Universidade Estadual de Maringá
Centro de Ciências Exatas
Departamento de Física
Programa de Pós-graduação em Física

Thiago Victor Moreno

Sensores de vidros calcogenetos para detecção de cloretos em águas residuais da atividade de mineração

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Tese submetida à Universidade Estadual de Maringá como requisito parcial para a obtenção do título de Doutor em Física

Orientador: Prof. Dr. Nelson Guilherme Castelli Astrath

Maringá

2018

Thiago Victor Moreno

Chalcogenide glass based sensors for chloride detection in mining wastewater

Thesis submitted to the Maringa State University in partial fulfilment of the requirements for the degree of Doctor in Physics.

Supervisor: Prof. Dr. Nelson Guilherme Castelli Astrath

Maringá

2018

Dados Internacionais de Catalogação na Publicação (CIP)
(Biblioteca Central - UEM, Maringá, PR, Brasil)

Moreno, Thiago Victor
M843s Sensores de vidros calcogenetos para detecção de cloretos em águas residuais da atividade de mineração. / Thiago Victor Moreno. -- Maringá, 2018.
xvi + 56 f.: il., color., figs., tabs.

Orientador(a): Prof. Dr. Nelson Guilherme Castelli Astrath.
Tese (doutorado) - Universidade Estadual de Maringá, Centro de Ciências Exatas, Departamento de Física, Programa de Pós-Graduação em Física, 2018.

1. Sensores potenciométricos. 2. Eletrodos seletivos de íons. 3. Detecção de cloretos. 4. Calibração. 5. Vidros calcogenetos. 6. Águas residuais. I. Astrath, Nelson Guilherme Castelli, orient. II. Universidade Estadual de Maringá. Centro de Ciências Exatas. Departamento de Física. Programa de Pós-Graduação em Física. III. Título.

CDD 21.ed. 549.4
AHS-CRB-9/1065

THIAGO VICTOR MORENO

CHALCOGENIDE GLASS BASED SENSORS FOR CHLORIDE DETECTION IN MINING WASTEWATER

Tese apresentada à Universidade Estadual de Maringá, como requisito parcial para a obtenção do título de doutor.

Aprovado em: Maringá, 08 de agosto 2018.

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Agradecimentos

Gostaria de iniciar agradecendo a minha esposa Evellen Lima por toda a paciência, compreensão, carinho e apoio dado ao longo destes mais de quatro anos de doutorado. Agradeço também meus pais, Santiago e Tania, e minhas irmãs, Talita e Tatiana, pelo suporte dado ao longo deste trabalho, e meus filhos de quatro patas Pitty, Princesa, Fred e Thor por me recepcionarem com alegria toda vez que chego em casa.

Quero agradecer o professor Dr. Nelson Guilherme Castelli Astrath pela orientação desta tese. Sou muito grato pelos conhecimentos que recebi, confiança depositada em mim e paciência durante a orientação deste trabalho. Agradeço também os professores Malacarne, Fran Sato, Medina, Wilson, Adauto, Jurandir, Mauro, Bento, Renio, Andressa, Nilson e Sanguino por terem de alguma forma me auxiliado neste doutorado. E gostaria também de agradecer o pessoal da secretaria, a Monica e o Zelito, por resolverem todos os problemas burocráticos que surgiram nestes quatro anos.

Gostaria de agradecer o Laboratório de Materiais Fotônicos (LAMF), do Instituto de Química da Unesp campus Araraquara, e em especial o professor Dr. Sidney Jose Lima Ribeiro, a Dra. Sílvia Helena Santagneli e o Dr. Danilo Manzani por terem aberto as portas do laboratório a mim e me ensinado a arte de fazer vidros calcogenetos, tarefa essencial para o desenvolvimento deste trabalho.

Quero agradecer o Dr. Jun Shen pela orientação durante o meu período no *National Research Council* (NRC) no Canadá e aos colegas de NRC, Eben, Zhong, Wei, Jason, Orlando, Marco, Pathik, Cheng Hu, Kidus e Colin pelas discusões científicas, auxílio técnico e diversão ao longo dos seis meses em que residi em Vancouver. O desenvolvimento desse trabalho não seria possível sem a colaboração de cada um de vocês.

Não poderia esquecer dos colegas da pós, Otávio, Vitor, Anderson, Vinicius, Gabriel, Elton, Patrik, Pablo, Thiago Petrucci, Renan, Jaci, Vanessa, Leandro, Robson, Getúlio, Marcelo e Raquel pela companhia nas aulas, futebol, ajuda com o trabalho, companhia nos cafés, e

discussões físicas e não físicas em momentos oportunos.

Agradeço também os amigos não físicos brasileiros, Kairo, Marcel, Jean, Ulysses, Marcelo e Lukas pelos bons papos, cervejas e descontração, e os canadenses Nafees, Davide, Greta, Aidin, Betsee, Stefan e Juan pelos momentos de aventura e montanhas subidas.

Quero agradecer o apoio financeiro prestado pelo CNPQ, Capes e Fundação Araucária, e por fim à UEM e ao PFI pela oportunidade de desenvolver este trabalho, e ao *National Research Council Canada* por me aceitar em meu período de estágio no exterior.

Enfim, agradeço a todos que diretamente ou indiretamente contribuíram para este trabalho e para minha formação pessoal e acadêmica.

Muito Obrigado!

Resumo

Sensores potenciométricos, especialmente os Eletrodos Seletivos de Íons (ISE[1]), são um subgrupo atraente de sensores electroquímicos para aplicações práticas devido à sua simplicidade, baixo consumo de energia, tamanho diminuto, portabilidade e custo relativamente baixo. Além disso, esta classe de sensores não altera a composição da amostra em contato com o sensor e, por isso, pode ser usado para medições no local. Devido a estas características, estes sensores são amplamente utilizados em diagnósticos clínicos e no monitoramento ambiental. Aplicações modernas em ambos os campos necessitam de melhorias na construção de novos sensores e do desempenho dos sensores convencionais. Tendências para futuro apontam para sistemas de diagnósticos portáteis, diagnósticos no local e detecção autônoma em locais remotos. A importância da sustentabilidade dos recursos naturais torna o campo de aplicações ambientais atraente, representando uma grande oportunidade para o desenvolvimento de uma variedade de ISEs. Uma das preocupações públicas mais comuns sobre as indústrias de mineração é a contaminação da água, que inclui o elevado nível de salinidade como um dos principais problemas ambientais. Neste sentido, este trabalho visa desenvolver um protótipo para o monitoramento de Cl^- em águas residuais da atividade de mineração. Amostras de vidros calcogenetos baseados no sistema AgX-Ag_2S-As_2S_3 (X = Cl or Br) foram preparadas para serem usadas como membrana sensível dos ISEs. Fabricamos vários eletrodos para a detecção de íons de cloro em solução e a resposta e o limite de detecção de cada um dos sensores foram avaliados. O mais sensível foi acoplado com um sensor de referência em um protótipo de baixo custo. O protótipo mostrou uma resposta linear em até 4 ordens de magnitude da concentração de Cl^- com uma sensibilidade de 7 mV/pCl^-. O protótipo foi desenvolvido para monitoramento remoto e em tempo real de águas residuais da extração de petróleo.

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[1] Do inglês *Ion Selective Electrode*

Abstract

Potentiometric sensors, specially the Ions-Selective Electrodes, are an attractive subgroup of electrochemical sensors for practical applications because of their simplicity, low power consumption, small size, portability and relatively low cost. Also, this class of sensors do not change the composition of the sample in contact with the sensor, and can be used for on-site measurements. Due to these characteristics, Ion-Selective Electrodes are extensively used in clinical diagnostics and in environmental monitoring. Modern applications in both fields require improvements in conventional construction and sensor performance, as trends are for portable diagnostics, on-site diagnostics and autonomous sensing in remote locations. The importance of natural resources sustainability makes the field of environmental applications demanding, representing a great opportunity for the development of a variety of ISEs. One of the most common public concerns about mining industries is water contamination, which includes the elevated level of salinity as one of the major environmental issues. In this sense, this work aims to develop a sensor prototype for Cl^- monitoring in mining wastewaters. We prepared several chalcogenide glass samples based on $AgX\text{-}Ag_2S\text{-}As_2S_3$ (X = Cl or Br) glass system to use as ISE's sensitive membranes. We fabricated several electrodes for measurement of chloride ion in solution and response slope and detection limit of each ISE were evaluated. The most sensitive one was built in a low cost sensor prototype, which consisted of an ISE, a reference electrode, and a flow-cell system. The sensor prototype showed a linear vs. logarithm behavior of up to 4 orders of magnitude to Cl^- ion concentration with a slope of 7 mV/pCl^-. The prototype was designed for real-time and remote monitoring of oil wastewater.

