Development of a solid state ion sensor for the quantification of potassium ions in soil

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1. INTRODUCTION

In the field of agriculture, the quantification of essential nutrients for plant growth is fundamental to provide efficient agricultural production at low cost. In Madagascar, analytical measurements for the dosage of ions in agricultural soils are not common practice. This process is problematic in a context where the agricultural area per family decreases from year to year and the response obtained about the concentration of ions must be made to make the necessary adjustments to obtain optimal growth of the plants. A solution to this problem would be the change in agricultural techniques towards the concept of precision agriculture. This new approach uses the principle of spatial and temporal quantification of resources essential to plant growth. This solution is not possible for large-scale distribution due to the significant implementation cost and the complexity of the technology.

The aim of this work is to find a way of precision dosing of potassium ions (K) using an electrochemical sensor. More precisely, the work consists on the adaptation and development of an electrochemical sensor for the dosage of potassium ions to achieve the following results:
   - Optimal selectivity for the ion to be quantified, the potassium ion in this work
   - Low implementation cost
   - Easy to carry and easy to use outside the laboratory

In the literature and on sale, there are several kinds of ion sensors. They use electrical or optical techniques. The most used electrical type sensors are ion-selective potentiometric electrodes. This sensor technology has several operating principles; the most common are ion-selective electrodes or ISE. They can be made from a working electrode or selective electrode composed of an electrode, an internal solution and an ion sensitive membrane or ionophore membrane. In relation to the purpose of this work, these types of electrodes present different weaknesses related to the use of internal solution, the life cycle of the sensor and the risk that the sensor physically breaks. To overcome these problems, the present study turned to sensors with solid contacts or solid state, the advantage of which is to allow the solidification of the sensor and the elimination of the internal solution. Thus, for the purposes of this work, the adaptation and development of a solid contact ionic sensor resulting from research already carried out in this area will be done. The operating principle of a solid contact ionic sensor and the technologies used from previous research will be studied first and then the modeling of an ionic sensor which meets the objectives set above.

2. ION SENSOR ELECTRODE MEASUREMENTS

In order to talk clearly and concretely about ion sensor electrode (ISE), we will divide them into two main groups: liquid state electrodes and solid state electrodes. Electrochemical sensors are based on the use of an ion-selective electrode which operates as a transducer and converts the ionic activity of an environment into electrical potential. The potential difference between the ion-selective electrode and a reference electrode is recorded by a voltmeter and this is dependent on the logarithm of the activity following the Nernst equation. In the case of electrodes with a solid state, the working electrode or selective electrode is composed of an electrode, a semiconductor polymer membrane added to the electrode and an ion sensitive membrane. The process of producing the potential is as follows. First, there is the ions transfer from the sample solution to the interface of the sensitive membrane. The ion goes through a desolvation step to get in the membrane. Second, ions are transported from the ion sensitive membrane to the interface between the ion sensitive membrane and the semiconductor polymer. Third, there is coupling of ions and transfer of electrons in the semiconductor polymer. The electrons are then transported from the semiconductor polymer membrane to the electrode. Once the transfer into the electronic system is complete, electrical measurement is possible. In other words, the potential developed at the membrane is the result of either an ion exchange process or an ion transport process occurring at each interface between the membrane and the solution analysis. The simplified graphic of a solid state electrode is shown in Figure 1.
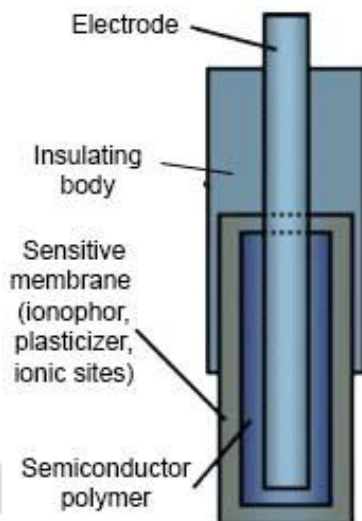
Fig -1: Solid state ion sensitive electrode

2.1 Ion exchange process

In order to construct an ion-selective electrode; for exemple with a liquid state electrode [1]; we would add an inner reference solution to the other side of the membrane. This solution would contain a fixed concentration of the ion of interest, K^+ in this work. This is typically accomplished by placing a thin membrane at the end of the plastic tube and filling the tube with a standard (known concentration) solution of the analyte. As shown in figure 3, a reference electrode is placed in the inner solution and a second reference electrode is in contact with the analyte (outer) solution. At each solution-membrane interface, an ion-exchange equilibrium is established. The of partitioning K+ between the aqueous solution phase and the membrane phase depends on its activity, or concentration. The resulting charge separation at each interface results in a phase-boundary potential. If the analyte ion concentration on each side of the membrane was equal, the potential difference across the membrane would be zero. However, if the concentrations are not equal, a membrane potential will develop. The two reference electrodes measure the potential difference across the membrane.

