in the aqueous phase.
Figure 4-7: Debye lengths of each phase as a function of KCl concentration in the aqueous phase.

\[ \frac{c_{\text{HCO}_3(0+)}(\infty)}{c_{\text{HCO}_3(0+)}} = \frac{c_k(\infty)}{c_k(0+)} \]  

(4.12)

Knowing the bulk carbonate concentration, we can now solve for the carbonate concentration at the interface. Taking the logarithm of this value yields the pH at the interface for each salt-ionophore concentration (Figure 4-4).

One thing to notice from Figure 4-4 is that as the salt-ionophore ratio increases, at a given concentration of potassium in the aqueous phases, the pH at the interface becomes more acidic. Given that one of the predominant theories surrounding the origin of the detection limit involves interference from hydrogen ions at the interface, this model would therefore suggest that higher salt-ionophore concentrations suffer from higher detection limits. In Chapter 6, we attempt to confirm this result with empirical data relating the salt-ionophore ratio to the detection limit and respective selectivity coefficients for H+. 

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Figure 4-8: Schematic showing how the potential drop from the interface to the bulk relates the concentrations of protons at the interface and in the bulk.

Figure 4-9: Interfacial pH as a function of the KCL concentration in the aqueous phase for different ratios of salt to ionophore.
4.1.5 Limitations and Future Work

While our model correctly predicts the Nernstian response for an ideal ion-specific membrane, it does not include the deviation from Nernstian behavior associated with interfering ion complexation, which ultimately gives rise to the detection limit. In the near future we hope to incorporate this into our model so that we can more fully predict the response of ion-specific membranes and enable us to modify parameters for optimizing performance.

4.2 Sensitivity Analysis

The purpose of this model is to the answer the question: "Just how accurate do our sensor potential readings need to be to accommodate 80% predictive accuracy?"

As per the product contract, users valued accuracy as one of their top product attributes. To that end, we benchmarked our accuracy with respect to commercial blood glucometers, which operate on a similar principle. Since blood glucometers typically achieve an accuracy around +/- 10% with respect to true values, we wanted to ensure that our soil potassium measurement was similarly accurate. But given that it is universally common to decompose soil analyte measurements into four of five "bins" - i.e. "Low", "Medium", "High", "Excessive" - our prediction accuracy should be measured ultimately as to whether or not the incorporated device measures the bin correctly, not necessarily the actual value. Thus, with a goal of an 80% bin prediction accuracy, this model sets out to uncover what the required potential reading accuracy must be.

The first step in the model is to model a typical response curve of a potassium ISE. Shown in Figure 4-10, the curves are represented with respect to the concentration of potassium as well as the logarithm of the concentration of the potassium ion. Notably, we neglect Debye-Huckel factors relating concentration to activity here. The equation relating the potential to the concentration of potassium in the solution as represented is an empirical form of the Nernst equation:
Figure 4-10: Typical EMF responses of potassium selective ISEs with respect to molarity and the logarithm of molarity of potassium.
\[ EMF = 25.6\ln M + C \] (4.13)

Where \( C \) is a constant shifting the curve up or down.

In order to determine the sensitivity of our measurements for a given potential, we take the partial derivative of the concentration with respect to the potential, and then multiply that by the factor relating concentration in molarity (M) to concentration in parts per million (ppm). For potassium, this is 39090, which is the product of the atomic weight (39.09 g/mol) multiplied by the conversion of ppm to mg/L (1000).

\[
\frac{\partial ppm}{\partial EMF} = 39090 \times \frac{5}{128} \times e^{\frac{5(EMF-C)}{128}}
\] (4.14)

Once we have the partial derivative of ppm with respect to EMF, we can multiply that by the standard error in potential (\( \Delta EMF \)) to determine the error in concentration as a function of the error in EMF measurement. A graph of a set of these curves for \( +/- 1, 5, \) and \( 10 \) mV can be found in Figure 4-12. As shown in the figure, the error curve is exponentially increasing, meaning that deviations in concentration are particularly large as the EMF value increases. We expect, therefore, that errors in bin prediction will be more frequent for more concentrated soil samples.

For the next part of the analysis, we attempt to predict the accuracy in bin prediction as a function of a standard error in the EMF measurement. First, we take into consideration a normal distribution (std dev: 150ppm, mean: 225 ppm) of soil samples, which typically vary from 1-800 ppm for potassium. Notably, this range is dependent on the soil extraction solution used, which varies from the Bray, Mehlich, Keliowna and Olsen extracts - to name a few.

The range of potassium levels is further divided up into five bins:

1. **Bin 1 ("Low")**: 1 - 50 ppm K+
2. **Bin 2 ("Low-Medium")**: 51 - 150 ppm K+
Figure 4-11: Partial derivative of the potassium concentration in ppm with respect to the measured EMF.
Figure 4-12: Partial derivative of the potassium concentration in ppm with respect to the measured EMF.
Figure 4-13: Normal distribution typical of soil potassium samples, with an average of 225ppm and standard deviation of 150ppm.
3. **Bin 3** ("Medium"): 151 - 250 ppm K+

4. **Bin 4** ("High"): 251 - 800 ppm K+

5. **Bin 5** ("Excessive"): > 800 ppm K+

Using the normal distribution of soil samples, the algorithm for calculating the prediction accuracy as a function of potential error is as follows: First, the code converts every ppm value to an EMF measurement. The code then adds/subtracts the standard error in potential measurement, ranging from 0 to 10 mV (i.e. 0 to 20 mV "swings"). Using the resultant EMFs the code recalculates a corresponding set of ppm values, and then checks if those values are in the same bin as the original EMF. For each positive result, the code weighs that value in accordance to the expected frequency of that soil ppm value in the normal distribution of Figure 4-13. Dividing the weighted count of correct predictions by the total number of iterations gives the predicted accuracy rate. We can do this same analysis for results that end up being one or two bins away from the actual result (Figure 4-14).

As seen in Figure 4-14, for a standard error of +/- 5mV, we would achieve an 83% accuracy rate for measurements within 1 bin away and for an error of +/-5.4 mV we would hit the target of 80% accuracy. For errors less than +/- 10mV there is a negligible (<1% of samples) error constituting a 2 bin prediction error. What this tells us that in order to achieve the product attribute of accuracy desired by users, a +/- 5.4 mV standard deviation in measurement would be required. For such a deviation we would be incorrect only 20% of the time, and even when our system would provide an incorrect prediction, it would never be off by more than 1 bin. This ensures that with such a variance, the soil fertilizer recommendations would not be significantly different even in the cases of incorrect bin prediction.

Given that total system error with the WE, RE, and reader is given by:

$$\sqrt{\sigma_{total}^2} = \sqrt{\sigma_{RE}^2 + \sigma_{WE}^2 + \sigma_{Reader}^2} \quad (4.15)$$
Figure 4-14: Predicted bin accuracy as a function of the standard error deviation in EMF potential measurements of the ISE for (Top) 1 bin error and (Bottom) 2 bin error.
We now have a bounds that the square root of the sum of the squares of the standard deviations for each of the individual components of the system (WE, RE, reader) should be less than 5.4 mV.
Chapter 5

Electrode and Sensor Fabrication

5.1 Electrochemistry

5.1.1 Materials

Screenprintable inks - specifically, the 5874 silver/silver chloride (Ag/AgCl) conductor as well as the 7102 carbon nanotube (CNT) conductor paste - were purchased directly from DuPont Microelectronics. The inks were spread through a 0.003” thick low-tack mask purchased from Grafix onto a 0.015” clear polycarbonate substrate (McMaster) with the aid of an 80 durometer polyurethane squeegee from Speedball.

Polyvinyl chloride ion selective membrane components, including valinomycin (potassium ionophore I), potassium tetrakis 4-chlorophenyl borate (KTPClB), polyvinyl chloride (PVC), 2-Nitrophenyl octyl ether (o-NPOE), and tetrahydrofuran (THF) were purchased from Sigma. Similarly, butyl acrylate (BA) ion selective membrane (ISM) components, including tetrakis(4-chlorophenyl)borate tetradecylammonium salt (ETH500), butyl acrylate (BA), 2,2-dimethoxy-2-phenylacetophenone (DMPP), and hexane-1,6 diol diacrylate (HDDA) were purchased from Sigma as well.

For the final RE design, reference membrane components, namely, polyvinyl butyral (PVB), was also purchased form Sigma. The membrane cocktails were dropcast through a mask made of a 0.005” (5mil) ultra-high molecular weight polyethylene (UHMW PE) sheet with an acrylic adhesive backing (McMaster). Earlier RE itera-
tions had an additional hydrogel layer comprised of hexamethyl ethyl methacrylate (HEMA), tetraethylene glycol (TEG), as well as ethylene glycol (EG) - all purchased from Sigma.

Analytical grade salts of potassium chloride ($KCl$), sodium chloride ($NaCl$), ammonium chloride ($NH_4Cl$), lithium chloride ($LiCl$), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), and lithium acetate ($LiOAc$) for potentiometric analyses were purchased from Sigma. All aqueous electrolyte solutions were prepared using 18.2 $M\Omega$ Millipore deionized (DI) water.

### 5.1.2 Electrode Fabrication

Prior to screen printing, the sensors were designed in Adobe illustrator. A two-electrode system wherein the silver chloride reference electrode serves also as the counter electrode was chosen to simplify circuit design. The two-electrode system is a common construction for low-current open circuit voltammetric electrochemical sensing.$^{72}$

The size of the working and reference electrodes were 1.25 mm (W) x 28 mm (H). At the top of the electrodes the width increased to 1.5875 mm and were spaced 7.5 mm apart so as to accommodate the required edge card reader spacing inside of the printed circuit board. Centered on the bottom end of the working and reference electrodes were two circular holes of 4.5 mm diameter for the CNT ink, comprising a $28.3\ mm^2$ working area. Notably, the diameter of the Ag/AgCl layer and the dropcast mask diameter was reduced to 4 mm and 3.5 mm respectively so as to accommodate for inaccuracies in manual mask placement and ensure that the Ag/AgCl layer or ISM were always in contact with the CNT layer beneath.