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List of Symbols

Symbol	**Description**
a, a_i	Single ion activity
a_p	Activity of the products
a_r	Activity of the reagents
c_i	Ion i concentration
$c_i^{(S)}$	Concentration of ions i at the solution phase
$c_i^{(M)}$	Concentration of ions i at the membrane phase
$c_i(x,t)$	Ion i concentration at position x and time t
d	Membrane thickness
D_i	Diffusion coefficient
E	Electric potential
E^0	Standard electrode potential
E_0	Standard sensor potential
$E(x,t)$	Electric field
E_i	Electric potential of a pure ion i solution
E_D	Diffusion potential
E_M	Membrane potential
$E_M(t)$	Electric potential at a membrane in a time t
E_{PB}	Phase boundary potential
F	Farady constant
ΔG	Gibbs free energy
ΔG^0	Gibbs free energy under standard condition
$I(t)$	Current density
$J_i(x,t)$	Particle flux

Symbol	**Description**
k_{ij}	Equilibrium constant
K_{ij}	Selectivity coefficient
R	Universal gas constant
S	Sensor sensitivity
t	Time
T	Absolute temperature
T_g	Glass transition temperature
x	Spatial coordinate
z, z_i	Ion charge
ϵ	Dielectric permittivity
μ_0	Chemical potential under standard conditions
μ_i	Chemical potential of an ion specie i
$\overline{\mu_i}$	Electrochemical potential of an ion specie i at the phase boundary
$\overline{\mu_i}^{(S)}$	Electrochemical potential of an ion specie i at the bulk of sample solution phase
$\overline{\mu_i}^{(M)}$	Electrochemical potential of an ion specie i at the membrane phase
$\overline{\overline{\mu_i}}$	Mobility of an ion specie i
$\nu_i(x, t)$	Drift velocity of an ion specie i at position x and time t

List of Abbreviations

Abbreviation	**Description**
AES	Auger Electron Spectroscopy
ET	Electronic Tongue
FIM	Fixed Interference Method
GDP	Gross Domestic Product
GPS	Glass Pellet Sensor
GSS	Glass Slice Sensor
ICP	Inductively Coupled Plasma
ISA	Ionic Strength Adjuster
ISE	Ion Selective Electrode
μISE	micro Ion Selective Electrode
ISFET	Ion Selective Field Effect Transistor
IUPAC	International Union of Pure and Applied Chemistry
LoD	Limit of Detection
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
MSL	Modified Surface Layer
NE	Nikolsky-Eisenman
NPP	Nernst-Planck-Poison
PBM	Phase Boundary Model
PLD	Pulsed Laser Deposition
RBS	Rutherford Backscattering Spectrometry
RE	Reference Electrode
RF	Radio Frequency
SEM	Scanning Electron Microscopy
SSM	Separated Solution Method

Abbreviation	**Description**
WE	Working Electrode
XRD	X-Ray Diffractometer

Contents

Chapter 1

Introduction

Mining is an essential activity for modern life. From cell phones to airplanes, from building structures to coins, ores are ingredients for a variety of everyday items. In order to provide the basic raw material for the production of these various products, mining is of great importance in the world economy, representing in 2016 approximately 2% of GDP[1] produced worldwide and generating approximately 1.5 trillion dollars in gross revenue, according to the World Bank [1]. However, there are questions about the sustainability of the economic results of this activity, given that social and environmental problems are intrinsically associated [2].

From the environmental point of view, mining has a considerable impact. It greatly alters the mined area and the sites where tailings deposits are made [3]. These wastes typically contain metals rich in sulfides and heavy metals such as arsenic, lead, mercury, cadmium, chromium, zinc, nickel and copper, all of which pose risks to human health and the environment itself [4, 5].

Over the past 50 years the concentration of heavy metals in the environment has grown significantly, most likely caused by mining [6]. There are more than 100 thousands abandoned or inactive mines only in the United States [7], and many of these mines are considered by the US Environmental Protection Agency as dumping sites for extremely toxic materials [8].

Perhaps the most significant impact of mining is on water quality. Even in small amounts heavy metals can be extremely toxic. Loaded by water, these metals can travel far away, contaminating rivers, lakes and groundwater [9]. In Brazil, an accident involving the mining company Samarco dumped approximately 32.6 million m^3 of tailings in the Doce river

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[1] Gross Domestic Product

basin [10]. The tailings were loaded by the river over 650 km to the Atlantic Ocean, damaging the entire aquatic ecosystem. The population of cities, whose water supply is collected in this river, remained for days without drinking water supply. Therefore, monitoring water quality is a key task for the mining industry. The quality of water, both on the surface and within the subsoil, in the vicinity of the sites where the mining wastes are deposited and in areas of environmental recovery, after extractive activity, should be monitored to ensure a sustainable ecosystem functioning [11] and, consequently, the proper supply to the population. It is estimated that of all the water on the planet, only 0.77 % is not saline and is in the rivers, lakes, swamps and subsoil [12], whose treatment is affordable. Therefore, such monitoring becomes critical.

Measurement of the activity of heavy metal ions in aqueous systems is of great environmental importance because of their toxicity. This type of measurement is relevant in the control of pollutants present in the mining tailings. Traditional monitoring of contaminants is usually performed with techniques that require the removal of samples from the site and the transport of the contaminants to specific laboratories. Unfortunately, because speciation can change rapidly as a result of chemical, physical and biological reactions, long delays associated with this process are unacceptable [13]. Therefore, the best way to do these preventive measures is to quickly determine the contaminants by making the measurement on site, which is a crucial issue regarding environmental monitoring. For this, monitoring systems need to be developed [14].

Potentiometric sensors represent an interesting approach in environmental monitoring. The use of these sensors to monitor water quality has been a reality for some time. There are papers in the literature that have employed these sensors to measure various heavy metal cations in aquatic systems [15]. It is a low-cost option that demands low power consumption, has relative simplicity in the software/hardware interface and is portable, enabling the transportation of the equipment to the measurement site.

In potentiometric sensors, the analytical information is obtained by the conversion of ionic recognition into an electrical signal [16]. Among the types of potentiometric sensors, Ion-Selective Electrodes (ISE) and Ion-Sensitive Field Effect Transistors (ISFET) stand out. Local equilibrium is established by the sensitive membrane present in the sensor, leading to a electric potential variation in it. The analytical information is obtained from the potential difference between the ion selective electrode and a Reference Electrode (RE), which are interconnected by a high impedance voltmeter. The measured potential is a function of the species activity

[17].

Both ISEs and ISFETs are typically designed to have sensitivity to a particular major ion. However, other species may interfere in the measured signal, leading to uncertainties about what is actually being detected. Such interference is known as cross-sensitivity [18]. This could be a problem when designing a sensor sensitive to a single species, since real samples are complex and have several species that can interfere with the signal.

As the electrical signal is dependent on the interaction of the selective membrane with the solution under analysis, different membranes will display different responses to the same species or will have sensitivity to different species. Thus, by changing the composition of the membranes one can obtain sensors with responses to different ions, making this type of sensor an attractive alternative for environmental monitoring. The most common materials for membranes are polymers, crystals and glasses. The class of chalcogenide glasses are particularly interesting for membranes.

Since the 1970s, chalcogenide glasses have been successfully used as sensitive membranes in potentiometric sensors [19]. Chalcogenite glasses can be manufactured with varied compositions, resulting in membranes with different properties and characteristics [20, 21]. These materials have high chemical stability that enables the manufacture of solid state and thin film sensors, which allows for microfabrication techniques to be used for the production of small scale sensors [22]. From the electrical point of view, the low impedance of thin films, compared to bulk materials, allow the use of poor conductive glasses to make these sensors [14].

Moreover, studies have shown that sensors produced with chalcogenide glasses have better stability and detection limits comparable to crystalline membrane sensors [23]. Compared with polymer membrane sensors, sensors using chalcogenide glasses, such as a sensitive membrane, perform poorly on the limit of detection. However, they are better as regards to chemical stability and mechanical durability [24]. Another important factor is that chalcogenide glass sensors exhibit better strength and durability when operating in corrosive environments [25].

Potentiometric sensors of the ISE and ISFET type usually show cross-sensitivity to some ions. Until the 1990's, a lot of effort was invested to improve the sensitivity of these sensors and tp develop membranes with low cross-sensitivity [26]. In principle, this could be a problem since it is desirable to have a selective sensor to only one single ion. However, if for an isolated sensor this is a problem, when a set of sensors work as an array, cross-sensitivity may be the solution. After 1990's researchers began to work with these sensors arrays. Coupled with advanced mathematical methods for signal processing, these sets of sensors proved to be promising and stablished thereafter as Electronic Tongue (ET) [27].

Sensors that present greater cross-sensitivity are promising candidates for ET. The coupling of these properties with appropriate algorithms results in better signal resolution. In this way, ET devices are ineheritable to cross-sensitivity, allowing only one device to analyze several species in solution and thus to characterize complex liquid samples [28]. For the past three dacades, several applications for these devices have emerged for the analysis of beverages such as mineral water [29], wines [30–32], beers [33, 34], milk [35–38] and juices [39, 40], industrial processes (mainly in the food [41] and pharmaceutical industry [42–44]), and also in environmental monitoring [45, 46].

Althoug ET sensors may be used for monitoring water quality associated with environmental mining activities, there is still the need to carry out the measurements "in loco". Considering the vast area comprised by a mine and the entire aquatic ecosystem in the surroundings, local monitoring becomes impractical. An alternative approach for such challenging problem is a network remote monitoring system. Stations consisting of sensors for measurements, batteries, photovoltaic systems for power generation and antennas for data transmission, would represent an important step towards this goal. These network stations could be placed over a wide area and could be monitored in real time from a central station, connected to the individual stations over a wireless network [47, 48]. The main advantages of this strategy are the low cost associated with conventional techniques and the increase of spatial and temporal resolutions, allowing the creation of a fast and efficient alarm system. Most toxic metals in ambient waters can vary in concentration over a time scale of less than one hour [49]. Therefore, monitoring remotely and in real time becomes necessary. In the case of the Samarco disaster, for instance, an adequate ecosystem monitoring system in the vicinity of the affected area would have detected previous leaks, and actions could have been taken in time.

The aim of this work is to develop, construct and characterize ISEs sensors for chloride detection in solution, with potential application in the monitoring of water quality in areas of mining tailings and environmental recovery. To achieve this we have performed an extensive literature review on potentiometric sensors with chalcogenide glasses, the synthesis of chalcogenide glass samples to make the electrode membranes, the sensor response characterization and the development of the flow-cell and prototype.

The next chapter of this thesis brings a literature review of ISEs based on chalcogenide glass membranes for various ions detection, mainly heavy metal cations. In chapter 3 we present the glass synthesis, the sensors construction, and the prototype development. Finally, a general conclusion of this work is presented in chapter 4.