In the following ion exchange process, a potassium cation displaces a H^+ cation from the organic anion, R^- :

$$HR + K^+ \leftrightarrow KR + H^+$$
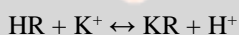
We can imbed the lipophilic R in a membrane, as shown in figure 2, and place it in a solution of K^+.

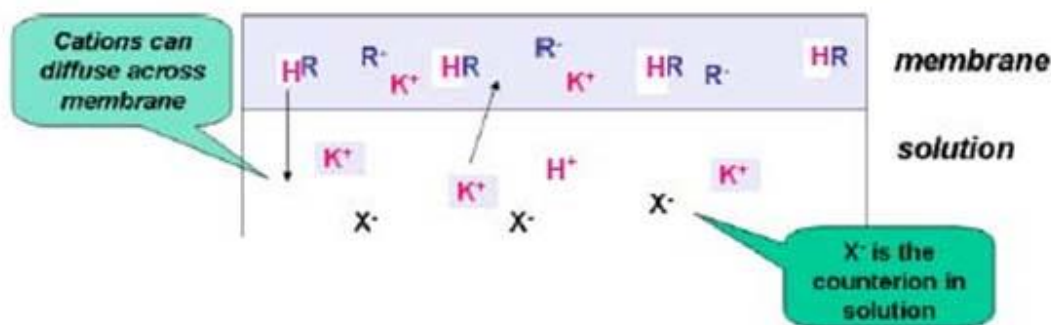$$HR_{(mem)} + K^+_{(aq)} \leftrightarrow KR_{(mem)} + H^+_{(aq)}$$
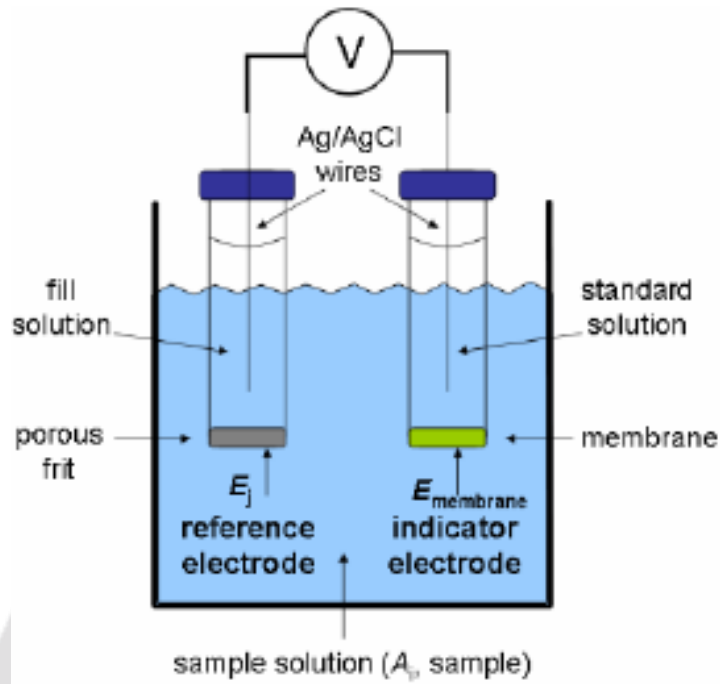

Fig -2 : Ion exchange process

Fig -3 : Electrochemical cell for making a potentiometric measurement with an ISE

2.2 Ion transport with an ionophore

With a liquid contact ISE, let's put a membrane, containing an ionophore[1], between an "unknown" analyte solution and a "known" reference solution (Figure 4). The analyte is A. The ionophore is a neutral "carrier" molecule represented by the blue oval. Figure 5 shows the chemical structure of two ionophores. The ionophore cannot diffuse out of the membrane and but can "trap" the analyte ion (A) at the interface between the solution and membrane. Without the ionophore, the analyte would be unable to partition into the organic membrane.
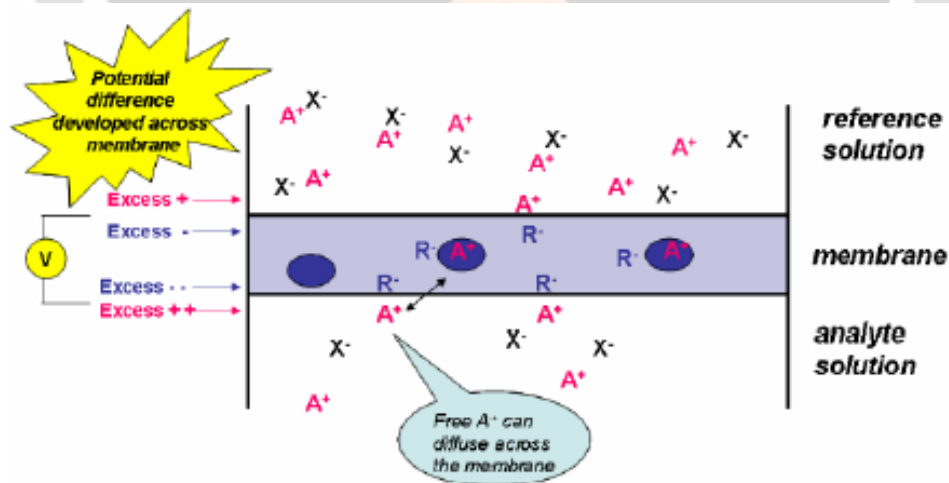