The design for a single ISE system was multiplied to fit into a standard 8.5 by 11 inch sheet. For a single sheet, 96 individual electrodes (i.e. 24 strips of four sensors) can be produced. Outlines of the 8.5 by 11 sheets of electrodes were saved as the CNT masks, Ag/AgCl masks, and final ISM dropcasting mask, respectively. Screenprinting masks were made of Grafix paper while the ISM dropcasting mask was made of UHMW PE. All masks were laser cut using a 60W CO2 laser cutter (Epilog).
Figure 5-1: The construction of the ion selective electrode system, designed in Adobe Illustrator. 96 electrodes fit in the area of a single 8.5 x 11 inch sheet.
The screen printing process first consisted of the bottom carbon nanotube layer. Briefly, the polycarbonate sheets were cut down to 8.5 x 11in sheets with a shear. The CNT mask was carefully peeled off the adhesive back, placed onto the polycarbonate substrate, and flattened out gently with a pie roller. The masked polycarbonate was then taped down onto a flat substrate, and 1g of the 7102 CNT paste was spread on top. With the squeegee, the ink was carefully spread across the mask in a reciprocating motion to ensure adequate and uniform coverage. The ink was then cured in the oven at 70 degrees celsius for 10 minutes. Finally, the CNT mask was peeled off and disposed.

The Ag/AgCl screenprinting process was markedly similar. The only exception was that 1g of the paste was spread in small aliquots of approximately 20uL dabbed on with a disposable spatula. In addition, to avoid permanent adherence of the low-tack glue on the CNT layer underneath, the heating time was reduced only to 5 minutes, with the remainder of the time air dried until all the solvent evaporated.

With the CNT and Ag/AgCl layers complete, the UHMW PE dropcast mask was carefully applied by hand to ensure that all of the holes lined up with the CNT or Ag/AgCl layers underneath. The masked polycarbonate was then placed in a heated plastic lamination machine (Scotch) to ensure a complete seal between the acrylic adhesive and the substrate.

To our knowledge, our electrodes are the simplest all solid state, complete ISE system reported in literature. The screen printing methodology vastly reduces the need for expensive equipment; only a lasercut mask and a squeegee are needed. From a construction standpoint, the fact that the CNT layer serves both as the transducer and the conductor layer in one simplifies the design significantly. The heat-laminated UHMW polyethylene mask also uniquely serves the multiple functions of protection and insulation of the electrodes, as well as outlining the barriers of the dropcasting step. Of course, it is expected that scaling up manufacturing will increase the complexity and cost of the equipment, but our simple process underscores the ability for scientists to rapidly prototype ISEs in lab using readily available equipment and manual processes.
5.1.3 Ion Selective Membrane Preparation

The polyvinyl chloride (PVC) K+ ISM cocktail was prepared as follows: 100 mg of 2wt% valinomycin, 1wt% KTpClB, 66wt% o-NPOE, 32wt% PVC were dissolved in 1mL of THF. 2uL were dropcasted with a manual repeating pipette (USA Scientific) and left to dry overnight.

The butyl acrylate (BA) K+ ISM cocktail was prepared as follows: 12mg of valinomycin, 3mg of KTpClB, 3 mg of ETH500, 7mg of DMPP were weighed and dissolved in a stock mixture containing 500uL of BA with 2uL of HDDA. 2uL of the ISM cocktail were dropcasted through the mask in an Argon glovebox using a manual repeating pipette. Following dropcasting, the membranes were cured for 8 minutes under 365nm UV light via two handheld UV lamps (Spectraline) situated 3.25 inches above a 8.5 x 11 in substrate coated with aluminum foil to enhance uniform irradiation.

After curing, the individual WE membranes were removed from the glovebox and left overnight before conditioning in 10^{-3} M KCl for 12 hours. After the main conditioning step, dry membranes were stored in a ziplock bag. No preconditioning was necessary prior to electrochemical measurements.
5.1.4 Reference Membrane Preparation

For early studies on REs employing BA based membranes, two layers were created. The first layer consisted of a hydrogel membrane comprised of 2100 uL HEMA, 1200 uL EG, 40 uL of TEG and 40 mg of KCl. 2uL of this layer were dropcasted above the CNT layer beneath and UV cured in Argon for 8 minutes using the UV lamp setup aforementioned. Following deposition of this layer, a second layer consisted of an ionophore-free BA cocktail: 500 uL BA, 1.5 uL HDDA, 3 mg ETH500, and 3mg KTpC1B. 2uL of this layer were deposited above the HEMA layer in the same fashion.

The final PVB reference membrane cocktail consisted of 79.1 mg of PVB and 50 mg of NaCl dissolved in 1mL of methanol. The mixture was sonicated at 75 Hz in a sonicator bath. 10uL of the reference junction cocktail was dropcasted using a positive displacement pipette (VWR) and left to dry for 12 hours. The reference membranes were placed in the conditioning bath for 12 hours in 10^{-3} M KCl. Following the first conditioning step, RE were conditioned for 3 more hours 10^{-2} M Sr_{2}Cl. After this conditioning step, the REs were rinsed fully with DI water and left in dry storage prior to use.

For full ISEs the dropcasting and conditioning steps of the RE and WEs were parallelized. First, REs were dropcasted and left to dry for 12 hours. Then WEs were dropcasted and cured. Together, the WEs and REs were then conditioned for 12 hours in 10^{-3} M KCl, followed by 3 more hours 10^{-2} M Sr_{2}Cl. Full ISEs were then rinsed with DI water and left in dry storage prior to use without the need of preconditioning.

A summary of the manufacturing process can be found in Figure 5-4.

5.1.5 Electrochemical Characterization

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were carried out by using a 2-channel high impedance potentiostat (Biologic) in a single compartment three-electrode cell where the electrode under study was the working electrode in 10^{-3} M KCl solution. The reference and auxiliary electrodes were
take CNT mask & polycarbonate substrate

place CNT mask on polycarbonate and flatten out gently

heat in oven at 65 celsius for 10 min

peel off CNT mask

repeat 1-6 for AGCL

place down dropcast mask

insert into scotch laminator

dropcast WE/RE cocktails

UV cure WE membrane in Argon

condition membranes in KCL

Figure 5-3: A schematic of the manufacturing process.
Ag/AgCl (3 M KCl) and graphite rod, respectively. Impedance measurements were taken over the range of 1mHz to 1MHz with a 30 second rest step prior to each membrane measurement, and each frequency measurement reported as the mean of triplicates.

Resistance and capacitance values were tabulated from a Nyquist plot representation of the imaginary and real parts of the membrane impedance at different input frequencies. Using a simple RC circuit fit to the data to simulate the double layer at membrane side of the interface, resistance and capacitance values were tabulated. For all electrochemical measurements, 14 samples were tested, and compared with their potentiometric performance values.

Potentiometric measurements were performed by the electrochemical workstation at room temperature with a double-junction setup with two beakers: one for the WE and the other for the RE. The RE (3 M KCl, Gamry Instruments) was immersed in a $10^{-2}$ M KCl solution, and was connected to the working electrode sample bath via a 1.5 cm by 20 cm filter paper salt bridge hydrated with 200uL of 1M LiOAc. Concentrations of the primary ion were varied by adding fixed amounts of different molarity stock solutions to achieve decade-increases in concentrations of the sample bath. All potentiometric values were corrected for the liquid-junction potentials according to the Henderson equation, and the ion activities were calculated by the Debye Huckle equation.

Selectivity measurements were completed via the fixed interference method (FIM). The FIM entails a very similar experimental procedure to the potentiometric studies above, except that the sample bath is in a background of a fixed activity of the interfering ion. In this case, the fixed activity of all interfering ions was 1mM, which is representative of typical soil analyte concentrations. $\log K_{ij}$ selectivity constants were calculated for all interfering ions as the activity corresponding to the intersection of the potentiometric titration curve with and without the interfering ion present. Required selectivity coefficients were calculated using the respective typical concentration of the interfering ion in soil, and a critical percent error of 0.1%.
5.1.6 Physical characterization

Physical characterization of the membranes consisted mostly of profilometry measurements using a Dektak XT Profilometer. Average height measurements and surface roughness measurements were calculated after a two point linear fit filter.

Scanning electron micrograph (SEM) images were taken using a Zeiss Merlin Gemini SEM. ISEs were sliced with a razor blade to expose a cross section collinear with the center of the ISM. 5nm of gold was sputtered directly onto the electrodes at a vacuum pressure of $10^{-6}$ Torr.

5.1.7 Soil Sampling and Analysis

Samples from 30 locations around the MIT campus were collected at 20cm depth (about 6in) with a soil core. For each respective sample, 5 sub-samples were combined and mixed into one to provide a representative sample. The samples were air dried and sieved to less than 2 mm after crushing aggregates manually. Particles greater than 2 mm (pebbles and stones) were discarded.

2g of air dried soil was placed in a 50mL vial and extracted with 20 mL of the 0.02M $SrCl_2$ extraction solution (1:10 soil-weight:solution-volume). Vials were placed on a rotary mixer for 15 minutes at 180 oscillations per minute. Filtrates were collected using a Whatman 4 filter paper, and diluted at a 10/3 ratio with a 2% nitric acid solution. 1, 10, and 100ppm standards were matrix matched and diluted equivalently with the same nitric acid solution. Standards and samples were measured on the Agilent 5100 ICP-OES and calculated via a three-point linear regression.

5.2 Reader Design and Fabrication

5.2.1 PCB Design

Two op-amp stages were used realize the project. The initial stage of the circuit is a buffer module to allow for the measurement of voltage while preventing current from flowing into or out of the solution through the edge card. A specialized op-amp was
needed for this task, the selection of which is described in the component selection section. Eight buffers were needed, one for both the RE and WE for each of the four sensors.

A differential op-amp circuit was used to take the difference between the working electrode voltage level less the reference electrode voltage level. The result is fed into ADC pins on the micro-controller. This ordering was used since the analog to digital converter gives a reading of 0V for negative voltage. For the measurement of potassium this setup was sufficient, as the calibration solution would never give a negative potential and if the working electrode did read a negative voltage relative to the reference electrode, it would mean that the concentration was low enough that giving a reporting of the lowest bin value would be an accurate result. For other ion measurements, it may be necessary in the future to give a positive voltage offset of the difference or to use an analog inverter to allow for the ADC to read the proper value.