Chapter 2

Potentiometric sensors with chalcogenide glasses as sensitive membranes: a short review[1]

Nowadays there exists a large variety of Ion Selective Electrodes with chalcogenide glasses as sensitive membrane. This short review paper will discuss the development of these sensors for the last almost fifty years. The glass compositions, response modelling, construction methods, parameters evaluation and applications are reviewed. Research breakthroughs and remaining problems on chalcogenide glass Ion Selective Electrodes are discussed.

2.1 Introduction

Potentiometric sensors are widely used in many areas, such as environmental monitoring [47, 50–52], industrial factories [53], clinical and biomedical analysis [54–56], wearable sensors [57–59], etc. They are stable and easy to use, and the interpretation of their signals is straightforward. The sensing signal of this type of sensor is, basically, a potential generated at a membrane in contact with a solution in which a specific ion of interest is dissolved. Thereafter, the membrane plays a crucial role in the sensors. In fact, changing the membrane composition will change the sensor characteristics thus making these sensors interesting for

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[1] Reprinted from *Journal of Non-Crystalline Solids* 495, Potentiometric sensors with chalcogenide glasses as sensitive membranes: a short review, pages 8-18, Copyright © 2018, with permission from Elsevier.

many areas of scientific research and industrial applications.

The largest group of potentiometric sensors is the Ion Selective Electrodes. The first developed and most widely used ISE is the pH-sensitive glass electrode, which was proposed by Haber and Klemensiewicz in 1909 [60]. Since then a large number of membrane materials were developed for ISE applications. These include oxide and chalcogenide glasses, crystalline membranes, liquid and plasticized organic polymeric compositions containing ion exchangers or neutral carriers [61]. With the advance of thin film and microfabrication technologies, the possibility of making miniaturized sensors becomes a reality. The traditional ISEs could be miniaturized to a few microns by the use of thin films techniques to make the sensitive membranes. These sensors are called μISE. Other class of potentiometric sensors is the Ion Selective Field Effect Transistors which is a traditional Metal Oxide Semiconductor Field Effect Transistor (MOSFET) with the gate terminal replaced by an ion sensitive membrane. Like the μISE, the ISFET can be easily fabricated by microelectronic technology. However, the main problem associated with ISFET is its stability and short lifetime [62]. After years of research and development, there is a variety of commercial ISEs available for determining concentrations of different ions in liquid samples of different natures [17]. In fact, over the past half-century ISEs have evolved to well-established routine analytical tool [63].

All these sensors have in common the same detection mechanism employed by measuring a potential over a membrane in contact with the test solution. Membranes play an important role in the sensor characteristics, as different material compositions provide the sensitivity to different ions in the solution. One important class of membranes is based on chalcogenide glasses.

Chalcogenide glass-based ISEs were introduced by Baker and Trachtenberg in the 1970's [64,65]. Since then these glasses have been studied as membranes for potentiometric detection of metal cations like Fe^{3+}, Cd^{2+}, Pb^{2+} and others. The chalcogenide glasses have a number of advantages:

- The possibility of being synthesized with continuously variable compositions provides a wide spectrum of material properties [20, 21]. Since the chalcogenide glasses possess considerable glass-forming ability with several elements, it is possible to make minor changes in the glass compositions to adjust their physical, chemical and electrochemical properties.

- The glasses can be used for fabricating solid-contact sensors.

- They have high chemical stability, which leads to chemical durability.
- It is possible to make the glasses into thin films, constructing miniaturized sensors [22]. Furthermore, the low impedance of a thin film compared to that of the corresponding bulk material enables the use of poor conducting glass [14].

These features make chalcogenide glasses attractive for potentiometric sensor membranes for the applications in harsh environments and possible to use microfabrication techniques for mass production. Consequently, ISEs with chalcogenide glasses as sensitive membranes are widely used for determination of heavy metal ions concentration in solutions [19, 66].

However, the main challenge when working with chalcogenide glass sensors is the cross sensitivity, which can induce incorrect interpretations of the measurements. One way to overcome this problem is to construct a sensing system called electronic tongue. The ET system is an array of several chemical sensors that uses advanced mathematical algorithm for signal processing. ETs were developed in an attempt to mimic the human gustatory system. There are some important reviews about ET systems in the literature [46, 67–69], therefore ET system is not covered in this particular review.

Although the research on chalcogenide glass ISEs has decreased over the past few years, recently, Li et al. [70] have developed an Ag^+ sensitive chalcogenide glass ISE with nanomolar detection limit and almost no cross sensitivity, showing the current research interest in the development and improvement of chalcogenide membrane sensors. This chapter will discuss the progress in the development of the ISEs and ISFETs sensors based on chalcogenide glassy membranes and the theory foundation of the sensor response. The paper starts with a brief overview of techniques for chalcogenide glass synthesis, followed by a review on the theory and response modelling and discussions on sensors' construction and development for different ions detection. At the end of this paper, a conclusion of the progress and future perspectives and challenges will be presented.

2.2 Chalcogenide Glass Synthesis

The typical high temperature synthesis process is applied depending on the type of glass. According to desired composition - pure elemental or salt components are used as precursors for making the glasses. They are proportional weighted, mixed and sealed in an evacuated quartz ampoule. The ampoule is then heated to 600-1200 k for hours and is quenched in water or air to form the desired glasses. A thermal treatment process follows at a temperature below the glass-transition temperature (T_g) for a few hours up to several days to remove the stresses of the sample. Because of the different physicochemical properties of the initial components, intermediated compounds and a final glass, the temperature range should be carefully selected to ensure a complete interaction between the elements and keep the vapor pressure under a critical value to avoid the quartz ampoule explosion [19].

The glass state can be verified by XRD and/or electron microscopy analysis. X-ray microprobe, Auger Electron Spectroscopy (AES) and Infrared Spectroscopy are used to study the material homogeneity on the surface and within the bulk. Physicochemical parameters such as glass transition, crystallization and melting temperatures, density, microhardness, module of elasticity and so on are of great importance and should be determined [19, 71, 72]. From the electrochemical point of view, doping a chalcogenide glass with Ag above a certain threshold concentration can change it from semiconductor to fast ionic conductor, increasing its conductivity up to 8-10 orders of magnitude. High ionic conductivity and ion transport are necessary characteristics for achieving ion sensitivity of the sensor membranes [73, 74].

2.3 Theory for electrochemical sensor response

Electrochemical sensor response is a time-dependent phenomenon that depends on the membrane material and the solution under investigation. The electrical signal is produced by a sensing membrane when contacting a solution. The thermodynamic and kinetic properties of the membrane-solution interface play important roles in the signal generation. Modelling the sensor response serves two roles. The first one, centered on basic principles and simple mathematical equations, supports sensor users in applications and quantitative measurements. The second is to model the sensor response with advanced mathematical equations based on electrochemical theory to provide a fundamental understanding of the response [75] and to map electric potential and ion concentration changes in space and time, which could be helpful for the development of sensor membranes.

In the next subsections, some principles and mathematical models will be discussed in different levels of details and complexity. The models assume that: (i) the sensors are under open-circuit conditions in an electrochemical cell that is consisted of two electrodes, an ISE and a reference electrode, separated by an electrolyte, the solution under investigation; (ii) The electrodes are connected to a high impedance voltmeter as showed in Figure 2.1a; (iii)

The sensor scheme is sample/ion-sensitive membrane/internal contact (e.g. solution, gel, solid contact) represented by the schemes in Figures 2.1b and 2.1c. As a start, the Nernst equation is presented. It describes oxidation-reduction processes and serves as a basic model for the sensor response. Moreover, it is a background for the classical models, which avoid mathematical, numerical and computational difficulties stemmed from solving nonlinear equations inherent to advanced models. Classical models are easier to comprehend. However, the use of advanced models is the only way to achieve a fundamental understanding of a sensor response [75].

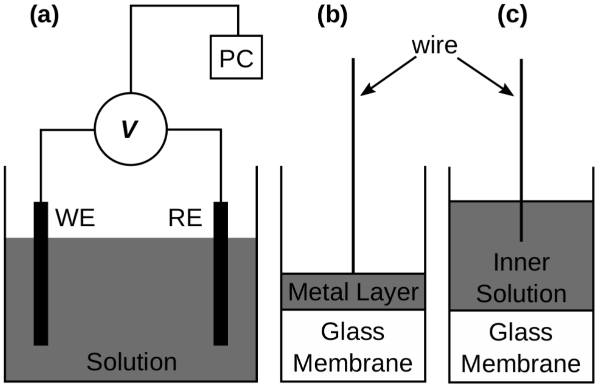

Figure 2.1: (a) Scheme of an ISE operation, (b) solid-contact ISE and (c) ISE with inner liquid contact. RE = Reference Electrode, WE = Working Electrode.

2.3.1 The Nernst Equation

The Nernst equation indicates that the reduction potential of an electrochemical reaction depends on the standard electrode potential, temperature, and activities of the chemical species undergoing reduction and oxidation. In a reversible electrochemical cell, the Gibbs energy change under non-standard conditions can be related to the standard Gibbs energy change by

$$\Delta G = \Delta G^{\circ} + RT \ln\left(\frac{a_p}{a_r}\right). \tag{2.1}$$

Here ΔG is the Gibbs free energy or the chemical potential variation of the solution, ΔG° the Gibbs free energy under standard condition, R is the universal gas constant, T the absolute temperature, a_p is the activity of the products, and a_r is the activity of the reagents. The relationship between free energy and cell potential is defined by

$$-\Delta G = zFE, \tag{2.2}$$

where z is the ions charge, F is the Faraday constant, and E is the electric potential. Substituting equation 2.1 into equation 2.2, we have

$$E = E^0 - \frac{RT}{zF} \ln\left(\frac{a_p}{a_r}\right), \tag{2.3}$$

which can be written as

$$E = E^0 - \frac{RT}{zF} \ln a, \tag{2.4}$$

which is the Nernst equation. E^0 is the standard electrode potential, a is the activity of the ion with a charge z in the solution and the activity of the reagents inside the membrane is considered to be 1. The Nernst equation can be used to calculate the potential of an ion-selective membrane.