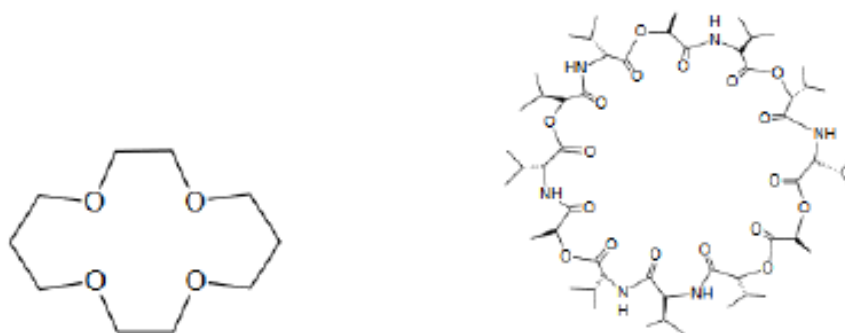**Fig -4 : Propagation of particles into the ISE membrane**.

Fig -5 : Chemical structures of a crown ether (left) and of valinomycin (right), two ionophores.

As with the ion-exchange process, equilibrium is established at both solution-membrane interfaces. The resulting charge separation at each interface leads to a phase-boundary potential.

Now that we have developed an electrical potential across the membrane, we need to find a way to measure it. As before, we put an internal reference electrode in the internal reference solution and an external reference electrode in the analyte solution, as shown in Figure 6. The potential difference measured at these two electrodes is the membrane potential.
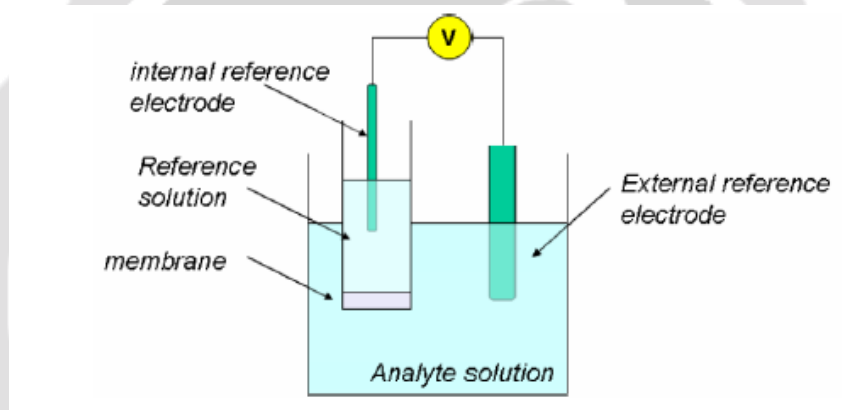

Fig -6 : Electrochemical cell for a potentiometric measurement with an ISE

2.3 Development of a potentiel at the sensitive membrane

The propagation of charged particles results in a potential difference, ΔE. The electrical work W is the product of the charge q and the potential ΔE:

$$W = q \times \Delta E \tag{1}$$

W in joules, q in coulombs and ΔE in volts.

According to thermodynamics [1], the reaction variation in free enthalpy, $\Delta_r G$, is:

$$\Delta_r G = -W = -q \times \Delta E \tag{2}$$

In an electrochemical reaction, the electric charge q relates to the number of electrons transferred per elementary n. Considering that each mole of electrons has an electric charge of 96485 C; Faraday constant, F:

$$q = n \times F \tag{3}$$

Thus,

$$\Delta_r G = -n \times F \times \Delta E \tag{4}$$

In standard state :

$$\Delta_r G^0 = -n \text{ x } F \times \Delta E^0 \tag{5}$$

According to thermodynamics [1],

$$\Delta_r G = \Delta_r G° + RT \times \ln K \tag{6}$$

Where R is the constant of the ideal gases, T is the temperature in kelvins, K is the equilibrium constant.