Preliminary designs also had a 4th order Sallen-Key Topology Filter done by cascading two 2nd order filters. The filters are used to stabilize the output of the differential amplifier and offer a better average of the measurement voltage. Later on, though, it was determined that no analog filter module would be implemented, as after a period of settling the device output is characterized by relatively low noise, allowing software filtering to be a more effective alternative. In addition to slightly increasing cost and size, a hardware filter would introduce an additional source of error that would be hard to minimize. Thus, the unfiltered amplified output is finally sent to an ADC on the microcontroller (ATMEGA328P) for further processing.

Another ADC also takes the input from a simple thermistor, allowing calculations to take into account the temperature of the system. The thermistor has a 3 pin header that allows it to stick out of the device, so that it reads the temperature of the outside rather than potentially higher temperatures inside the device.

A micro-controller was used to deal with interactions with the user and to calculate the appropriate result. It takes inputs from the differential op-amp module, thermistor temperature sensor, and a simple push button. The button connects the
pin to ground when pushed causing a reading of LOW. When open, this is open, and internal pull-up resistors inside the micro-controller cause a reading of +5V, or HIGH. Output is given form the micro-controller to an LED with a current-limiting resistor of 10 kΩ going to ground. The LED flashes when the device is measuring and is left on when a task must be performed or results are ready. An LCD is also controlled, which can report to the users the solution that needs to be measured, the time remaining, and the result. A Hitachi HD44780 controller is built in to the LCD, limiting the number of pins required and greatly simplifying the software and hardware. The contrast for the LCD was connected to ground.

Several components require a voltage to be provided at +5V, such as op-amps, the micro-controller, the LCD, and temperature sensor. A buck converter was used to take the ≈ 9V provided by a 9V battery passed through a rocker switch that must be turned on to allow for a functioning circuit, and give an output of 5V regardless of variation in input voltage.

For the op-amps, negative voltage was also required to provide adequate power to the rails and give a correct result. A CMOS DC-DC voltage converter was set up to provide -5V, as shown below, with an input to V+ of +5V.

Figures 5-5 and 5-6 show the schematic and board designs of the circuit.

5.2.2 Component Selection

The op-amp selected was the LF353-N, a dual chip JFET op-omp with an internaltly compensated offset voltage. The JFET input device provides wide bandwidth, low input bias currents and offset currents. What would be a negligible level of current in other applications could in this instance cause a significant change in voltage level as a result of using open-circuit potentiometry. By experimentation, a general purpose op-amp, such as a 741, allows enough current to pass through in order to change the concentration of ions being measured, so that over the relatively short period of time needed to measure the voltage potential would change this value. It was therefore determined that the standard internal input impedance of general purpose op amps, 10⁶Ω, was insufficient for our purpose as it resulted in a typical input bias current
Figure 5-4: The board design of the PCB circuit.
of 80 nA, and a maximum of 200nA at 25°C. However, op-amps with a higher level of input impedance, at $10^{12}\Omega$, was sufficient for these purposes, resulting in a typical input bias current of 50pA, which was found to be low enough for our purposes. The 353 also has an internally trimmed offset voltage to reduce error, and is very low cost.

The ATMEGA 644 micro-controller was used because of its familiar Arduino programming environment, easy setup, and wide range of features. It has an internal oscillator, saving the additional hardware of an external crystal oscillator and appropriate capacitors. It also has 7 analog to digital converters and an additional 3 banks of 8 general purpose digital input/output pins, providing adequate scope for the entire project. It also provided more than enough programming memory for our project.

The buck converter used was a L7805CV, since it was low cost and easy to implement. It had a output voltage tolerance of 2% and high temperature range.

The TL7660 was used for the voltage converter, as it had several features. It is simple to implement, requiring only two external capacitors that do not require a high level of accuracy. No external diode is needed. It has a typical power efficiency of 98%
and a 99.9% voltage conversion efficiency, providing more than adequate accuracy for our purposes.

The thermistor used was MCP9700, as it was easy to implement and provided necessary range and accuracy for our purposes.

The LCD used was the LCM-S01602DTR/M, as it had an internal Hitachi HD44780 controller and was relatively low cost. It has a display format of 16x2 characters.

The edge card reader used was a EBC20DRAS, bi-directional 40 pin (two rows of 20) female edge card connector that used right-angle output pins, which were necessary for the PCB so that the cards could be connected from the bottom while soaked in the solution being measured.

5.2.3 Software Programming

The program begins immediately upon receiving power by initializing the general purpose IO ports, the LCD and the ADCs for future use. The number '1' is displayed in the middle of the LCD, representing the step that the user is on. When the button is pressed, a countdown of 60 seconds begins, which is displayed on the second line of the LCD. For the last 30 seconds, values are recorded from all four ADCs. When the countdown is proceeding, the LED begins flashing. It will remain solid when the user must perform an action or the result is ready. Step 2 and Step 3 continue in a similar manner, with Step 2 only lasting 10 seconds and recording no data as it is the wash step. Obvious outliers are then removed from the dataset, and averages are taken to determine the bin, ranging from the lowest bin "A" to excessive nutrients in bin "E". Cutoffs are hardcoded. For testing purposes, the button may be held down for 10 seconds to display the averages from each of the four ADC's for both the soil solution and calibration solution steps. The average type and value are displayed one at a time, and may be scrolled through by pushing the button. At any point, the program may be restarted by turning off and on the rocker switch. No data will be saved in this instance.
5.2.4 Reader Error Analysis

There are two principle sources of error: the differential module and quantization resulting from the analog to digital converter. Noise will be effectively minimized by removing outliers and averaging a large number of samples. Resistors with 1% tolerance and equal values were used for the differential module. This results in a total tolerance of 3%, or 6mV for a input difference of 200mV. Typical error will be lower. The ADC gives values over a range of 1024 steps, ranging from 0V to 2.56 V using internal reference in the micro-controller. This results in a maximum possible error of 2.5 mV, and a typical error of 1.25 mV. The actual voltage will always be larger than the reported voltage by up to these levels.

5.2.5 Case Design

The case of the reader was designed in Solidworks, using the board design from Eagle as a guideline. The case is comprised of two shells, each 3D printed on the Ultimaker+ using default settings and PLA filament (Ultimaker). The shape of the shells were roughly rectangular, with slight 10 degree depressions on the sides to afford gripping. The shells were adorned with cut extrusions which delineated where PCB components (i.e. buttons, LEDs, temperature sensor, on/off switch) extend outside. Rectangular holes are found on the bottom of the case to accommodate mating with the peg protrusions on the walls of the receptacle, which is used for containing the solutions for soil testing (Figure 5-10).

The two shells were connected together via a lip/groove formulation and some low tack Dot Shot Pro adhesive (Staples). M4 screws (McMaster) held together the PCB against the back case along with the aid of threaded brass plastic inserts (McMaster) which press-fit into boss extrusions in the back for extra stiffness. Finally, the battery of the PCB fit into a walled extrusion in the backside of the PCB, which ensured the battery did not disconnect from the power cables and did not move during operation.

Figure 5-8 below shows the isometric and side views of both the case assembly and the PCB assembly which fit inside the case. Figure 5-9 shows the case with the
Figure 5-6: Solidworks model of the PCB and case design, later exported into an STL for 3D printing.

sensor inserted as well as the case opened up, revealing the PCB inside. Figure 5-10 shows a collage of pictures of final 3D printed product.

5.2.6 Soil K measurement with the full kit

With the case and the programming fully complete, the user experience was fully defined. For soil testing with the reader and the strip, it consists of the following steps (Any equipment mentioned can be seen in Figure 5-10).

1. Aliquot 2.5 mL of soil using the soil scooper and add it to compartment 1 of the receptacle (demarcated with an etched "1" on the bottom)

2. Add 12.5 mL of solution 1 (extraction solution) by taking the beaker marked "1" and adding solution up to the fill line (demarcated with an etched line on the side of the receptacle)

3. Use the same spoon for aliquoting to mix the solution intermittently for 5 minutes to allow for full extraction of the ions

4. Take an ISE strip and insert it into the bottom of the reader where the edgecard lies
Figure 5-7: Case with the sensor inserted as well as the case opened up, revealing the PCB inside.

5. Turn on the reader by switching on the rocker switch at the top of the reader; a "1" will show at the center of the screen indicating the user should be performing steps relating to solution 1 and compartment 1 of the receptacle.

6. Place the reader with the strip into solution by mating the pegs at the top of the compartment 1 with the holes inside the case; this forms a stable connection for stable electrochemical measurement.

7. Press the button at the center of the reader to initialize the measurement; a countdown on the screen will occur for 60 seconds for which the last 30 seconds the microprocessor takes an average measurement across the four channels and saves each individual channel potential; at the end of this measurement a "2" will appear on the screen indicating it is time to move to compartment 2.

8. Add solution 2 (DI water) by taking the beaker marked "2" and adding solution to compartment 2 up to the fill line.
Figure 5-8: A collage of photos showing the final 3D printed reader and PCB assembly.
Figure 5-9: The full kit: reader, solution beakers, soil scooper, and receptacle.
9. Place the reader with the strip into solution by mating the pegs at the top of the compartment 2 with the holes inside the case; this forms a stable connection for stable electrochemical measurement.

10. Press the button at the center of the reader to initialize the measurement; a countdown on the screen will occur for only 10 seconds; at the end of this measurement a "3" will appear on the screen indicating it is time to move to compartment 3.

11. Add solution 3 (calibration solution) by taking the beaker marked "3" and adding solution to compartment 3 up to the fill line.

12. Place the reader with the strip into solution by mating the pegs at the top of the compartment 3 with the holes inside the case; this forms a stable connection for stable electrochemical measurement.

13. Press the button at the center of the reader to initialize the measurement; a countdown on the screen will occur for 60 seconds for which the last 30 seconds the microprocessor takes an average measurement across the four channels and saves each individual channel potential; at the end of this measurement a letter ("A", "B", "C", "D", "E") will appear on the screen indicating the result of the soil testing measurement.