2.3.2 The Classical Models or Total Equilibrium Models

Classical models give the simplest description of a sensor response. It assumes a steady-state sensor working and that the electrical potential (E_M) is a sum of the boundary potential (E_{PB}) at the sample/ion-sensitive membrane boundary and the diffusion potential inside the membrane (E_D),

$$E_M = E_{PB} + E_D. \tag{2.5}$$

The simplest model assumes that the interface between an analyzed solution and a sensor membrane is a potential generating system, and there are no ions diffusion along the membrane (E_D = 0). This model is known as *Phase Boundary Model* (PBM). Two main assumptions are considered. The first is the *electroneutrality assumption*, which means that the migration effects are ignored and the sensor response is a potential at the phase boundary (interface between membrane and solution). The second is the *total equilibrium assumption*, which means that electrochemical equilibrium exists at the membrane interface. Using these two assumptions, Guggenheim developed a concept of electrochemical potential [76], which can be implemented as

$$\overline{\mu_i} = \mu_i + z_i F E = \mu_0 + RT \ln a_i + z_i F E \tag{2.6}$$

where $\overline{\mu_i}$ represents the electrochemical potential at the phase boundary for ion specie i, μ_i is the chemical potential, μ_0 is the chemical potential under standard conditions, a_i represents single free ion activity and z_i is its charge.

For the simplest model, some idealizing assumptions are needed:

- Ideal selectivity - only an ion "i" can be transferred through the interface.
- Infinite kinetics - the ion transfer is fast and reversible.
- Ideal immiscibility - the phases are immiscible and have distinct chemical properties.
- Ideal phase - the single ion activity (a_i) in each phase is equal to its concentration (c_i).
- Solvent impermeability - there is no flux of solvent through the membrane.

With these assumptions, it is possible to use the Guggenheim's theory to obtain E_{PB} as a function of c_i. Using the condition of chemical equilibrium between two chemically distinct phases ($\overline{\mu_i}^{(S)} = \overline{\mu_i}^{(M)}$), for example, the bulk of sample solution (S) and the membrane phase (M), the membrane potential E_M can be written as follows

$$\begin{aligned} E_M = E_{PB} &= \frac{\mu_0^{(S)} - \mu_0^{(M)}}{z_i F} + \frac{RT}{z_i F} \ln \left(\frac{c_i^{(S)}}{c_i^{(M)}} \right) \\ &= const + \frac{RT}{z_i F} \ln \left(\frac{c_i^{(S)}}{c_i^{(M)}} \right), \end{aligned} \tag{2.7}$$

which is a Nernst-like equation. The PBM model was proposed in 1937 by Nikolsky [77] to describe the response of a pH glass sensor in contact with a solution containing ions H$^+$ (i) as preferred ions and Na$^+$ (j) as interference ions. The membrane potential derived was

$$E_M = E_{PB} = const + \frac{RT}{z_i F} \ln \left(c_i^{(S)} + k_{ij} c_j^{(S)} \right), \tag{2.8}$$

where k_{ij} is the equilibrium constant and is given by

$$k_{ij} = \frac{c_i^{(S)} c_j^{(M)}}{c_i^{(M)} c_j^{(S)}}. \tag{2.9}$$

The next step is to consider that some ions can diffuse through the membrane, extending the Nikolsky's equation to a non-zero diffusion potential in the membrane ($E_D \neq 0$). This equation was obtained by Eisenman three decades later [78, 79] and has the form

$$E_M = E_{PB} + E_D = const + \frac{RT}{z_i F} \ln \left(c_i^{(S)} + \frac{\overline{\overline{\mu_j}}}{\overline{\overline{\mu_i}}} k_{ij} c_j^{(S)} \right), \tag{2.10}$$

where $\overline{\overline{\mu_i}}$ and $\overline{\overline{\mu_j}}$ are the mobilities of the respective ions. Both Nikolsky and Eisenman equations are available only for ions, the main and interfering ones, of equal charges ($z_i = z_j$).

2.3.3 Advanced Nonequilibrium Models

The models described above fails in numerous situations due to the two constitutive conditions: electroneutrality and total equilibrium. These conditions are not considered and are the main feature of the advanced nonequilibrium models. It can be done by employing the Nernst-Planck-Poisson (NPP) equations system. This equation system works explicitly with the space and time domains, and is general and rich enough in a physical sense to describe the generation of the membrane potential and can be written as

$$J_i\left(x,t\right) = D_i \frac{\partial c_i\left(x,t\right)}{\partial x} - \frac{F}{RT} D_i z_i c_i\left(x,t\right) E\left(x,t\right) + c_i\left(x,t\right) v(x,t), \tag{2.11}$$

where $J_i(x,t)$ is the flux of particles through the membrane, $c_i(x,t)$ is the concentration, $v_i(x,t)$ is the drift velocity, $E(x,t)$ is the electric field, D_i is the diffusion coefficient, x is the spatial coordinate and t is the time. To solve this equation two additional equations are used; the law of mass conservation

$$\frac{\partial c_i\left(x,t\right)}{\partial t} = \frac{\partial J_i\left(x,t\right)}{\partial x}, \tag{2.12}$$

and the Poisson equation

$$I(t) = F \sum_i z_i J_i\left(x,t\right) + \epsilon \frac{\partial E(x,t)}{\partial t}, \tag{2.13}$$

where ϵ is the dielectric permittivity and $I(t)$ is the current density. Finally, the electrical potential $E_M(t)$ is calculated as the integral of electric field over space

$$E_M\left(t\right) = -\int_0^d E(x,t)dx, \tag{2.14}$$

where d is the membrane thickness.

Due to its complexity, the NPP model can only be solved numerically, which makes this approach difficult for users to solve it for every analysis. Nevertheless, this model provides profound insight into the fundamental principle of ISE that have intrigued scientists for decades and was not possible using the classical models. There are some alternative intermediate models for the PBM and NPP such as the Diffusion Layer Models [75].

2.3.4 Semiempirical Equation

For laboratory purposes, the Nernst equation fulfils the basic needs of ISE applications, and the Nikolsky's and Eisenman's models provide analytical equations valid just for two ions with the same charge. The Total Equilibrium Model does not work for the description of membrane potential for ions with unequal charges. To cover such cases, the arbitral decision of International Union of Pure and Applied Chemistry (IUPAC) defined a semi-empirical equation, which is known today as Nikolsky-Eiseman (NE) equation [80], as

$$E = E_0 \pm \frac{RT}{z_i F} \ln\left(c_i + \sum_j K_{ij} {c_j}^{z_i/z_j}\right), \tag{2.15}$$

where E_0 is the standard potential of the sensor, the indexes i and j refer to the ion to be determined and the interfering ones, respectively, and K_{ij} is the selectivity coefficient. The sign "$+$" corresponds to cation selective and "$-$" to anion selective sensors. If there is only one ion to be determined in the solution, equation 2.15 reduces to the Nernst equation. However, a calibration of the sensor is necessary for the semiempirical approach [80].

2.3.5 Sensor calibration and parameters measurements

The sensor calibration can be performed by measuring the electric potential between the sensor and a reference electrode in different solutions with varying concentrations of the ion of interest. Figure 2.2 shows an example of a calibration curve.

To calibrate a new ISE, some parameters must be determined. The first one is the sensitivity (S) which is the linear coefficient for the linear part of the fitting line in Figure 2.2, which should be $S = 2.3RT/z_iF$, although it is not always necessary to obey this relation [81]. In a standard condition at 25°C, the sensitivity is approximately equal 59 mV/pM$_i$ (millivolt per negative log of molar concentration of ion i) for an ion of $+1$ charge. Indeed, in real life, the sensitivity could differ from this value and could be different for different membranes. So the value of S is a characteristic of each individual sensor. Sensors that have S values near 59.9 mV/pM$_i$ are said to have Nernstian response and those with $S > 59$ mV/pM$_i$ ($S < 59$ mV/pM$_i$) are said to have super-Nernstian (sub-Nernstian) behavior.

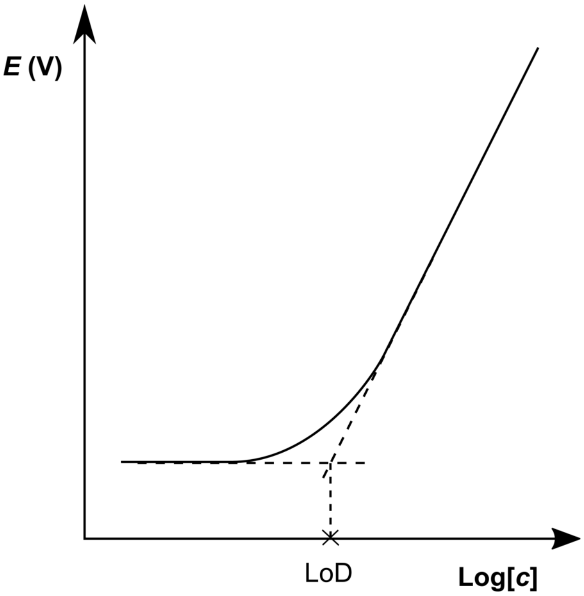

Figure 2.2: ISE calibration curve. LoD = Limit of Detection.

The second important parameter to determine is the Limit of Detection (LoD), which is the lowest concentration the sensor could measure. According to IUPAC recommendations [80], the LoD is equal to the concentration where the potential differs by 18/z_i mV/pM$_i$ (z_i is the charge of the ion i) from its Nernst response, or it could be determined by the intersection of the extension of the two linear parts of the response curve as shown in Figure 2.2.