Combining equation (3), (4) and (5), we have the following equation:

$$-n \times F \times \Delta E = -n \times F \times \Delta E^0 + RT \times \ln K \tag{7}$$

By rewriting the formula, we obtain the potential developed in the membrane:

$$E = E^0 - \frac{RT}{nF} \ln K \tag{8}$$

Where E is the electrochemical potential.

2.4 The ionophore membrane

Types of ionophores that are ion selective include crown ethers and the antibiotic valinomycin (see Figure 5). One of the characteristics of these neutral carrier molecules is its cavity which has dimensions approximately those of a molecule or an ion. The valinomycin electrode was one of the first polymer membrane electrodes and is commonly used to determine potassium.

The electron-rich center of valinomycin efficiently extracts K^+ ions due to the similarity between the diameter of K^+ and the interior diameter of the valinomycin molecule. The outer lipophilic portion of the valinomycin molecule allows it to remain within the polymer membrane.

2.5 Reference electrodes

To measure the change in potential difference across the ion-selective membrane as the ionic concentration changes, it is necessary to include in the circuit a constant reference voltage that acts as a half-cell from which the relative differences are measured. This reference voltage is obtained with a reference electrode.

The most common and simplest reference system is the silver/silver chloride (Ag/AgCl) single junction reference electrode. The silver/silver chloride reference electrode consists of a silver wire, sometimes coated with a layer of solid silver chloride, immersed in a saturated solution of potassium chloride and silver chloride. In electrochemistry the half-reaction is represented by:

$$AgCl \text{ (s)} + e^- \longrightarrow Ag \text{ (s)} + Cl^-$$

The electrode potential of this half-cell is +0.2046 V compared to the standard hydrogen electrode at 25°C. Another reference system is the saturated calomel electrode, it is composed of mercury chloride (Hg_2Cl_2, calomel). The half-reaction is presented by:

$$Hg_2Cl_2(s) + 2 e^- = 2Hg(l) + 2Cl^-_{(satd)}$$
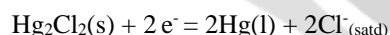
With an electrode potential of +0.244 V.

3. DEVELOPMENT OF THE SENSOR

Ion sensors are mainly made up of ion-selective electrodes. These electrodes come in various configurations which have already been the subject of several researches [2] and summarized in the following paragraphs.

• Electrodes with a quasi-liquid structure: the main component of this type of electrode is a selective membrane which is located between two electrolytic solutions, one of which serves as a reference solution as shown in Figure 7. A membrane separates two electrolytic solutions and the potential difference established between the two sides of the membrane is measured using the two reference electrodes.
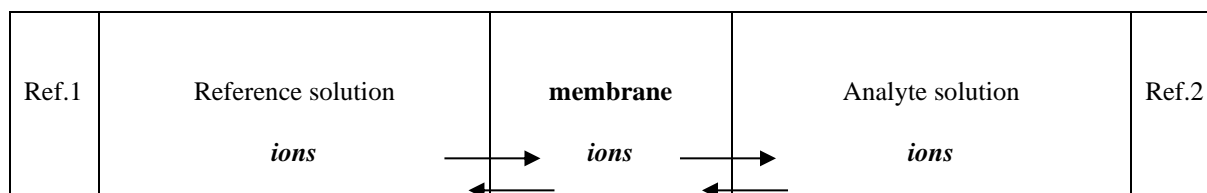
Ref.1	Reference solution	membrane	Analyte solution	Ref.2
	ions →	*ions* →	*ions*	
	←	←		

Fig -6 : Electrodes with a quasi-liquid structure

The disadvantage of using this type of configuration is that the presence of the internal filling solution prevents miniaturization. In addition there are also problems linked to the fragility of the electrode.

- Coated Wire Electrodes (CWE) : These are electronic conductive substrates (metallic in most cases) where the selective membrane is directly deposited as shown in Figure 7.
In the literature, the advantages of these electrodes compared to the previous one are based their low cost and their mechanical flexibility (they can be used horizontally or vertically).
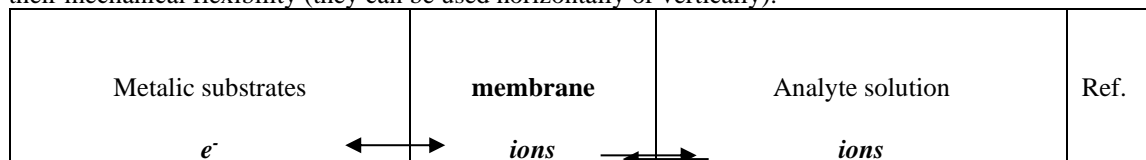
Metalic substrates	membrane	Analyte solution	Ref.
e^-	ions	ions	

Fig -7 : Simplified graphic of a CWE in contact with the analyte to be detected

However, problems with the stability of the equilibrium potential and noise are very common. Buck [3], attributed this behavior to contact problems at the membrane/metal interface. He considered this interface "blocked" because no transfer of ions or electrons can take place. The answer to all these problems came by developing a solid electrode with a "sandwich" structure.