14. At the end of the measurement, operators other than the user can access the individual channel potentials for the sample and the calibration solutions (1 and 3) by pressing the central button for 10 seconds continuously and then clicking through the values named "C0-3" or "S0-3".
Chapter 6

Ion Selective Electrode Performance

6.0.7 Working Electrodes

PVC-based WEs

Given that PVC-based ion selective membranes are archtypical in the industry, these were the first type of membranes study. Beyond mechanical durability and chemical stability of PVC based membranes, another advantage was their relatively simple manufacturing method: open-air solution casting. Unfortunately, though, PVC membranes were found to suffer non-uniformity issues, as well as irreproducibility issues. As demonstrated in Figure 6-1, the SEM image and profilometry data together suggest inhomogeneity in the thickness and coverage of the final PVC matrix over the CNT layer after evaporation of the solvent. This is likely attributed to the Marangoni effect, wherein solute transfer occurs across regions where perturbations in surface tension during solvent evaporation lead to surface tension gradients - and ultimately, inhomogeneous thicknesses.

Thicknesses of solution-cast PVC membranes showed a percent standard deviation with respect to the mean of 19.13%. Figure 6-2 shows that indeed the potentiometric performance of PVC based membranes are thickness dependent, with thinner membranes corresponding to better potentiometric performance. This suggests that the non-uniform thickness associated with solvent casting may not be ideal for highly reproducible ISEs. Even the best performing solvent cast PVC membranes suffered
from relatively high limits of detection (around $10^{-4}$ M K+) and sub-nernstian slopes, around 43 mV/decade of potassium activity.

It is hypothesized that one of the underlying mechanisms for sub-par potentiometric performance (specifically with respect to the detection limit) is ionophore leakage into the aqueous phase, most likely a result of the highly inhomogeneous PVC-plasticizer network. Essentially, vesicles of plasticizer within the solid PVC matrix are likely areas of high ionophore leakage, serving to reduce the detection limit and degrade potentiometric performance. Sub-nernstian slopes can also be attributed to the inhomogeneous network of PVC and plasticizer, as vesicles of water may form in the matrix during the conditioning step, thereby inducing a sample dependence of the membrane on aqueous potassium concentration and reducing the Nernstian slope. The conclusion from this phase of the project was that PVC-based ISEs should be replaced with a more suitable polymer matrix.
Figure 6-2: (Left) Potential versus time and (Right) Potential versus logarithm of activity of potassium for PVC-based membranes of different dropcast volumes.
Figure 6-3: Logarithm of the limit of detection (LOD) and selectivity coefficient ($K_{ij}$) versus salt-ionophore ratio (wt%). For all experiments valinomycin was kept at 12mg/500uL membrane solution. Selectivity coefficients were determined via the fixed interference method (FIM), at an interference of 1mM HCl.

Butyl acrylate-based WEs

Butyl acrylate (BA) membranes were the next membranes to be examined. BA membranes offer the advantage of "self-plasticization" - meaning, they do not require any plasticizer to achieve suitable glass transition temperatures. They also offer the advantage of UV-curability, allowing for faster manufacturing times.

Optimal salt-ionophore ratio  The first investigation into BA membranes aimed to determine the optimal salt-ionophore loading ratio, and further compare this experimental result to the output of the theoretical model. Valinomycin was kept at 12mg/500uL of membrane solution and the amount of KTpClB was varied in accordance to the specific salt-ionophore ratio.

As shown in Figure 6-3, experimentally determined detection limits are stable up until ratios of 0.5, but then significantly increased with higher salt loading. Experimentally verified selectivity coefficients for hydrogen show a similar trend, with a point of inflection at salt-ionophore ratios around 0.5. These two plots together demonstrate a correlation between membrane selectivity coefficients for hydrogen.
and the detection limit, thereby experimentally verifying that detection limits are connected to concentration of hydrogen ion at the aqueous side of the interface.

But this is not the full story. According to theory, it is not purely the selectivity coefficient for hydrogen that is the limiting factor, but rather the product of the selectivity coefficient with the interfacial pH. This product represents the amount of hydrogen ions which can interact with valinomycin, and thereby decrease the free-valinomycin content within the membrane.

The reason for detection limit dependence on salt-ionophore loading is likely due to two factors: (1) the increased pH at the interface of the electrode is a function of the salt-ionophore ratio (as dictated by the model) and (2) the saturation of ionophore sites, leading to a reduced free valinomycin concentration within the double layer of the membrane phase. With non-zero selectivity for hydrogen ions at the interface, such high pH values at the interface would yield reduced detection limits.

Given that $a_{DL} = K_{ij} \cdot a_H$, it is possible to validate the predictive ability of the model with experimentally determined detection limits and selectivity coefficients. Figure 6-4 represents the interfacial pH predicted by the model, measured at the experimentally determined detection limit, compared with the logarithm of the quotient of the detection limit with respect to the hydrogen ion activity as given by the equation above. Figure 6-4 therefore demonstrates that indeed, the model can accurately predict the interfacial pH, and furthermore validates the theory that detection limits are predicated by the selectivity of the membranes with respect to hydrogen.

**Optimal conditioning protocol** Once the optimal membrane chemistry was determined, the next step in the manufacturing process to optimize was the conditioning protocol. Conditioning ISMs is crucial to ensure a stable response, void of drift due to ion exchange of anionic or cationic impurities in the membrane phase into the aqueous solution. Conditioning also serves to minimize transmembrane fluxes of free potassium within the membrane by giving it enough time to equilibrate fully across the membrane phase when in the presence of a phase concentrated with potassium ions.
Figure 6-4: Comparison of theoretically predicted interfacial pH and experimentally determined interfacial pH.
Given the above mechanism's dependence on diffusion, we sought to control the two parameters fundamental to Fick's first and second laws to determine the optimal conditioning protocol: time and concentration gradient. Increased concentrations of conditioning solution were hypothesized to be more effective conditioning agents as they further increased the electrochemical potential gradient acting as the driving force of impurity diffusion into the aqueous phase. Meanwhile, time was also varied so as to give the free potassium inside the membrane sufficient time to equilibrate uniformly across the cross section of the membrane.

As seen in Figure 6-5, increasing the conditioning solution concentration and incubation time yields more Nernstian slopes and more stable responses. BA ISEs which were not conditioned demonstrated particularly unstable potentials as well as low slopes (30.8 mV/decade), whereas the same membranes conditioned in 1mM KCl for 12 hours demonstrated both stable potentials and nearly ideally Nernstian slopes (58.4 mV/decade). In terms of incubation time, it was shown to have little effect on low ionic strength conditioning solutions and exacerbate the effect of high ionic strength conditioning solutions on the ISEs. For example, while increasing incubation time from 3 to 12 hours for 1uM conditioning solutions decreased the slope an insignificant 1.8 mV/decade, the same time increase for 1mM conditioning solutions served to increase the slope 6 mV/decade. In the end, due to the near ideal Nernstian behavior of BA ISEs in 1mM conditioning baths for 12 hours, this protocol was chosen moving forward.

**Selectivity** The results indicated from Table 6-1 show that for nearly all interfering ions of interest, the BA ISEs demonstrate sufficient selectivity towards potassium so as not to induce a significant error in the potentiometric measurement. The only ion which posed a potential issue was ammonia as ammonia is typically found in high concentrations in soil and soil fertilizers.

**Electrochemical and Physical Characterization** The final step for the individual ISMs on the WE was characterizing their electrochemical and physical properties.
Figure 6-5: (Left) Potential versus time and potential versus logarithm of activity for BA ISEs exposed to different conditioning protocols. (Right) Bar graph representing the effect that conditioning protocol has on the slope of the BA ISEs.

No conditioning. Slope: 30.81
10^{-3} M KCl, 3hr, Slope: 52.33
10^{-6} M KCl, 12hr, Slope: 51.45
10^{-3} M KCl, 12hr, Slope: 58.7
10^{-6} M KCl, 12hr, Slope: 48.92

Ideal Nernstian slope
In terms of physical parameters, we characterized the thickness and morphology of each layer with the SEM (Figure 6-6) and the profilometer. For the electrode contacts, the carbon nanotube (CNT) and silver chloride (AgCl) exhibited rough morphologies and thicknesses of $31.29 \pm 3.29 \mu m$ and $39.13 \pm 5.46 \mu m$, respectively. With both layers screen-printed through masks of equivalent dimensions, it makes sense that respective layer thicknesses would be similar, with differences likely attributed to the higher mass fraction of solid in the AgCl ink.

Meanwhile the drop-casted butyl acrylate (BA) ion selective membrane (ISM) showed a mostly smooth morphology with highly reproducible thicknesses of $127.09 \pm 12.35 \mu m$. The RE membrane, on the other hand, was much rougher but despite this, demonstrated similar thickness reproducibility at $138.2 \pm 13.7 \mu m$.

In terms of electrochemical metrics, the mean resistance and capacitance values of the ISMs were $11.47 \pm 0.70 \, M\Omega$ and $12.07 \pm 0.47 \, pF/cm^2$, which is consistent with literature values. Meanwhile, the thickness of the sensors was $157.0 \pm 6.6$ microns.
Figure 6-7 shows representative electrochemical impedance plots and profilometry plots.

Regressions of the resistance or capacitance (Figure 6-8) with respect to potentiometric performance parameters - namely, slope and detection limit (LOD) - showed no significant correlations ($R^2$ values all below 0.1). This suggests that the potentiometric performance of the ISMs are likely not correlated to electrochemical parameters such as resistance and capacitance. Similar regressions with thickness also yielded no correlation. Indeed if such parameters are correlated, it may be that a multiplicity of parameters effect performance, rather than a single parameter by itself.
Figure 6-8: Regressions of potentiometric performance metrics versus electrochemical and physical properties of the WE ISMs, $N = 14$. 
Working Electrode Reproducibility  One of the main objectives of this research project is to create reliable, repeatable soil diagnostic measurements. As such, reproducibility studies were carried out for the WE, RE, and full devices. For the WE, it is particularly important that the slope be repeatable, given a two point calibration likely to be used by the end user. Absolute values are not relevant as it is expected that for a particular sensor the potential deviation with respect to the RE will be consistent.