Another parameter to establish is the response time of an ISE sensor. Response time is the time required for the electrode to take a stable potential value after its transfer from one working solution to another with a different ionic concentration [81]. This parameter depends on the electrode type, presence of interfering ions, concentration difference between the solutions, and if the concentration of the new solution is higher or lower than the initial one.

When interfering ions are present, the response should obey equation 2.15 (NE equation). The selectivity coefficients define the ability of an ISE to distinguish one ion (i) from another (j). The smaller it is the greater is the electrode's preference for the principal ion. It could be determined from the NE equation by different measurement methods like *Fixed Interference*

Method (FIM) and *Separated Solutions Method* (SSM). In the first method, a calibration plot is done with a solution containing a fixed concentration of the interference ion j. By the same way as to determine the LoD in a calibration plot with a solution containing only the primary ion i, the intersection of the extrapolation of the two linear portions of this plot indicates the value of c_i that should be used in the equation

$$K_{ij} = \frac{c_i}{{c_j}^{z_i/z_j}} \tag{2.16}$$

to determine K_{ij}. The SSM relies on separate measurement of the E in pure solution of the primary and interfering ion (E_i and E_j) with equal values of ions concentrations ($c_i = c_j$). Then, the value of K_{ij} can be calculated by

$$\ln K_{ij} = \frac{E_i - E_j}{S} + \left(1 - \frac{z_i}{z_j}\right) \ln c_i. \tag{2.17}$$

Other way to measure by SSM is doing E measurements of pure solutions of the primary and interfering ions and for any pair of c_i and c_j with $E_i = E_j$ the selectivity coefficient can be calculated by

$$K_{ij} = \frac{c_i}{{c_j}^{z_i/z_j}} \tag{2.18}$$

which is the same expression used in the FIM. It is important to note that both methods are useful only when the sensor exhibits a Nernstian behavior to both principal and interfering ions.

2.3.6 The Modified Surface Layer Model

The Modified Surface Layer (MLS) model, originally proposed by Vlasov [82], is a qualitative model that is largely used in literature to explain the response of chalcogenide glass ISEs. This model proposes that there is a partial destruction of the glass network in contact with the solution creating a modified surface layer. The sensor sensitivity depends on the direct exchange of the ions between the solution and this layer combined with an oxi-reduction process of these ions in the glass network. This model was first proposed to explain the sensitivity of a Cu^{2+} ion detection with a chalcogenide glass sensor. The sensor showed a slope of around 60 mV/pM$_i$, which should be a slope for ions with a $+1$ charge according to the Nernst-equation like models. The structural defects of the surface layer make the Cu^{2+} ions migrate through it. The exchange sites are formed by oxidation of Cu^{+} ions in the glass network. This model was confirmed by some experiments [23, 25, 83, 84], such as using x-ray photo-electron and Auger electron spectroscopy to detect the defects of the glass matrix formed in the modified surface and the presence of Cu^{2+} and Cu^{+} ions in that surface.

2.4 Glass Sensors

Glass sensors are possible types of sensors that can be made using chalcogenide glasses as sensitive layer. Figure 2.1 already presented two types of traditional ISEs, a solid-contact one (Figure 2.1b) and an electrode with an inner liquid contact (Figure 2.1c). Figure 2.1a shows a scheme of the galvanic cell, with which the potential (E) against the concentration of the interested ion in solution is measured. Figure 2.3 illustrates two types of miniaturized devices, which can be made by microelectronic techniques. Figure 2.3a shows an ISFET sensor, which is an electronic device like a MOSFET with a gate which responses to the ion concentration in the solution, and Figure 2.3b shows a μISE which is made by evaporation of different material layers over a silicon or glass substrate to make the sensor.

To make the ISE sensor, a glass disc of 6-10 mm in diameter and 1-2 mm thickness is cut and polished with very fine diamond paste. The disc is put on the end of a PVC or glass tube and sealed with epoxy resin. The solid-state contact could be obtained by deposition of a conductive metal layer, usually silver on the inner side of the membrane, and attaching a wire by micro-adhesive or conductive bond, as shown in Figure 2.1b.

The liquid contact could be made by filling the inner side with a solution, usually 0.01M $AgNO_3$/0.1M KNO_3, and putting a wire in contact with this liquid as inner reference electrode, as illustrated in Figure 2.1c. The potential measurement can be made with a standard reference electrode, usually Ag/AgCl, with the following electrochemical cell equation [85]

$$Ag, AgCl|KCl_{sat}||KNO_3(0.1mol/l)||\text{test solution}|\text{Glass}|AgNO_3(0.1mol/l)|Ag \tag{2.19}$$

for electrodes with liquid inner solution, and

$$Ag, AgCl|KCl_{sat}||KNO_3(0.1mol/l)||\text{test solution}|\text{Glass}|Ag \tag{2.20}$$

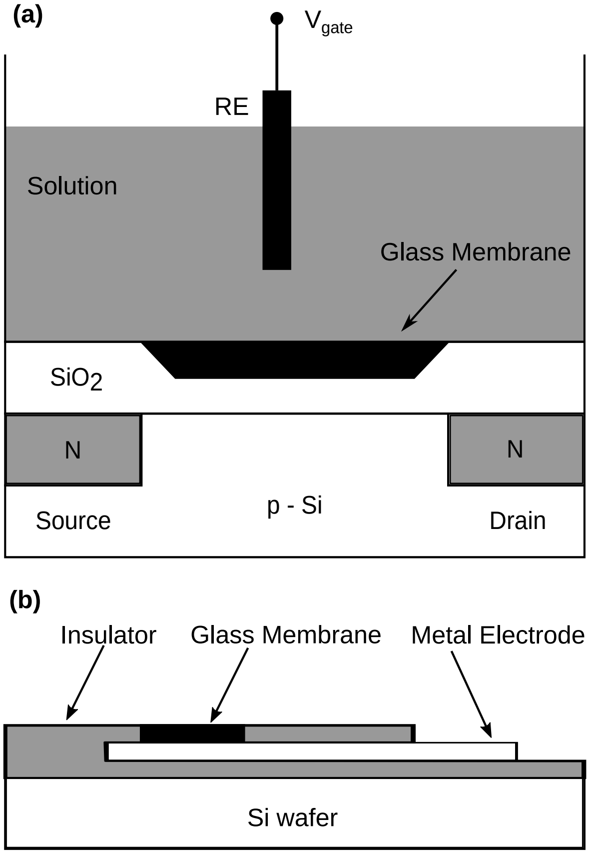

Figure 2.3: (a) ISFET and (b) μISE. RE = Reference Electrode.

for solid-contact sensors.

As shown in Figure 2.3b, a μISE sensor can be made by a superposition of a sensitive membrane layer and a metal layer over a substrate, which can be made of silicon, glass, graphite and others. Utilizing evaporation techniques, a metal layer is deposited over a substrate to make the electric contact, and a chalcogenide glass thin film is deposited over the metal-substrate assembly. Some techniques like spin-coating technique or sol-gel process [86], high-frequency [87], radio frequency (RF) co-sputtering of glass and dopant [88], pulsed laser deposition (PLD) [89, 90], vacuum evaporation [91], and others have been used to prepare these thin films. The film quality can be evaluated by means of Scanning Electron Microscopy (SEM), Auger electron spectroscopy and Rutherford Backscattering Spectrometry (RBS) techniques, and the potentiometric response is measured in a similar way as ISEs with the help of a reference electrode.

The fabrication process of an ISFET device is the same of that a MOSFET without the gate metal layer. In place of this layer, a layer of sensitive membrane (in this case, a chalcogenide glass) is evaporated. The technique to make the thin glassy layer is the same as those used for the μISEs.

Tables 2.1 and 2.2, updated from Ref. [92], list some works found in the literature organized by the ions that the sensors were developed to detect. These works will be reviewed in this paper according to the ions to be detected.

2.4.1 Fe^{3+}

The $Se_{60}Ge_{28}Sb_{12}$ glass composition doped with Fe^0 was used as sensitive material to evaluate Fe^{3+} ions in solution. Both solid-contact sensor and a sensor with inner liquid contact were developed and both configurations have similar results [65]. The sensors had a super-Nernstian slope of approximately 60 mV and the optimum doping level found was 2% Fe^0. According to the Nernst equation, this slope should be approximately 20 mV because of the charge $+3$ of the studied cation. However, in that case, the measured slope implies that a redox potential involving the Fe^{3+}/Fe^{2+} couple determined the potential instead of an ion exchange process. Therefore, Fe^{2+} must be in the glass or generated at its surface. These sensors have no response to Na^+, K^+, NH_4^+, Ca^{2+}, Ba^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cr^{3+}, NO_4^-, Cl^- and SO_4^{2-}, but have a strong sensitivity to Ag^+ [65]. Furthermore, the storage condition of the electrodes between measurements can influence the results, complicating the operation of the sensors for continuous measurements [109]. These sensors have wide applicability in monitoring wastewater quality and technological electrolytes and in nuclear plant safety, where the copper and iron content in high purity water can be an indicator of a corrosion process occurring and causing damage in a reactor [108].

2.4.2 Cu^{2+}

To detect Cu^{2+} ions in a solution, a $Se_{60}Ge_{28}Sb_{12}$ glass composition doped with Co^0 was proposed, and the sensor showed sensitive to storage conditions, which is undesirable for continuous monitoring applications [64, 65]. The $Cu_x(As_2(Se_{0.5}Te_{0.5})_3)_{100-x}$, $Cu_x(As_2S_3)_{100-x}$ and $Cu_x(As_2Se_3)_{100-x}$ glass compositions were used to develop cupric ions sensitive electrodes [103, 104]. The copper arsenic trisulphide glass membrane showed no response to the interferences of Ca^{2+}, Pb^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}, but had sensitivities to Fe^{3+} and Ag^+ ions.