- Electrode with a "sandwich" structure : It consists of two superimposed films. The first is the selective membrane which is in contact with the analyte to be detected. It is mainly made of PVC but other polymers have also been used [2]. The second film is an intermediate film between the ionosensitive part and the metal surface which serves as a transducer. It makes it possible to transform an "ionic signal" of interaction into "electrical signal". The configuration is shown in Figure 8.
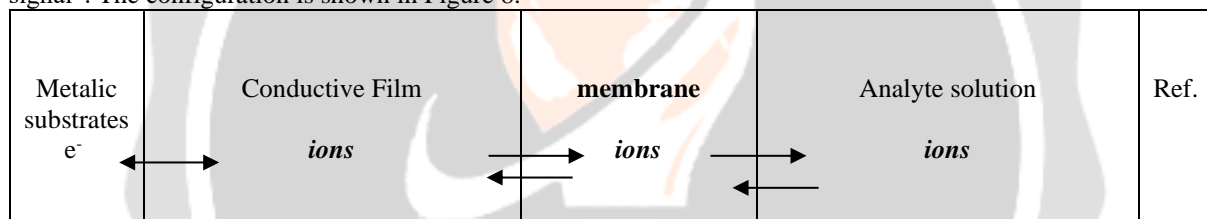
Metalic substrates	Conductive Film	membrane	Analyte solution	Ref.
e^-	ions	ions	ions	

Fig -8 : Simplified graphic of an electrode with a "sandwitch" and the analyte to be detected

The conductive layer is most often a conductive polymer.
- Single component electrode: Single-component electrodes have a configuration between membrane-covered (CWE) and sandwich-structured electrodes. The ionosensitive part can be a selective membrane containing a conductive polymer or a conductive polymer doped with ionosensitive particles (ionophores). The transduction of the ionic signal into an electronic signal takes place in the same film. It was designed to simplify the two-layer structure seen previously. Figure 9 shows a the configuration of such an electrode.
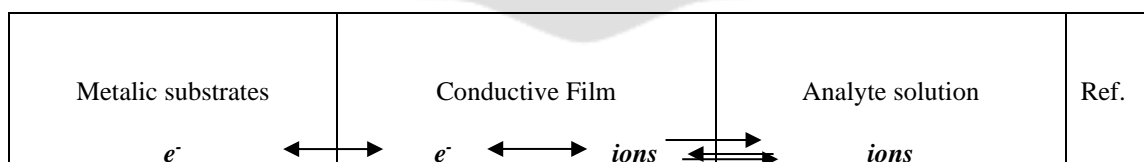
Metalic substrates	Conductive Film	Analyte solution	Ref.
e^-	e^- ions	ions	

Fig -9 : Structure of an electrode containing an ionic and electronic conductive film

According to research, the lack of selectivity means that these types of polymers cannot be directly used for the detection of a specific ion.

3.1 Electrode configuration

Following several analyzes based on research that has previously been done on solid contact electrodes and also not to deviate from the conventional configuration of ISEs (electrolyte/membrane/electrolyte). We opted to use the configuration of sandwich structure electrodes for further this study. Thus, the essential element of the

working electrode is a selective membrane which is in contact with the analyte to be detected and the other surface of the membrane is in contact with the conductive film.

3.2 The polymer

Among the polymers mainly cited in the literature wich are: membranes based on polyvinyl chloride (PVC), and membranes based on elastomer. The choice fell on the use of a high molar mass polyvinyl chloride (PVC) matrix. The problems linked to the glass transition temperature of PVC require the use of a plasticizer making the membrane more flexible and easy to handle. Most elastomer-based membranes such as polychloroprene-based membranes have a structure very close to that of PVC, but this polymer has never been used as a material for selective membranes.
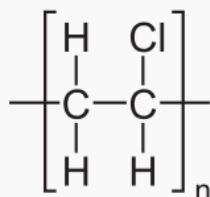

Fig -10 : Chemical structure of PVC

Several criteria must be considered for the choice of plasticizer such as the compatibility of the plasticizer and the polymer, the valence number of the ion to be measured. For this study, dioctyl phthalate (DOP) is chosen as plasticizer.
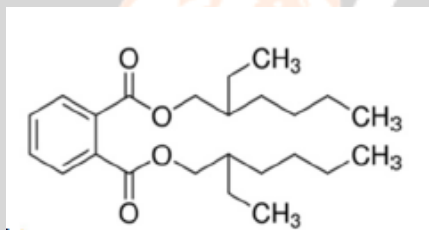