Figure 6-9 depicts the WE reproducibility study, wherein 17 ISMs were studied for their potentiometric performance. For this batch of ISMs, the mean slope was a sub-Nernstian 53.29 +/- 2.78 mV/decade and the mean detection limit was $10^{-6.22}$ M. With a calibration solution of $10^{-2}$ M KCl and soil samples typically within 2 decades in concentration of one another ($10^{-4}M$ to $10^{-2}M$), a standard deviation of 2.78 mV/decade for these individual WEs is nearly sufficient to remain within the bounday of +/- 5.4 mV error necessary for an 80% predictive accuracy as highlighted by the error analysis model. Detection limits of $10^{-6.22}$ M KCl are well within the range for soil K+, which is minimally $10^{-4.5}$ M.

6.0.8 Reference Electrodes

A lateral study of reference electrodes of different materials and constructions was considered. The two constructions are detailed in Figure 6-10. Both constructions include AgCl and CNT screen printed layers above a PC substrate. Above these two layers, construction 1 has a hydrogel polymerized HEMA layer doped with KCl (pHEMA/KCl) as well as an ionophore-free butyl acrylate layer (BA), signified as X so as to represent multiple explored variations of this layer.

Figure 6-11 details the potentiometric performance of the investigated RE designs. Neither of the electrodes utilizing construction 1 were able to obtain satisfactory stability over the potentiometric titration. The gold standard of reference electrodes is typically a slope of less than 2 mV/decade during the course of a potentiometric titration; as these are close to typical values for commercial PVC-based full-cell ISEs. The exposed ionophore-free BA layer indeed showed a cationic response of 21.6
Figure 6-9: (Top) Reproducibility study of Butyl Acrylate ISMs (Center) Distribution of detection limits (Bottom) Distribution of slope values.
mV/decade, suggesting that BA itself complexes cations naturally without the aid of any ionophore. While the DuPont 5018A screen printable dielectric had an improved performance of 17 mV/decade, it still did not provide satisfactory stability for the REs.

Although moving towards construction 2 provided a simplified manufacturing method (only 1 layer needed to be dropcasted rather than 2), it did not achieve ideal reference electrode stability. Graphene in particular showed poor performance (average 23 mV/decade change), likely due to intercalation of potassium into the graphitic layers. Blends of cellulose acetate and polyurethane (CA/PU) have been shown to be promising candidates for stable reference electrodes. Indeed CA/PU blends were the best performing reference electrodes (7 mV/decade slope) but still did not reach the desired 2 mV/decade goal.

**PVB REs**

**PVB conditioning** One final design iteration was considered utilizing construction 2: polyvinyl butyral (PVB) doped with sodium chloride (NaCl). PVB is a porous polymer which hydrates and complexes chloride when in contact with an aqueous
Figure 6-11: (Top left) Butyl acrylate (BA) based RE using construction 1, (Top right) Cellulose acetate/polyurethane blend (CA/PU) based RE using construction 2, (Bottom left) 5018A screen print based RE using construction 1, (Bottom right) Graphene based RE using construction 2. Aqueous KCl concentrations varied from $10^{-6}$ to $10^{-2}$, with decade increases at each 2 minute intervals for CA/PU and graphene and 5 minute intervals for BA and 5018A.
sample containing chloride ion. Notably, this complexation is not fully reversible, meaning that after contact with a conditioning solution bath containing chloride, the PVB can maintain a constant chloride ion activity above the Ag/AgCl layer. Importantly, though, PVB RE performance is highly dependent on the conditioning time. Figure 6-12 shows that increasing conditioning time in 1mM KCl up to 6 hours increases RE stability, but there is the chance of overconditioning once 18 hours is reached. Thus, the optimal conditioning time was chosen to be 12 hours, as this could be parallelized with the WE.

**Potentiometric Performance and Reproducibility**  Figure 6-13 shows the superior, repeatable potentiometric performance of the PVB based REs in potassium chloride solutions. Notably, there is a calculated distinction between the reported slope values and the reported average difference values. Slope values correspond to
the slope of the linear least-squares fit, whereas the average difference values takes the average of the potential jumps recorded immediately before and after a concentration change. In essence, the average difference values correspond to the immediate potential shift associated with a concentration change, without the effect of any drift. The average slope and difference values for the 9 reported PVB REs were 0.25 mV/decade and 3.10 mV, respectively, both within the acceptable range.

**PVB RE Selectivity** Importantly, the PVB REs must not only perform well in KCl solutions, but also in the presence of other salts with different ionic mobilities between the cation and the anion in the salt pair. Such difference in mobilities could yield to measurable diffusion potentials, for example, on the order of a few mV. Figure 6-14 shows the performance of the PVB REs in the presence of a various different chloride containing salts.

As shown in Figure 6-14, with exception of CaCl₂, all of the salts with interfering ions yielded sub-10mV shifts over the potentiometric titration from 10⁻⁶ to 10⁻² M. Referring to the error analysis model in Chapter 4, which concluded that the maxi-
Figure 6-14: Stability analysis of PVB REs in the presence of numerous salts with representative interfering cations typical in Soil. Note: Plots were shifted up or down to increase readability.

The minimum error in the complete ISE system had to be sub-10mV, these results themselves show that indeed the PVB REs alone fall within this range. However, given that the total error in the system is given by:

\[ \sqrt{\sigma_{total}^2} = \sqrt{\sigma_{RE}^2 + \sigma_{WE}^2 + \sigma_{Reader}^2} \]  

(6.1)

These results would conclude that the WEs and Reader would need to have close to zero standard deviation in error. Given the high improbability of such a condition, this suggests that improved RE stability may be needed.

6.0.9 Extraction system

One possible way to overcome this issue is to utilize the extraction solution background as a stabilizing agent for the REs. As discussed in Chapter 3, there are many types of UES available for soil scientists to use. An ideal UES for use with ISEs would ensure that the both the WE and RE remain unaffected by the ions present in the
Figure 6-15: Potentiometric performance of BA WEs with differing universal extraction solutions (UES) as backgrounds.

UES. Starting with the WEs, Figure 6-15 shows that of all the UES, Strontium Chloride (SrCl$_2$) had the most minimal effect on potentiometric performance of the WEs. While SrCl$_2$ only degraded the LOD of the WEs by less than 1 order of magnitude, Modified Morgan and Morgan UES degraded detection limits by nearly 2 orders of magnitude.

Another thing to note is the change in slope associated with different UES backgrounds. SrCl$_2$, for example, increased the sensitivity of the WEs, raising the slope from a sub-Nernstian 51.04mV/decade in a DI background (similar to the 53.2 mV/decade measured in the reproducibility plot) to a super-Nernstian slope of 67 mV/decade. While this deviates from the ideal 59.2 mV/decade, with an $R^2$ value of 0.989, the linearity of the WE slope suggests that this non-ideality can be controlled for in the software of the reader.
SrCl₂ also offered the advantage of increasing the stability of the PVB REs due to the high molarity of Cl⁻ in the solution. Figure 6-16 shows a comparison of the REs with a background of DI water to the same ones in the background of SrCl₂. Errors reduced from nearly 10mV/decade to sub-mV shifts. REs for LiCl and NaCl in fact shifted only on the order of tens to hundreds of microvolts which is particularly ideal.

**Morgan versus Strontium chloride extract performance**

As described in Chapter 3, SrCl₂ is typically not the standard UES for soil analyte measurement. Rather, ammonium acetate, Morgan, or Modified Morgan extracts are preferred as they are highly efficient ion extractants, and as such soil recommendations are typically in terms of total extractable K⁺ from the aforementioned UESs. In order to ensure that SrCl₂ was an appropriate UES for this application, Morgan and SrCl₂ extraction protocols were compared on the ICP. Figure 6-17 shows that while SrCl₂ is a less effective UES than Morgan (Morgan is 34.9% more efficient in extracting K⁺), the highly linear fit ($R^2 = 0.9575$) suggests this inefficiency can be accounted for in either the reader software or in reducing the threshold for K⁺ bins associated with the recommendation process.
Figure 6-17: Extracting protocols of Morgan UES and $SrCl_2$ compared on the ISE for potassium.

6.0.10 Full ISE system

With the extraction solution, RE and WE fully characterized and optimized, the final step in the process was in characterizing the potentiometric performance of the full ISE system. Rather than using an external RE, the potentials on the WE were measured with respect to the potentials on the RE in the background of the $SrCl_2$ extraction solution.

As seen in Figure 6-18, the full ISE system showed highly reproducible potentiometric performance. Standard deviation of LODs of the full ISE system, for example, varied only 1.59%, or 0.08 decades in molarity. Meanwhile, the most important value, the slope, had a standard deviation of 3.24 mV/decade. With soil potassium values spanning approximately two decades of concentration, this would suggest that the full ISE system (WE and RE) variability would constitute a total standard error of 6.28 mV.

6.0.11 ISE performance versus ICP

The final part of experimentation was dedicated to testing the performance of the full ISE system with respect a control, the ICP. Figure 6-19 shows regressions of
Figure 6-18: Reproducibility of the full ISE system in a background of $SrC{l_2}$. 

158
calculated potassium ppm values of 30 soil samples measured using full ISEs on either the potentiostat or the reader. All measurements were taken using a two point calibration with $10^{-2}$ M KCl in a background of 0.02 M $SrCl_2$, waiting 90 seconds after insertion of ISE into solution to avoid transient responses. ISE responses measured on the potentiostat showed an $R^2$ of 0.962 with respect to ICP samples, while those measured on the reader device showed an $R^2$ of 0.898. The likely cause of the reader correlation being lower is due to the additional 1.25-2.5 mV error introduced by the components, as discussed in the reader error analysis section in the methods chapter. Together, though the highly correlated responses of the ICP results with those of the ISEs on the potentiostat and the reader demonstrate that indeed the ISEs can provide reliable measurement of soil potassium.
Chapter 7

Usability Study

This chapter describes the usability study which took place in Hubli, Karnataka in July, 2016. The purpose of the study was to answer the following questions:

1. "How usable and intuitive is the soil testing user experience with the sensors and the reader?"

2. "How do demographic factors such as age, education, and landholdings affect the usability of the devices?"

The hypothesis was that users would perform worse than the control (myself), and that factors such as increased age, decreased education, and decreased landholdings (a proxy for decreased wealth) would negatively correlate with usability performance data.