Ion	Chalcogenide glass material	Sensitivity (mV/pX)	LoD (mol/L)	Ref.
Ag^+	Ag-As-S,Ag-As-Se	56-60	10^{-7}	[93]
	AgGeSe	56±5	5×10^{-8}	[94]
	$AgAsS_2$-Ni	59±8	10^{-7}	[95]
	$AgCl\text{-}Ag_2S\text{-}As_2S_3$	54.5±0.5	1.89×10^{-9}	[70]
Br^-	$AgBr\text{-}Ag_2S\text{-}As_2S_3$	57-60	5×10^{-7}	[96]
Cd^{2+}	$CdS\text{-}Ag_2S\text{-}As_2S_3$,$CdI_2\text{-}Ag_2S\text{-}As_2S_3$	25-28	10^{-7}	[23]
	CdS-GeTeSe	≈30	–	[97]
	$GeSe_2\text{-}Sb_2Te_3\text{-}CdSe$	22-24	$1.6\text{-}2\times10^{-5}$	[98]
	$CdSe\text{-}AgI\text{-}As_2S_3$	24-26	3×10^{-7}	[99]
	$CdS\text{-}AgI\text{-}Ag_2S\text{-}As_2S_3$	>30	$\approx10^{-7}$	[100, 101]
Cr^{6+}	Composition not given	30-60	10^{-7}	[102]
Cu^{2+}	Cu-Ag-As-Se	27-29	10^{-7}	[83]
	Fe+SeGeSb	27-62	$\approx10^{-5}$	[64, 65]
	$Cu\text{-}As_2S_3$	30-50	$\approx10^{-5}\text{-}10^{-6}$	[103]
	$Cu\text{-}As_2S_3$,$Cu\text{-}As_2(SeTe)_3$	28-30	$<10^{-5}$	[104]
	$Cu_{10}(As_2S_3)_{90}$	30	$\approx10^{-6}$	[105]
	Cu-As-Se	≈30	-	[23]
	$Cu_2Se\text{-}As_2Se_3$	≈30	-	[97]
	Cu+SeGeSb	31	$<10^{-5}$	[106]
	Cu-As-S	30	10^{-6}	[107]
	AgGeSe	60-70	3×10^{-7}	[74]
	(CuAg)GeSe	45-60	10^{-7}	[74]
Fe^{3+}	Composition not given	20-60	5×10^{-6}	[108]
	FeSeGeSb	57.6±2.9	$\approx10^{-6}$	[65, 109]
Hg^{2+}	Composition not given	45-50	10^{-7}	[108]
	HgS+GeTeSe	≈30	-	[97]
Na^+	$NaCl\text{-}Ga_2S_3\text{-}Ge_2S$	50-55	10^{-5}	[82]
Pb^{2+}	$PbI_2\text{-}Ag_2S\text{-}As_2S_3$,$PbS\text{-}Ag_2S\text{-}As_2S_3$	26-29	10^{-7}	[25, 110]
	$PbS\text{-}AgI\text{-}As_2S_3$	26-29	10^{-7}	[25, 110]
	$PbI_2\text{-}AgAsS_2$	30	$\approx10^{-5}$	[111]
	Pb(AsSe)	30	$<10^{-6}$	[104]
	PbCu(AsSe)	30	$<10^{-5}$	[104]
	$GeSe_2$-PbSe-PbTe	12-25.8	$(3.5\text{-}7.9)\times10^{-6}$	[112]
Tl^+	Composition not given	55-59	10^{-7}	[113]
	$TlI\text{-}Ag_2S\text{-}As_2S_3$	57	3×10^{-6}	[114, 115]
Zn^{2+}	$GeSe_2\text{-}Sb_2Se_3\text{-}ZnSe$	25-39	$\approx10^{-5}$	[116]
	$GeSe_2$-ZnSe-ZnTe, $As_2Se_3\text{-}Sb_2Se_3\text{-}ZnSe$	22-41	$\approx10^{-6}$	[117]

Table 2.1: Chalcogenide glass materials as sensor membranes used for ISEs and corresponding electrochemical characteristics.

Ion	Chalcogenide glass material	Method	Sensitivity (mV/pX)	LoD (mol/L)	Ref.
Ag^+	Ag-As-S	d	≈59	$\approx 10^{-5}$	[118, 119]
	Ag-As-S	f	56-60	$<10^{-6}$	[120–122]
	AgGeSe	f	56±5	5×10^{-8}	[94]
	$AgI-As_2S_3$	f	46.1±4.5	2×10^{-7}	[123]
Cd^{2+}	$CdS-Ag_2S-As_2S_3$	b	25	$\approx 10^{-5}$	[124]
	$CdS-AgI-Sb_2S_3$	e	≈24	$\approx 10^{-7}$	[91]
	Cd-S-Ag-I-As	f	26-28	4×10^{-7}	[21, 89, 110, 125–129]
	$CdS-AgI-As_2S_3$	f	20	3.8×10^{-6}	[130]
	$CdS-AgI-As_2S_3$	f	25.5±0.9	4×10^{-7}	[123]
Cu^{2+}	As_2S_3:Cu	a	26-30	10^{-6}	[131]
	Cu-As-Se	a	27-30	$\approx 10^{-6}$	[88, 132]
	Cu-Ge-Sb-Se:microsensor	a	30	5×10^{-7}	[133, 134]
	Cu-Ge-Sb-Se:ISFET	a	28	10^{-6}	[133, 134]
	Cu-Ge-Sb-Se	c	30	10^{-6}	[105]
	As_2S_3+As,Se,Cu	c	25-31	$<10^{-5}$	[135]
	Cu-Ag-As-S	d	23-29	10^{-5}	[62, 119, 136]
	Cu-Ag-As-Se	d	23-29	10^{-6}	[62, 119, 136]
	Cu-Ag-As-Se	f	27-29	10^{-7}	[21, 121, 126, 130]
	Cu-Ag-As-Se	f	31.9±0.4	4×10^{-8}	[123]
	Cu-Ag-As-Se-Te	f	27-30	10^{-7}	[21, 89, 110, 120, 122, 127, 129]
Hg^{2+}	HgTe-GeTe-Se	e	24	3×10^{-6}	[137]
	$AgBr-Ag_2S-As_2S_3$	e	90-110	$\approx 10^{-6}$	[138]
Pb^{2+}	Pb-Ag-As-S	d	25	10^{-5}	[119, 139]
	Pb-S-Ag-I-As-S	f	26-29	10^{-7}	[89, 110, 120, 121, 125–127, 140]
	$PbS-AgI-As_2S_3$	f	23	5×10^{-6}	[130]
Tl^+	Tl-Ag-As-I-S	f	54-60	3×10^{-5}	[21, 89, 110, 125, 127, 129]

Table 2.2: Chalcogenide glass materials as thin-film sensor membranes for ISEs and field-effect devices deposited by means of thin-film preparation techniques. a: RF co-sputter process, b: RF magnetron sputter process, c: RF sputter process/ion-implantation, d: vacuum deposition/photodoping, e: vacuum evaporation process, f: pulsed laser deposition.

A sensor made with $Cu_{10}(As_2S_3)_{90}$ glass membrane was successfully used to detect copper ions in wastewater [105].

The glasses of composition $Cu_xAg_{25-x}As_{37.5}Se_{37.5}$, with x varying from 0 to 25, were used as sensitive membranes for ISEs for cupric ion detection. The sensor with the $Ag_{25}As_{37.5}Se_{37.5}$

membrane appeared to be Cu^{2+} sensitive even without any copper in its composition. These electrodes were 10-30 times more sensitive in strongly acid media than the respective crystalline ones and were superior to the Cu^{+} selenide electrode in selectivity and resistance to acids and oxidation [83]. The sensitivity and Nernstian range of the solid-contact sensors and sensors with inner solution were similar, but the solid-contact one showed better potential stability. These sensors showed no response to the alkali and alkali-earth metals Ca^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}. However, considerable interference of Ag^{+} and Fe^{3+} were observed [83].

Two glass compositions of AgGeSe and (AgCu)GeSe were used as selective membranes for copper ISEs. It seemed that the response of the electrodes was controlled by the amount of Ag in the membrane, and the addition of Cu to the membrane composition did not improve the sensitivity of the electrodes. As silver content in the membranes increases, the slope increases, the LoD is shifted towards lower concentrations and the linear range is shortened [74].

A miniaturized device to detect copper ions was made with a chalcogenide Cu-doped As_2Se_3 thin film membrane. The film was fabricated by the RF co-sputtering technique and the sensor is an ISFET type [131]. To explain the mechanism of this sensor, the existence of a modified surface layer in a traditional ISE was considered due to the ion-exchange mechanism in the membrane/electrolyte solution interface. This ISFET sensor showed properties similar to the conventional chalcogenide glass based ISE [131]. Another miniaturized ISFETs with Cu-doped membranes made of As_2S_3 or As_2Se_3 glasses by vacuum evaporation technique showed good properties [62]. The Cu-doping was performed using a photo-doping process. Light exposure caused photochemical reactions and Ag and Cu photo-doping in the As_2S_3 glass matrix. Decreased response time and improvement in the reproducibility of these sensors were observed, probably resulted from the photochemical reactions. A pulsed laser deposition technique was used to fabricate thin film sensors with the Cu-Ag-As-Se [121, 123, 126] and Cu-Ag-As-Se-Te [89, 120] glasses as sensitive membranes. These sensors were also sensitive to Ag^{+} and Hg^{2+} interferences [21].

Germanate glassy systems, Cu-Ge-Sb-Se [133, 134] and AgGeSe [94] were also used to make miniaturized sensors by using of RF sputtering and PLD techniques to make thin film membranes, respectively. The thin film sensors exhibited the same properties as bulk membranes, indicating that these chalcogenide glasses have great potential for miniaturization. These sensors showed drastic potential decrease in basic solutions caused by the slow dissolution of the membrane. In neutral or acid solutions, the sensors had a constant potential.