Fig -11 : Chemical structure of DOP

3.3 The ionophore

As noted above, the ionophore best known to be selective for potassium ions is valinomycin. Its chemical formula is shown in Figure 12.
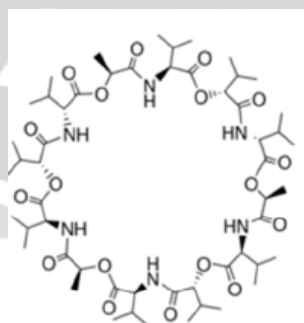

Fig -12 : Chemical structure of valinomycin

Tetrakis salt (4-chlorophenyl) potassium borate (TCPB) is used as the ionic site. It is added to the ionophore, polymer and plasticizer composition and makes it possible to obtain an ionic site/ionophore molar ratio of 1:1.8. The purity of the ionophore and the ionic site used for the membrane is important to have good selectivity.
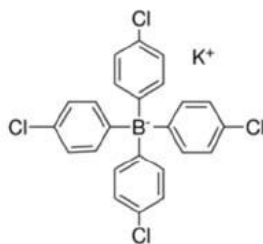
Fig -13 : Chemical structure of TCPB

3.4 The conductive film

As a conductive layer, polypryrole is chosen since there are several researches and literature regarding its properties and operating mechanisms. Polypyrrole is both ionic and electronic conductors [2] [4] that is to say they can transport ions or electrons depending on certain parameters. This behavior can be explained by its chemical structure presented in Figure 14.
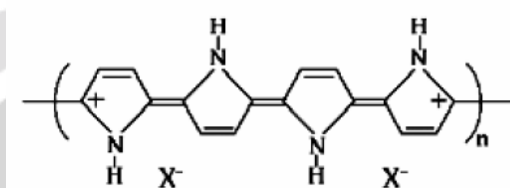
Fig -14 : Chemical structure of polypyrrole. X- is the counter ion (dopant) used during polymerization

3.5 The insulating body

To achieve the objectives this work. The insulating body consists of a two-core ceramic rod 6 centimeters long. The two electrical wires which constitute the electrode are inserted into the two cores. The ends of the wires are then dipped in a thin layer of conductive film then in the ionophore, polymer, plasticizer and ionic site composition to form a bulb 0.5 cm long.
The quantity of elements for the development of the entire sensor is detailed in the research carried out by Pénélope Liatsi [2] and Charles-Olivier Normandeau [4]

4. MEASUREMENT TECHNIQUE

In order to study the operation of the sensor, potentiometry allow to study its response. It is the main and universal method of characterizing these systems to demonstrate the Nernstien character or not.

4.1 The potentiometry

Potentiometry consists of measuring the potential difference established on both sides of the membrane when it is in contact with the analyte to be detected. It is the key technique for characterizing selective electrodes and evaluating the performances achieved. Before carrying out any measurement, this sensor must be calibrated by dosing the analyte to be detected in a wide range of concentrations. This calibration is initially used to check whether the system responds by following Nernst's law. Indeed, a calibration curve having a slope of 59 mV per decade of concentration indicates a Nernstian response. This can then be used to determine the concentration of the ion considered in a sample to be analyzed.

The calibration of the electrode was done in aqueous solutions for a range of concentrations between 10-6 and 10-1 mole in KCl. the electrochemical cell consists of a reference electrode saturated with calomel (ESC) immersed in the solution to be analyzed and the working electrode with a ceramic insulating body doped with a valinomycin ionophore. The electrochemical chain is:

Electrode / Conductive film / membrane / Analyte solution / ECS (Reference electrode)
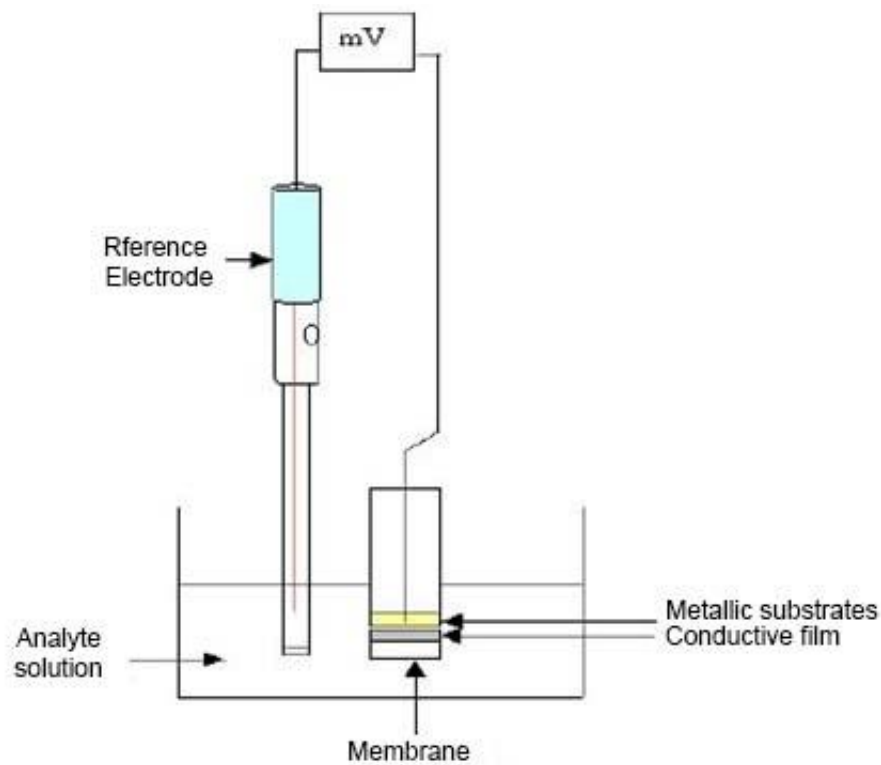The figure below shows the system assembly .

Fig -15 : Experimental device for potentiometric measurements with a solid state electrode..

The membrane potential is separated into three potentials, which contribute to the total potential:
- Two interface potential and
- A diffusion potential inside the membrane.

One of the three potentials can be considered to be independent of the concentration of the ion analyzed, whether the semiconductor polymer membrane interface potential. But, research has shown that the potential for diffusion is negligible in the majority of cases.

So the measured potential, E_{meas}, is the difference between the two interface potentials, between the analyte side (E_{outer}) of the membrane and the reference side (E_{inner}) of the membrane.

$$E_{meas} = E_{outer} - E_{inner} \tag{9}$$

The potential on each side is related to the activity (A) or concentration as described by the Nernst equation (equation 7), where z is the charge of the ion of interest:

$$E_{outer} = E^0 - \left(\frac{RT}{zF}\right) \log 1/A_{unk} \tag{10}$$

$$E_{inner} = E^0 - \left(\frac{RT}{zF}\right) \log 1/A_{ref} \tag{11}$$

With A_{unk}, activity or concentration of the K^+ ion in the analyte and as the semiconductor polymer membrane interface potential being independent of the concentration of the ion analyzed. E_{inner}, A_{ref} and E^0 are all constants (equation 10).

If equations 9 and 10 are combined with equation 8, we have the following equation:

$$E_{meas} = const - \left(\frac{RT}{zF}\right) \log 1/[K^+] \tag{12}$$

$$E_{meas} = const + \left(\frac{RT}{zF}\right) \log[K^+] \tag{13}$$

This equation 12 presents the measured potential at the terminal of the working electrode which is proportional to the change in the K^+ ion concentration in the analyte solution.

4.2 Evaluation of sensor selectivity

When using ion-selective electrodes in complex environment, the response of the electrode to the primary ion (equation 12) can be influenced by other ions of identical charge present in the solution to be analyze. In order to

have precise measurements, a correction of measured values is required. This is the role of a selectivity coefficient, K_{ij} which represents a quantitative expression of the capacity of an electrode to respond to the primary ion in the presence of other interfering ions of the same charge. The selectivity coefficient is defined by the Nikolsky-Eisenman equation:

$$E_{meas} = const + \left(\frac{0,05916}{z}\right)\log(A_i + k_{ij} A_j^{\frac{z_i}{z_j}})$$ (14)

Where :
z_i et z_j the charges of the primary ions i and the interfering ion j
A_i et A_j activities of ions i and j
K_{ij} the selectivity coefficient

For this study, the result of research [1] on the interference of ions most likely to interfere with a membrane containing valinomycin is used (table 1).

Analyte ion (i)	Interfering ion (j)	K_{ij}
K^+ (valinomycin)	Na^+	10^{-4}
	Ca^{2+}, Mg^{2+}	10^{-7}

Tableau 1- Selectivity coefficient of the analyte ion K^+ (valinomycin)

If an electrode has equivalent responses to the two ions i and j then $k=1$, the smaller the values of k, the less impact the interfering ion j will have on the measured potential.

5. APPLICATION AND MEASUREMENT

The result of the first measurement was obtained using a KCl solution in a concentration range between 10^{-6} and 1 mole. The reference electrode used is an electrode saturated with calomel, its electrode potential is $E_{ref} = 0,244V$. The standard electrode potential E^0 for K^+/K est de -2,93V.

For a measurement carried out at 25°C. The table below shows the value of the parameters.