Unfortunately a software glitch during the study made it impossible to collect accurate potassium measurements. As such, this study is limited to usability data only.

7.0.12 Study Design

The study was designed as follows: 64 farmers, in batches of 6, came into a central room for a demo on how to use the devices and the strip. After a 20 minute question
and answer period, users were given the opportunity to use the devices *independently* to test an actual composite soil sample (collected the day prior) for soil potassium.

During this independent activity period, workshop coordinators watched objectively while the users performed the necessary steps to take a measurement, and gave them a score of 0 or 1 if they performed a step correctly. Once the users completed the test, coordinators took down their time and calculated the total score as the sum of the individual step scores. With 10 steps in total, the maximum score, therefore, would be 10. The delineation of steps was as follows:

1. **Step 1:** Scoop soil (2.5 mL)
2. **Step 2:** Add solution 1 (extraction solution) to compartment 1 (12.5 mL)
3. **Step 3:** Stir solution intermittently for 5 minutes
4. **Step 4:** Turn on PCB
5. **Step 5:** Insert strip into reader
6. **Step 6:** Measure solution 1
7. **Step 7:** Add solution 2 (DI water) to compartment 2 (12.5 mL)
8. **Step 8:** Wash with DI
9. **Step 9:** Add solution 3 (calibration solution) to compartment 3 (12.5 mL)
10. **Step 10:** Measure solution 3

A "usability index" was generated by dividing the total score across all the steps by the total time. In this way, the index was designed to take into account both the ease of the user experience as well as the degree of intuitiveness, reflected in the time. Usability indices were normalized with respect to my own performance as the control. My usability index was 10/9 as my total score of 10 and a completion time of 9 minutes. Normalized usability indices were used throughout the study, on a scale of 0-1 with 1 being of equal performance to the control.
Figure 7-1: Collage of pictures of the workshop coordinators and participants throughout the week.
Demographic information was collected in the form of age, sex, education, and landholdings for each user. This information was used in regressions generated later in this section.

A copy of the sheet filled out by the coordinators is shown in the auxiliary section. It was highly important to get accurate translations for each of the steps so that all coordinator scores were not affected by interpretation error. Translations can be found beneath the English explanations for each query.

### 7.0.13 Study Results

The results of the study are presented in Figure 7-2,3 and Tables 7-1,2. Notably, regressions are only shown with respect to total score given that correlations were weaker with respect to the weighted usability index.
Beginning with the first question, "How usable and intuitive is the soil testing user experience with the sensors and the reader?," Figure 7-2 shows the average step score for each individual step. The lowest performing steps were the card insertion step (Step 5, average score of 0.62) and the first button press (Step 4, average score of 0.73) to initialize the measurement. Users particularly struggled with correct card insertion without touching the sensors, so it is suggested to have some protective film on top of the sensors, and an ergonomic physical feature to guide users as to how to hold the strip. For the first button press users thought that the device would automatically start measurement when placed in the solution, so they asked to have some sort of clear audio or visual feedback to ensure they press the button for each of the three main steps in the process (extraction measurement, wash, and calibration measurement).

On the other hand, users had in fact perfect performance for the step of scooping the soil sample (Step 1, average score of 1) and aliquoting the correct amount. They also had particularly high scores for the second button press (Step 7, average score 0.96), which makes sense given the reminder that the workshop coordinators would have given on Step 4 if they had not had pressed the button for the first extraction solution measurement.

Table 7-1 shows the averages and standard deviations of the performance values for the 64 farmers in this study. The self-reported farmer rating, total score, usability indices (normalized to 10 as the maximum), and time are respectively 8.007 +/- 1.435, 8.091 +/-1.413, 7.158 +/- 1.649, 10.809 +/- 1.916.

The relatively high farmer ratings are encouraging. Furthermore, the fact that the average total score and farmer rating so closely match up with each other is further shows that farmers were relatively honest with their feedback. A farmer rating much higher than the objective score rating would indicate that farmers either thought the device was easier than it actually was, or they were providing dishonest feedback as to how they actually found device operation to be.

An average usability index of 7.158 can be interpreted as farmer performance being approximately 72% as good as control performance during a farmer’s first use.
This metric takes into account how intuitive device operation is with only a short demonstration and without any external aid. As with any task, muscle memory and active working memory develop over time, and so we expect that the usability index would increase over repeated use of the device. This would likely come in the form of both decreased times as well as increased total scores.

<table>
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<th>Metric</th>
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<th>Standard deviation</th>
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<td>1.435</td>
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<tr>
<td>Score</td>
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<td>1.413</td>
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<tr>
<td>Usability index</td>
<td>7.158</td>
<td>1.649</td>
</tr>
<tr>
<td>Time (min)</td>
<td>10.809</td>
<td>1.916</td>
</tr>
</tbody>
</table>

Table 7.1: Average values and standard deviations resulting from the usability study.

Now onto the second question: "How do demographic factors such as age, education, and landholdings affect the usability of the devices?"

As shown in Figure 7-2, correlations were quite weak across the board with respect to demographic information. $R^2$ values were 0.175, 0.087, 0.019 for age, education, and landholdings respectively. Of all the demographic predictors, age seemed to be the strongest.

This fact is corroborated by the results in Table 7-2, wherein T tests are individually run for data split along individual demographic lines. Data in the young versus old (above or below 35 years old), and educated versus uneducated (above or below 9 years of education) groups had mean differences of 0.97 and 0.9 respectively and p values of 0.007 and 0.027, which are very statistically significant. In other words, these data suggest that the younger group performed 9.7% better than the older group, and the higher educated group performed 9.0% better than the lower educated group.

Unlike our original hypothesis, usability index distributions had no significant differences between the high and low landholdings groups. In fact, on the basis solely of mean difference, the lower landholdings group performed better than the higher landholdings group - though notably, this difference is not statistically significant.
Figure 7-3: Linear regressions of age, education, and landholdings with respect to total farmer score.
With respect to usability index (Table 7-3), most of the t-tests are relatively similar in their statistical significance, with the exception of education superceding age. p-values and mean differences for education and age were 0.0089 and 0.0092 and 0.106 and 0.108, respectively. Thus, by taking in the time for users to complete the user experience, the relative performances of the younger and higher educated groups rose to 10.8% and 10.6% better compared to their respective counterparts.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Group 1</th>
<th>Group 2</th>
<th>p-value</th>
<th>t-value</th>
<th>Mean Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age</td>
<td>≤ 35 years</td>
<td>&gt; 35 years</td>
<td>0.0064</td>
<td>2.821</td>
<td>0.970</td>
</tr>
<tr>
<td>Education</td>
<td>≤ 9 years</td>
<td>&gt; 9 years</td>
<td>0.0127</td>
<td>2.564</td>
<td>0.900</td>
</tr>
<tr>
<td>Land</td>
<td>≤ 19 acres</td>
<td>&gt; 19 acres</td>
<td>0.759</td>
<td>0.307</td>
<td>-0.110</td>
</tr>
</tbody>
</table>

Table 7.2: T tests on demographic factors with respect to farmer score.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Group 1</th>
<th>Group 2</th>
<th>p-value</th>
<th>t-value</th>
<th>Mean Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age</td>
<td>≤ 35 years</td>
<td>&gt; 35 years</td>
<td>0.0092</td>
<td>2.691</td>
<td>0.106</td>
</tr>
<tr>
<td>Education</td>
<td>≤ 9 years</td>
<td>&gt; 9 years</td>
<td>0.0089</td>
<td>2.703</td>
<td>0.108</td>
</tr>
<tr>
<td>Land</td>
<td>≤ 19 acres</td>
<td>&gt; 19 acres</td>
<td>0.887</td>
<td>0.1423</td>
<td>-0.006</td>
</tr>
</tbody>
</table>

Table 7.3: T tests on demographic factors with respect to farmer usability indices.

### 7.0.14 Future Recommendations

This section combines the quantitative results of the usability study along with the qualitative feedback received from the farmers to give a list of the top suggested changes needed for future product development.

1. **Readability**: increase the size of the display and contrast, perhaps by using either a backlit display or a 7-segment numeric LED character display; ensure that the display can be read well in all light settings

2. **Auditory feedback**: add sound for when the device turns on, when a measurement is occurring, and when a measurement is done
3. **Visual feedback**: users preferred to have visual queues for each step to guide them so that they wouldn’t forget to initialize the measurement at each step (i.e. flashing LEDs going from red when step not the present step, to flashing green when step is the present step, then green when measurement is complete, and finally back to red when it is time for the next step)

4. **Timer**: for timed measurements, add a clock icon on the display accompanied with a second countdown rather than use the current abstracted timer representation of squares descending in number over time

5. **Power management**: the 9V battery used was unfamiliar, and although AA and AAA batteries were more common, many users expressed a dislike of the disposable batteries because of the cost and inconvenience; future designs should instead use a rechargeable system, perhaps with the micro USB charger often used for phones, to make it more convenient; add a feedback mechanism in the form of a red or yellow LED to indicate when charging is needed

6. **Insertion mechanism**: make the insertion mechanism ergonomic, smooth, and foolproof; ensure only one way of insertion and a feedback mechanism (i.e. sound or light indicator) telling the user if the strip was inserted correctly (this can be done with a small code on the strip and a photodiode and light source in the reader itself); add a protective layer to avoid sensor degradation due to improper handling

7. **Grouping**: instead of having one button for all three phases (extraction, washing, and calibration), users instead wanted three separate buttons or switches with corresponding flashing lights and color changes to indicate when a step is up next, active, and complete

8. **Soil sampling card**: given that soil testing accuracy is highly dependent on users’ ability to take an accuracy composite soil sample, it would be best to have a slot in the back of the reader detailing how to take a composite soil
sample, either completely pictographically (i.e. IKEA) or in the local language of the user.

9. **Receptacle design:** rather than have the current peg/hole configuration (which is also not waterproof) it would be best to have a tall, thin receptacle and a high surface area slot which the reader and strip slides in; the simple geometric mating fit would be easy to implement and stable with the high surface area connection.