These sensors showed high response to the interfering ions Hg^{2+}, Pb^{2+}, Fe^{3+} and Cr^{3+} but no response to Cd^{2+}, Ni^{2+}, Mg^{2+} and K^{+}.

2.4.3 Hg^{2+}

The chalcogenide glass system HgS-$Ge_{0.2}Te_{0.3}Se_{0.5}$ was used as a sensitive membrane of ISEs to detect Hg^{2+} ions. The glass host matrix $Ge_{0.2}Te_{0.3}Se_{0.5}$ alone did not respond to Hg^{2+} ions, but the sensor showed response to the mercury ions when doped with up to 10 mol % HgS. When tested with Cu^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+} and Fe^{3+} the sensor showed no response [97]. These sensors have already been successfully used for wastewater control [108]. The glass system HgTe-GeTeSe was also used to make thin films sensors by vacuum evaporation technique onto a chromium sputtered glass substrate. This sensor was very selective in solution containing Pb^{2+} and Cd^{2+} [137]. Using the same process, thin films of AgBr-Ag_2S-As_2S_3 glass system was made as a sensitive membrane for mercury ion detection. This particular sensor showed a super-Nernstian response of around 90-110 mV/pHg [138].

2.4.4 Pb^{2+}

The first effort trying to detect lead ion with chalcogenide glass was with the $Pb_{20}Cu_5(As_2Se_3)_{75}$ glass composition. The main problem is that this glass has very high resistivity and presented difficulties with potentiometric measurement [104]. This problem could be solved by adding silver to the glass composition. It was observed that a small amount of silver could improve the ionic conductivity of the glass by orders of magnitude. Glasses with silver in its composition, like $AgAsS_2$ and PbS-Ag_2S-As_2S_3, showed sensitivity to lead ion, good conductivity, and consequently good electrochemical properties [25, 141]. The glass of composition PbS-As_2S_3 exhibited sensitivity to this ion but compared with the Ag containing compositions it was less reproducible because an oxidation process in the surface of the membrane occurred. The PbS present in the membrane composition converted to PbO and/or other lead-oxygen compound, which did not display reasonable Pb ion sensitivity [141].

Another sensor with the $GeSe_2$-PbSe-PbTe glass system showed good lead sensitivity [112]. Glasses with $GeSe_2$ in its composition appeared to be more chemically resistant than glasses with As_2Se_3 and As_2S. Other advantage is that these glasses do not use arsenic in its composition. Vassilev [112] indicated that as a rule, chalcogenide ISEs are reversible to the metal ions that are included in the composition of the glassy alloy, and the ion-exchange process is favored by the increased ionic part of the conductivity, which can be ensured by adding PbSe and PbTe to the $GeSe_2$-glass. Moreover, these sensors showed good selectivity in presence of Cd^{2+}, Cu^{2+}, Zn^{2+} and Al^{3+} with the selectivity coefficients smaller than 10^{-5}.

A pulsed laser deposition technique was used to make μISE sensors with a thin layer of chalcogenide Pb-Ag-I-As-S glass on a silicon substrate [125]. To form the appropriate electrical contact, metallic layers were deposited by electron beam evaporation techniques. The sensor had a near Nernstian response to Pb ions for about five orders of Pb^{2+} concentration. It was observed that the thin-film had a polycrystalline structure in contrast to the amorphous structure of the target material. Comparing with the respective traditional ISE, this sensor showed good agreement with the calibration parameters [140]. These sensors have considerable sensitivity to Ag^{+} and Hg^{2+}, so these ions must be absent in the analyzed solution. They have almost no response to Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+} and Ca^{2+} [110]. Sensors with a thin film of Pb-Ag-As-S glass system made by thermal vacuum evaporation and photo-doping process were also developed [119, 139]. These sensors showed a detection limit two orders of magnitude lower than the ones made by PLD technique.

2.4.5 Ag^{+}

Sensors based on the Ag-As-Se-Te glasses exhibit sensitivity to silver ions. The sensors with low tellurium content demonstrated high Ag^{+} ion sensitivity, potential stability and reproducibility. Furthermore, these glass sensors demonstrated superior selectivity over their respective crystalline silver ion sensors in the presence of interfering ions [85]. The sensors with AgGeSe glass composition showed sensitivity to silver ion, but suffer interference from some cations like Hg^{2+}, Pb^{2+} and Fe^{3+} [94]. An Ag^{+} sensitive electrode improvement was made by Ni-implantation into $AgAsS_2$ membrane glasses in solid-contact devices [95]. The Ni^{+} implantation increased the p-type electronic conductivity by six orders of magnitude and the ionic conductivity by 2.5 orders of magnitude near the inner glass/metal interface providing high ionic and electronic exchange in this interface, leading to fast and reproducible sensor response [142]. This looks quite promising because low electronic conductivity makes it difficult to realize a reversible glass/metal interface at the inner side of the membrane and, consequently, to obtain solid-contact devices with high potential stability and fast response [95]. On the other hand, Vlasov [95] indicated that keeping the outside surface with a very small value of the electronic conductivity prevents electrochemical corrosion of the membrane surface and decreases the influence of redox couples in solution on the sensor response. Recently, Li *et al.* [70] published their results of a set of solid-contact sensors made with AgCl-Ag_2S-As_2S_3 glass system as sensitive membrane. They improved the sensor to nanomolar detection limit with a slope around 55 mV/pAg^+.

Thin films of As_2S_3 and AsSe glasses doped with silver were used to prepare micro sensors to detect silver ions by two different techniques. The first technique used was the spin-coating where the glasses should be previously dissolved in organic solvents. However, these sensors exhibited unsatisfactory response [143]. The second one was a vacuum evaporation technique, which was used to prepare ISFET sensors. The chalcogenide glass was previously deposited by vacuum evaporation and then silver was photo-doped into As_2S_3 thin films. It's observed that the sensor potential decreases with the increasing of the thickness of the layer until reaching a saturated value above 0.2 μm [118, 119]. Another micro sensor was made using the AgGeSe glass thin film as sensitive membrane [94]. The membrane was deposited by PLD and the sensor showed almost the same properties as the sensor made of bulk glass as membrane.

2.4.6 Tl^+

A thallium ion sensitive electrode was made using the TlI-Ag_2S-As_2S_3 glass system as a sensitive membrane [114, 115]. It was observed that the sensor with the membrane of a higher concentration of Ag showed the best analytical characteristics. The Tl^+ sensor was almost not interfered by alkali and alkali-earth cations, Mg^{2+}, Pb^{2+}, and Cd^{2+}, but could be strongly interfered by solutions containing Cu^{2+}. The thallium sensor was used to measure thallium content in natural and wastewater and showed selectivity two orders of magnitude better than a crystalline electrode [113].

The Tl-Ag-As-I-S glass system was evaporated by the PLD technique to form sensitive thin film layers [21, 89]. These sensors suffered strong interference from Hg^{2+} and Ag^+ ions [110], moderate interference from Cu^{2+}, Pb^{2+} and Cd^{2+} [129], and almost no interference from Mg^{2+}, Zn^{2+} and Ca^{2+} [127].

2.4.7 Zn^{2+}

The $GeSe_2$-ZnSe-ZnTe and As_2Se_3-Sb_2Se_3-ZnSe glasses were used for Zn^{2+} ions detection in solution [117]. The sensors have an unusual behavior because its calibration curve looked like that of a sensor for anion detection. The authors proposed a model based on structural changes on the glass matrix and consequently the diffusion of Zn ions in the matrix to explain the sensor response. A coated wire type sensor was made with the $GeSe_2$-Sb_2Te_3-ZnSe glass powder mixed with epoxy resin [116]. With this sensor, the ions Fe^{3+}, Pb^{2+}, Cd^{2+}, Na^+ and Cl^- did not interfere in the zinc ion measurement.

2.4.8 Cd^{2+}

The CdS-AgI-Ag_2S-As_2S_3 [100, 101] glassy system was used for cadmium ion detection. The sensor presented high selectivity in the presence of alkali and alkali-earth ions, but it was not suitable for working in mediums containing copper and sulphide ions. The sensor showed good sensitivity when tested in wastewater. The sensors with CdS-Ag_2S-As_2S_3 and CdI_2-Ag_2S-As_2S_3 glass membranes also responded to cadmium cations. With the second composition, the sensor showed slightly better electrode properties. Both sensors presented sensitivity to silver ion, but displayed good selectivity in the presence of Fe^{3+}, Cu^{2+}, Pb^{2+} and Tl^+ [23]. CdSe-AgI-As_2S_3 glass membrane electrode exhibited good sensitivity and detection limit for cadmium detection and almost no response to alkali and alkali-earth metals, but suffered strong interference by lead and copper ions [99]. Cd^{2+} ions could also be measured by a sensor with a $GeSe_2$-Sb_2Te_3-CdSe [98] glass system as a sensitive membrane. This sensor has good selectivity to cadmium ions in the presence of Na^+, Zn^{2+}, Sn^{2+}, and Al^{3+} ions.

Some miniaturized Cd^{2+} ions sensitive sensors were developed and the sensitive thin film of these sensors were deposited by thermal evaporation technique from the CdS-AgI-Sb_2S_3 glass system [91]. Silver and chromium were used as conductive layers. The response of the sensors with silver layer was more stable than the one with chromium, which could be explained by the better ion exchange at the interface Ag/glass. This sensor displayed poor selectivity in the presence of Pb^{2+} and Cu^{2+}.