Table 2-Parameters values

Descriptions	Symbol	Value
Gas constant	R	8.314(V.C)/(K.mol)
Temperature	T	25°C
Faraday constant	F	96,485 C/équivalent
Charge of the K^+ ion	z	1
Electrode potential of the calomel reference electrode	E_{ref}	0 ,244 V
Standard electrode potential(K^+/K)	E^0	-2,93 V

6. RESULTS

The calibration curve obtained in a KCl concentration range of 10^{-6} to 1 mole is presented in the figure below.
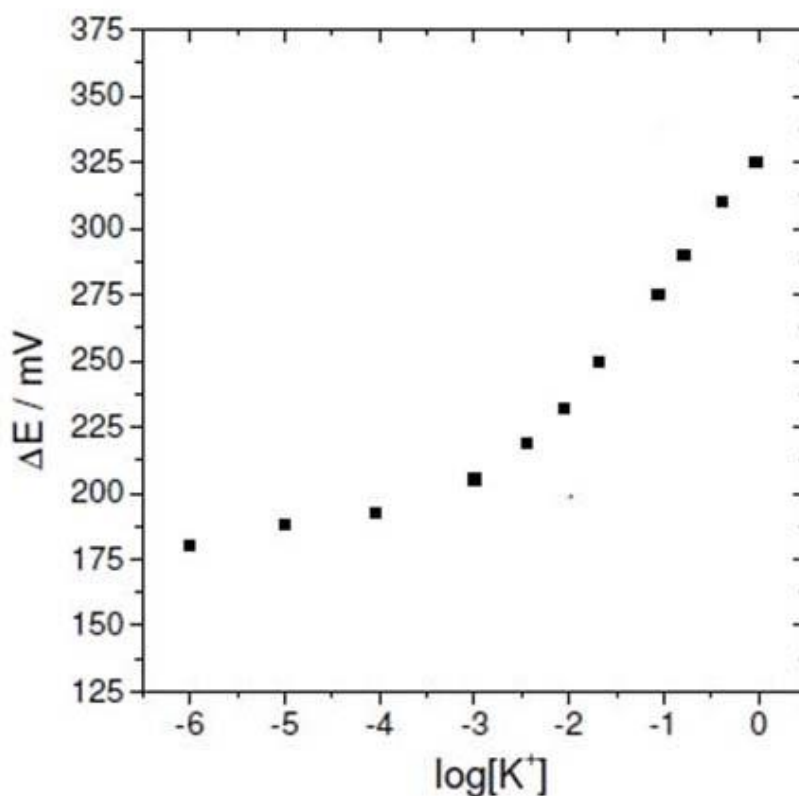
Fig -15 : Result of the calibration of a solid state electrode with a reference electrode in ECS

7. INTERPRETATION

It is noted on reading the results that the measurement in a range of 10^{-6} to 1 mole in KCl gives a non-Nernstian response of approximately 36.5 mV/decade. For this first measurement the system did not have a response according to Nernst's law. The calibration curve did not reach the slope around 59mV per decade of concentration.

According to the literature [2], the reason for this non-Nertian response is the failure to take into account the conditioning of the electrode before the first measurement because according to this same study , all membranes intended to the development of selective electrodes undergo pretreatment before any use as ionic sensors. This step seems to be necessary for the proper functioning of the electrode at least in terms of the potentiometric response. This pretreatment consists of conditioning the membrane in a solution of the ion to be detected, at a relatively high concentration, for a duration which can vary from 2 to 48 hours.

8. CONCLUSION

A solid structure ion sensor was investigated and developed in this present work.
Firstly, a review of the literature and the various researches which have been carried out in this field was carried out to constitute the constituent elements of the sensor. Following this research, a sandwich-type solid structure sensor was developed with the following different characteristics:

- A ceramic insulating body 6 cm long with a bulbous end of 0.5 cm containing the conductive film and the polymer membrane selective for potassium ions
- A PVC polymer with a dioctyl phthalate (DOP) plasticizer is added to the potassium ion-selective ionophore which is valinomycin.
- A conductive layer composed of polypryrole serves as a conductive film between the selective polymer membrane and the metal substrate which is connected directly to the measuring voltmeter.

A measurement to calibrate the sensor is then carried out with the potentiometer method and by associating the working electrode with a reference electrode saturated with calomel. The sensor has been calibrated in a wide range of potassium concentrations between 10^{-6} and 1mole of KCl. The result obtained from this measurement is a curve of 36.5 mv/decade which does not conform to the expected result of 59 mv/decade of concentration. After several researches, it was found that:

- Sensor conditioning was omitted before the first measurement.
- The electrode should be conditioned in a 0.1 mole of KCl solution for at least 24 hours.

For the remainder of this study, it is necessary to study in detail the influence of conditioning on solid configuration membrane electrodes.

9. REFERENCE

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