10. **Accommodating older demographics:** as suggested by the data, increased age had the highest correlation to with decreased device usability; with this information future designs should attempt to accommodate this age group by having large UX features (screens, buttons, lights, switches) and ensure ergonomic operation for the older age group.
Figure 7-4: Rendering of next generation prototype incorporating user feedback from usability study.
8.1 Summary of the Findings

Rural Indian farmers lack an actionable, available, affordable, and usable system for diagnosing soil health and receiving location and crop specific fertilizer recommendations. A combination of user interviews, field research, and interactive design workshops resulted in a solution agnostic product contract outlining user needs and resultant technical specifications of a soil diagnostic solution. Subsequent technical analysis including proof-of-concept experimentation and literature review revealed that ion selective electrodes were the most promising technical solution to fit user needs.

Prior to rigorous experimentation, a two-part theoretical framework was generated to understand (i) the underlying electrochemical phenomena which predicate optimal ISE performance, as well as (ii) the maximal system error (comprised of the WE, RE, and reader) allowable to accommodate user needs with respect to accuracy. These theoretical models not only provided the framework with which to explore solutions but also bounds necessary to constrain the solution space.

For the error analysis model, it was found that a total potential error of $\pm 5.4$ mV across the system is necessary to achieve an 80% error in soil K+ bin prediction. Notably, though, bin prediction error is only most frequent at the minima and maxima of each bin, and since bin prediction is nearly always (99.8%) only off by 1 bin, even
a standard system error of +/- 5.4 mV would not yield a problematic prediction. This suggests that it may be possible to introduce more leniency in the system and have higher total system error than the model predicts directly or perhaps have a software-based approach which takes into account higher error frequencies at higher concentrations.

For the electrochemical model, it was uncovered that the most important factor dictating ISE performance was the salt-to-ionophore ratio within the membrane. Specifically, it was found that ISE performance was dramatically degraded once salt-ionophore ratios exceed 0.5 (wt%). ISE cocktails containing such high ratios saw detection limits exponential reduce from sub-uM ($10^{-6.2}$ M) to closer to $10^{-4}$ M. Given that higher salt content in the membrane is necessary to ensure permselectivity of the membrane against interfering counterions, a final salt-ionophore ratio was chosen as 0.25. These membranes demonstrated an average detection limit of $10^{-6.2}$ M and a slope (albeit sub-Nernstian) of 53.3 mV/decade when in the presence of pure DI water.

It was also found that the interfacial pH is indeed the limiting factor dictating the detection limit of the WE ISMs. Experimentally calculated detection limits for variable salt-ionophore ratios were compared to theoretically predicted limits using the experimentally calculated $\log K_{ij}$ values with respect to hydrogen for each ratio. The high correlation between experimentally determined detection limits and those predicted by the model verify not only the model’s predictive ability, but also the role that interfacial pH has on ISE detection limits.

Meanwhile, conditioning solution molarity and incubation time were found to have the most significant affect on the other metric of potentiometric performance: slope. The optimal conditioning protocol was found to be 12 hours in $10^{-3}M$ KCl, followed by 3 hours in $10^{-3}M$ KCl in a background of $0.02M Sr_2Cl$. According to theory, the optimal slope of an ISE measurement is 59.2 mV/decade at room temperature, and such slopes (average of 61mV/decade) were achieved for the WE ISMs with this final conditioning protocol.

Important to any soil analyte measurement is the extraction of ions from the
charged colloidal soil complex. An ideal universal extraction solution in the context of ISE measurement can universally extract important macro and micronutrients from soil in parallel without compromising ISE performance. After exploring Kelowna, Morgan, Modified Morgan, and Strontium Chloride extracts, it was determined that Strontium Chloride had the least deleterious effect on the WE ISMs, reducing detection limits only by 1 order of magnitude as opposed to 2 or even 3 for some of the other extracts. And while Strontium Chloride was found to extract soil K+ at only 76% efficiency with respect to the standard Morgan extraction protocol, the highly linear relationship showed that fertilizer recommendations could easily be changed accordingly without introducing error in fertilizer application recommendations.

For the reference electrodes, a lateral exploration was conducted - including various layer-by-layer constructions and membrane formulations. After testing graphene, butyl acrylate, 5018A Dupont dielectric, cellulose/polyurethane blends, and polyvinyl butyral - it was found that the most stable reference electrode was comprised of a dropcasted polyvinyl butyral layer on top of a screen printed silver chloride layer. This RE construction demonstrated an average 2mV/decade stability across 6 decades in concentration of KCl in DI, and sub-mV changes when tested in a background of Strontium Chloride (which is ultimately how a final soil analyte measurement would take place). The fact that the high chloride ion content of the extraction solution stabilizes the electrochemical reduction reaction of silver at the RE is a further testament to the superior choice of Strontium Chloride as the UES.

Reproducibility analyses of the RE and WE and full ISE system together demonstrated bear commensurate standard error deviations to be within the bounds of the error model. Using a sample set of 20 full ISEs tested in a background of Strontium Chloride, the standard deviations in slope and detection limit were 3.24 mV/decade and 0.08 decades, respectively. Assuming 1.25 mV typical standard error introduced from the reader and typical soil K+ concentrations spanning only two decades of concentration, the total system error in such with the ISEs would be:
\[
\sqrt{\sigma_{\text{total}}^2} = \sqrt{\sigma_{\text{RE}}^2 + \sigma_{\text{WE}}^2 + \sigma_{\text{Reader}}^2} = \sqrt{\sigma_{\text{ISE}}^2 + \sigma_{\text{Reader}}^2} = \sqrt{6.28^2 + 1.25^2} = 6.35
\]

(8.1)

Which is slightly outside the bounds of 5.4 mV predicted by the error model. Such a system error would yield a 74% accuracy rate, not far out of the original bounds suggested from the product contract. But as suggested prior, the model may be too stringent and indeed such a system error may be commensurate for reliable soil fertilizer application recommendations. In addition, with increased mechanization as manufacturing ramps up, it is expected that the total system error resulting from the ISEs will likely dramatically reduce.

Selectivity analyses of the RE and WE showed that no ion typically found in a heterogeneous soil sample would meaningfully degrade ISE performance. For the WE, nearly all \(\log K_{ij}\) values were within the range required for less than 0.1% error (using typical concentrations of interfering ions for the calculations). Meanwhile, for the RE, when stabilized in a background of the UES, all interfering ions introduced less than sub-mV deviations in the measurement.

With the full ISE system optimized and characterized to completion, it was time for the development of a reader to transduce potential measurements into actual soil K+ concentrations. The reader was realized via a two-stage op-amp design - one for buffering the signal from the WE and RE and the other for taking the difference between the WE and RE and amplifying that to sufficiently high potentials to be read by the ADC of the microcontroller. A handheld physical case was also designed and 3D printed to encapsulate the PCB and accommodate an ergonomic user experience. Compared with the ICP, actual soil tests using the reader and the strips demonstrated an 0.898 correlation factor, suggesting that the system is robust enough to perform nearly as good as the gold standard in trace ion detection.

Finally, a usability study was conducted in July of 2016 with 64 farmers to test the usability of the devices and determine the affect of demographic factors (age, ed-
ucation, landholdings) on the user experience. Farmers scored an average 8.091 out of a total of 10 in terms of accurate completion of the steps of the user experience. Usability indices, which divided farmer scores by the total completion time and were then normalized by the control (myself) indicated farmer performance was approximately 72% as good as the control for their first time of use. Pure linear regressions based on age, education, and landholdings (a proxy to wealth) indicated that age and education had minorly significant affects on farmer scores, while landholdings did not. Meanwhile T-tests run on the young versus old (above or below 35 years old), and educated versus uneducated (above or below 9 years of education) had mean differences of 0.97 and 0.9 respectively in farmer score and p values of 0.007 and 0.027. In other words, these data suggest that the younger group statistically significantly performed 9.7% better than the older group, and the higher educated group similarly performed 9.0% better than the lower educated group.

Bringing it back full circle to the product contract, we can see that many of the constraints originally outlined have been successfully or nearly successfully met with this product:

**Accuracy:** Measure soil ppm values with 80% accuracy with respect to a typical KVK test.

Taking into account reproducibility errors, an average deviation of +/- 6.35 mV for the full ISE system across sensor batches would yield a 74% accurate bin prediction rate, just short of the target but likely to be improved with more refined manufacturing techniques.

**Usability:** Less than ten distinct steps to complete a soil test.

Indeed our process is right at the edge of this constraint, with 10 steps necessary for completion. Granted, this does not take into account composite soil sampling, but this would be necessary for any other soil testing solution, so it is plausible to discount this.

**Point of use:** Handheld operation.

As outlined, our devices can be used on site without the need of external equipment outside of the kit provided. It is a handheld device, so it can be done anywhere on
**Target user:** Rural small landholding farmers with adequate access to water resources and fertilizer distributors

**Use case:** Twice a year before planting in the Kharif and Rabi seasons, users take a composite soil sample representative of their farm, perform a soil test, and receive a customized soil fertilizer recommendation

<table>
<thead>
<tr>
<th>Product Contract</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>User data</strong></td>
</tr>
<tr>
<td>Accuracy is the most important aspect of a quality soil test</td>
</tr>
<tr>
<td>&quot;The current system is too slow, if I were able to get a result on my own fairly easily, I would do it&quot;</td>
</tr>
<tr>
<td>&quot;I had to travel 50km to the local KVK and I never got a soil test result back&quot;</td>
</tr>
<tr>
<td>&quot;We need more information about how much fertilizer to use, what crops to grow, and how to use inputs effectively&quot;</td>
</tr>
<tr>
<td>&quot;If the task takes me too much time I will not care anymore&quot;</td>
</tr>
<tr>
<td>&quot;I don't trust anyone but myself, and so I want to do the test myself&quot;</td>
</tr>
<tr>
<td>&quot;I don't mind paying if it's good quality&quot;</td>
</tr>
<tr>
<td>&quot;I can afford to buy this only once so longevity is important&quot;</td>
</tr>
<tr>
<td>&quot;We are used to spending many hours a day working in the field&quot;</td>
</tr>
</tbody>
</table>

Figure 8-1: Product contract describing attributes that determine technical and system design constraints.
the field or the farm.

**Time:** Less than 10 minutes.

Our process is right at the edge of this constraint, as average times from the usability study was 10.8 minutes. But since this metric was for the users' first time use, we expect this time to decrease as farmers use the device more and more.

**Longevity:** Lasts more than 100 soil tests.

While we did not conduct a reusability study on the strips themsevles, qualitatively we found that they can last easily up to 30 uses. That being said, the purpose of the strips are to be disposable, and so the metric here really applies mostly to the reader. We expect that the lifetime of the reader can exceed five years, based on similar electronic product lifetimes, and with recharging capabilities we foresee that our solution can easily fit within the bounds of this constraint.

**Labor Intensity:** Minimal labor to complete soil test.

Excluding soil sampling, this soluton requires very little physical work at all.

**Affordability:** < 60 INR per strip and < 600 INR per device.

Finally, in terms of cost, a bill of materials (BOM) calculation (Tables A-1, A-2) shows that the individual strips cost 0.26 USD each and that the reader costs 8.63 USD each. Notably, these BOM calculations take into account only material costs and not additional costs such as labor, manufacturing, packaging, distribution, and marketing. While these costs may significantly increase the final retail price of the product, we expect advances in manufacturing throughput and lower bulk prices to stabilize the price somewhat. In these ways, we hope to achieve the desired cost constraints expressed by users, with 60 INR (1 USD) per strip and under 600 INR (10 USD) for the reader.

In all, the results of this preliminary phase can be viewed a success in terms of realizing a desirable soil diagnostic solution which meets the appropriate user needs and corresponding technical specifications.
8.2 Future Work

This research is only the beginning of a comprehensive solution to the issue of poor soil health in rural India and the need for a point-of-use soil testing solution that is actionable, available, affordable, and usable.

In terms of the electrochemical theoretical model, the next steps required are considering H+ penetration into the membrane (and corresponding K+ exit out of the membrane), as well as H+ complexing with valinomycin based on its respective equilibrium constant with valinomycin as well as the conditions of thermodynamic equilibirum and no net ion flux at the interface. In this way, the model would be able to predict $\log K_{ij}$ values for hydrogen at different salt-ionophore ratios, which can be coupled with its current ability to predict the interfacial pH so as to determine the exact detection limit fully from theoretical foundations. This model output could then be compared to experimental data currently available on the salt-ionophore ratio affect on the detection limit.

The next most immediate step in terms of device development is expanding beyond just potassium measurement, but rather include the other three channels necessary for a complete macronutrient testing strip (NPKPh). Ionophores for N and H (pH) are widely available but those for P are less so. In this way, some time might be needed to research the optimal ionophore for P or pair up with a synthetic chemistry lab to synthesize the ionophore. Once a macronutrient strip is fully realized, a micronutrient strip which can test Boron, Zinc, Calcium, and Iron should also be developed since ionophores for these are commonly available as well.

In terms of the manufacturing of the strip, the most pressing need is finding a way to scale up production while simultaneously increasing the reproducibility of the full ISE system. Currently, while the manufacturing process is quite simple and robust, it is ultimately limited to manual deposition of both the screen printable inks and manual pipetting of the WE and RE solutions. This limits production to approximately 100 complete strips of 4 channels (i.e. 800 sensors) in a 36 hour period (including conditioning times). A small to medium size system which can produce
1000 sensors or so in a day while achieving the requisite reproducibility would be a major achievement moving forward. On such iteration of a system could come in the form of a roll to roll setup with doctor blade deposition of the inks and automatic pipetters with localized UV radiation to cure the WE membranes upon deposition. Another could remove the pipetting all together an instead solution cast and cure the RE and WE membranes in a batch and later on cut and adhere the individual sensors back onto the electrodes. Regardless of the iteration, slope reproducibility should be improved to ensure minimal predictive error in soil fertilizer application.

For the reader, the next generation prototype should incorporate the suggestions of the users from the usability study. Most importantly, it should improve the process of strip insertion in terms of ergonomics, protection of the membranes, and correct orientation and connection with the reader hardware. The next generation prototype should also incorporate more visual and auditory queues for guiding the user through the steps in the process, and indicate instances of misuse. Clearer groupings of the buttons and LEDs with the three main steps (extraction, washing, calibration) should also be realized, as well as the development of a rechargeable battery system which users most preferred.

Once the aforementioned tasks are complete, the products of this work would be ready to transition towards a full system on the ground. The most effective commercialization channel would likely be through partnerships with established institutions that have established manufacturing and distribution channels in India. Such partners could come in the form of private companies like mKrishi, whose mobile platform for agricultural information dissemination has successfully been piloted by 5000 farmers, and who plans to expand to 2 million farmers across India by 2023. They could also come in the form of NGOs such as the Desphande Foundation and Himmothan, who are highly trusted in their respective communities and are dedicated to disseminating new technologies which can alleviate poverty in rural India.
Appendix A

Supplementary Information
<table>
<thead>
<tr>
<th>Component</th>
<th>Unit cost (USD)</th>
<th>Calculation</th>
<th>Quantity</th>
<th>Vendor</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Val</td>
<td>940/g</td>
<td>12mg for 500uL cocktail, 8uL per strip</td>
<td>0.000960</td>
<td>AgScientific</td>
<td>0.0902</td>
</tr>
<tr>
<td>KTpClIB</td>
<td>117.8/g</td>
<td>3mg for 500uL cocktail, 8uL per strip</td>
<td>0.000024</td>
<td>TCI America</td>
<td>0.0028</td>
</tr>
<tr>
<td>PC</td>
<td>0.009/in²</td>
<td>24 strips per 8.5” x 11” sheet</td>
<td>3.895833</td>
<td>Grangier</td>
<td>0.0368</td>
</tr>
<tr>
<td>PE</td>
<td>0.011/in²</td>
<td>24 strips per 8.5” x 11” sheet</td>
<td>3.895833</td>
<td>Acme Plastic</td>
<td>0.0427</td>
</tr>
<tr>
<td>BA</td>
<td>16.27/L</td>
<td>8uL cocktail per strip</td>
<td>0.000008</td>
<td>Sigma</td>
<td>0.0001</td>
</tr>
<tr>
<td>CNT ink</td>
<td>1.04/g</td>
<td>0.5 g covers total electrode area</td>
<td>0.020833</td>
<td>DuPont</td>
<td>0.0216</td>
</tr>
<tr>
<td>AgCl ink</td>
<td>1.75/g</td>
<td>0.125 g covers total RE membrane area</td>
<td>0.010416</td>
<td>DuPont</td>
<td>0.0182</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.010/g</td>
<td>50mg for 1mL cocktail, 80uL per strip</td>
<td>0.004000</td>
<td>Sigma</td>
<td>4.048E-05</td>
</tr>
<tr>
<td>PVB</td>
<td>0.005/g</td>
<td>79.1mg for 1mL cocktail, 80uL per strip</td>
<td>0.00632</td>
<td>Ghangzhou</td>
<td>0.0003</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.554/L</td>
<td>80uL cocktail per strip</td>
<td>0.000080</td>
<td>Banhai</td>
<td>4.434E-05</td>
</tr>
<tr>
<td>Grafix mask</td>
<td>0.006/in²</td>
<td>24 strips per 8.5” x 11” sheet, 2 masks needed</td>
<td>7.791667</td>
<td>Grafix</td>
<td>0.0493</td>
</tr>
</tbody>
</table>

Table A.1: BOM calculation for the strips.
Table A.2: BOM calculation for the reader.

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit cost (USD)</th>
<th>Quantity</th>
<th>Vendor</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATMEGA 644</td>
<td>1.84</td>
<td>1</td>
<td>RX Electronics</td>
<td>1.84</td>
</tr>
<tr>
<td>L3563N Op-amp</td>
<td>0.15</td>
<td>6</td>
<td>Digikey</td>
<td>0.89</td>
</tr>
<tr>
<td>16x2 LCD</td>
<td>2</td>
<td>1</td>
<td>Shenzhen Saef</td>
<td>2</td>
</tr>
<tr>
<td>Temp. sensor</td>
<td>0.19</td>
<td>1</td>
<td>Digikey</td>
<td>0.19</td>
</tr>
<tr>
<td>Pushbutton</td>
<td>0.28</td>
<td>1</td>
<td>Digikey</td>
<td>0.28</td>
</tr>
<tr>
<td>Rocker switch</td>
<td>0.76</td>
<td>1</td>
<td>Digikey</td>
<td>0.76</td>
</tr>
<tr>
<td>9V Battery clip</td>
<td>0.19</td>
<td>1</td>
<td>Digikey</td>
<td>0.19</td>
</tr>
<tr>
<td>LED</td>
<td>0.1</td>
<td>1</td>
<td>Digikey</td>
<td>0.1</td>
</tr>
<tr>
<td>10K resistor</td>
<td>1.54E-3</td>
<td>1</td>
<td>Digikey</td>
<td>1.54E-3</td>
</tr>
<tr>
<td>1M resistor</td>
<td>1.73E-3</td>
<td>16</td>
<td>Digikey</td>
<td>1.73E-3</td>
</tr>
<tr>
<td>40POS Edge connector</td>
<td>1.08</td>
<td>1</td>
<td>Chip One Stop</td>
<td>1.08</td>
</tr>
<tr>
<td>Voltage regulator</td>
<td>0.17</td>
<td>1</td>
<td>Digikey</td>
<td>0.17</td>
</tr>
<tr>
<td>10uF capacitor</td>
<td>0.025</td>
<td>2</td>
<td>Digikey</td>
<td>0.05</td>
</tr>
<tr>
<td>9V Battery</td>
<td>0.577</td>
<td>1</td>
<td>Digikey</td>
<td>0.577</td>
</tr>
<tr>
<td>Inverter</td>
<td>0.52</td>
<td>1</td>
<td>Digikey</td>
<td>0.52</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>8.68</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure A-1: Example participant answer sheet for paper mockup exercise in Hindi.
USABILITY STUDY

Administrative:
Date
Session #
Coordinator
Translator (if not Kannada speaker)

Usability Study
Example:
Did the user open up the vial correctly?

Score (0/1)

User feedback and notes
user found it difficult to grasp the vial and couldn’t open

Farmer Demographics
Age: 
Sex: 
Education: 
Land (hectare): 

Figure A-2: The sheet filled out by workshop coordinators for the usability analysis.
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