By RF sputtering technique, a thin film of the system CdS-Ag_2S-As_2S_3 chalcogenide glass was deposited over an ISFET gate terminal [124]. The main problem of this configuration was its short lifetime, because the membrane peeled off from the gate terminal. The PLD technique was also used to prepare cadmium sensors with a membrane from the system Cd-Ag-As-I-S [110, 125]. ISFET and μISE sensors were produced, and the electrochemical parameters of both were in agreement with ISEs made with the same glass membrane [128]. It was observed that Ag^+, Cu^{2+}, and Hg^{2+} ions could strongly interfere with the sensor potential [129].

2.4.9 Summary

The sensors' developments for eight different ions were discussed in the text and the references for sensors development for other ions that were not discussed here are listed in Table 2.1. The devices developed up to now obey the NE equation and the calibration parameters were successfully measured. Nonetheless, only a qualitative describing of the response is given in literature and a quantitative modelling is missing. A quantitative modelling that describes the sensor response without any calibration will be a breakthrough in this research area.

The ISEs construction is well developed but the micro devices construction is indeed a challenge. Maintaining the stoichiometry of the targeted glass and the final thin film is an unsolved issue. Only the PLD technique has shown potentials to do it for now [89]. In addition, the fabrication of thin films with amorphous structure is quite difficult since the films tend to became polycrystalline in structure.

The recent advances in ISEs with polymeric membranes make a brief comparison with chalcogenide glass ISEs necessary. With regards to the electrochemical response, sensors with polymeric membranes have shown better electrochemical parameters, especially the detection limit that can reach picomolar and even fentomolar level for some ions, making ISEs with this type of membrane comparable to inductively coupled plasma (ICP)-based spectrometry [144, 145]. On the other hand, chalcogenide based ISEs has LoD in the order of μM-nM, as shown in Tables 2.1 and 2.2. However, the main problems with polymer membrane relay on its stability and relatively short life-time [146]. For continuous work in harsh environments, such as mining wastewater and most of industrial applications, chalcogenide glass ISEs has still being a better approach because the membranes are robust and stable comparing to polymers. The current state of research on chalcogenide glass ISEs requires lowering both LoD and cross sensitivity, which might be accomplished by improving the glass synthesis with possible new glass compositions and maintaining the stoichiometry of the thin film membrane.

2.5 Conclusion

The chalcogenide potentiometric sensors have been successfully applied in various areas, such as biomedical analysis, industrial factories, water pollutant monitoring, and many other application, especially due to the chemical stability, ease of use and data analysis.

Although chalcogenide glasses have considerable glass-forming ability with several elements, its synthesis process is not easy to do since the reaction is done inside quartz ampoules and the thermal regime should be well calculated to avoid the ampoule explosion, making the process quite delicate. In addition, the chalcogenide elements are toxic which needs some special care when working with it. The biggest challenge when synthesizing these glasses is the pressure control inside the ampoule and the quenching process. The melting should be contained to avoid explosion and the quenching should be good enough to avoid crystallization. More research on the preparation of these materials is fundamentally necessary.

Further research is needed, especially on the glass membranes to improve the electrochemical properties for various ion detections. Better sensitivity and lowest LoD are needed to achieve measurements that are more accurate and precisely detect small ions concentration in solutions. Furthermore, lowering the interference effects is desirable to make it possible to perform measurements in multi-ions solutions without measurement misinterpretation due to cross sensitivity.

Even with the development of numerous different chalcogenide glasses for membrane ISEs, the sensors with the glasses always showed some kind of cross sensitivity. The major interfering ions are silver and copper, and it is difficult to develop membranes that are not sensitive to them. This means that ions selective electrodes, ISEs, are not always selective. To overcome this problem, sensor arrays and the electronic tongues systems have been developed. By combining different sensors and analyzing their responses with mathematical algorithms, it is possible to identify the response due to the primary ion in the presence of the interference ones.

Although ISEs with chalcogenide glasses as sensitive membranes have been studied for almost half a century, deeper understanding of the response mechanism is still needed. In the literature, some theoretical models give quantitative narrative of the responses of some other types of ISEs. However, these models cannot adequately predict the responses of the ISEs with chalcogenide-glass membranes. There is a Modified Surface Model, which can only provide a qualitative explanation for these types of ISEs. Consequently, a model to describe quantitatively the ISEs is necessary to provide a better understanding of the roles of the membrane and its backing electrical contact in sensor response. This knowledge will be crucial for the optimization of the glasses for ISEs applications and certainly will be a breakthrough in this research area.

Chapter 3

Ion-sensitive electrodes with chalcogenide glass membranes for Cl^- ion measurement

We fabricated several ion-selective electrodes (ISEs) with chalcogenide glasses (AgX-Ag_2S-As_2S_3, X = Cl or Br) as ion-sensitive membranes for measurement of chloride ion in solution. Response slope and detection limit of each ISE were evaluated. The most sensitive one was built in a sensor prototype, which consisted of an ISE, a reference electrode, and a flow-cell system. The sensor prototype showed a linear vs. logarithm behavior of up to 4 orders of magnitude to Cl^- ion concentration with a slope of 7 mV/pCl^-.

3.1 Introduction

Ion Selective Electrode (ISE) sensors have a variety of applications in various areas, such as laboratory analysis, environmental monitoring, quality control processes, industrial factories, clinical and biomedical analysis, etc [15,45,56,75,147–149]. Its construction, calibration, usage and results interpretation are straightforward, which make this kind of sensor an attractive tool for solution analysis. The first developed and most widely used ISE is the pH-sensitive glass electrode, which was proposed by Haber and Klemensiewicz in 1909 [60]. Since then a large number of membrane materials were developed for ISE applications. These include oxide and chalcogenide glasses, crystalline membranes, liquid and plasticized organic polymeric compositions containing ion exchangers or neutral carriers [61].

The ion sensitive membrane plays an important role in the characteristics of the sensor. As the membrane stays in contact with the probed solution during the analysis, it should have proper electrochemical response and be robust enough to avoid damage in the solution. Due to the high chemical stability, chalcogenide and chalcohalide glasses are suitable membrane materials for ISEs designed to work in harsh environments, [14, 19, 20, 23, 74, 94, 100, 108] e.g. mining wastewater analysis.

The field of environmental applications is a demanding area [150], which represents a great opportunity for ISEs due to the importance of natural resources sustainability. ISEs can be used for remote water quality monitoring as sensors of a wireless sensor network [47]. Competing against other types of sensors in this scenario, ISEs have clear advantages: easy to use, low-cost for solution analysis, low power consumption, and almost 100 different detectable species [47, 50, 151].

One of the most common public concerns about mining industries is water contamination, which includes the elevated level of salinity as one of environmental issues [152]. Long-term sensing is required for such environmental monitoring. However, there is lack of maintenance free Cl^- sensors available for water quality monitoring in remote areas. To meet the needs, this work is aiming at developing a low-cost Cl^- sensor prototype, which consists of a solid-state working electrode (WE) with chalcogenide glass as a sensitive membrane and a reference electrode, as well as a flow-cell system, for automatic measurement of Cl^- ion concentration in a liquid medium. The flow-cell system is comprised of a flow cell, peristaltic pumps and valves, electronic circuits, and others.

3.2 Materials and Methods

3.2.1 Glass Synthesis

The glasses were prepared by conventional melt-quenched method. High pure elements (As, S) and compounds (Ag_2S, AgCl, AgBr) were used as precursor materials. These materials were proportional weighted, mixed and vacuum sealed in quartz ampoules. The ampoules were heated up to 920 °C with a heating rate of 3 °C/min in a rocking furnace. After 10 hours in that temperature the ampoules were quenched in water at room temperature to form the desired glasses. The obtained glass samples were then annealed at 100 °C for 4 hours to remove the stress generated during the quenching process. Six different glasses (C#4, C#5, C#6, C#7, C#8 and C#9) were prepared and their compositions are given in table 3.1. More details about the glasses synthesis and its characterization can be found in references [70, 153] and in appendix A.

Glass #	Glass Composition (mol %)
C#4	$(AgCl)_{0.5}(Ag_2S)_{0.325}(As_2S_3)_{0.175}$
C#5	$(AgCl)_{0.5}(Ag_2S)_{0.25}(As_2S_3)_{0.25}$
C#6	$(AgCl)_{0.5}(Ag_2S)_{0.1}(As_2S_3)_{0.4}$
C#7	$(AgBr)_{0.5}(Ag_2S)_{0.325}(As_2S_3)_{0.175}$
C#8	$(AgBr)_{0.5}(Ag_2S)_{0.25}(As_2S_3)_{0.25}$
C#9	$(AgBr)_{0.5}(Ag_2S)_{0.1}(As_2S_3)_{0.4}$

Table 3.1: Glass compositions.

3.2.2 Sensing Electrode Construction and Sensor Prototype

Two batches of sensing electrode were constructed with the prepared glasses as sensitive membranes: Glass Slice Sensing (GSS) electrode and Glass Pellet Sensing (GPS) electrode. In the first case a 1-2 mm thick slice was cut from the glass rod, while in the second case a pellet was made of some amount of a pulverized glass; the slice and the pellet were used as sensor sensitive membrane. Fig. 3.1 shows a schematic diagram of a constructed electrode. The membrane was electrically connected to the external circuit through its back side, while the front sides was left open for exposure to water samples. The membrane and an electrical wire were encased with epoxy.

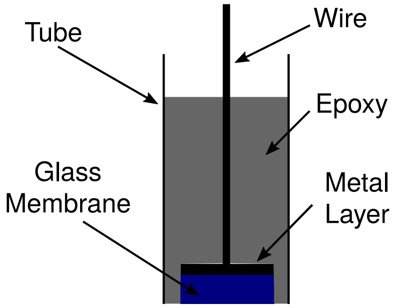

Figure 3.1: A schematic diagram of a solid-contact ISE constructed in this work.

Figure 3.2a presents a schematic diagram of a flow cell with a working electrode and a reference one implanted in. These two electrodes were facing each other with a gap of approximately 2 mm. A solution flowed between the electrodes, and the flux could be adjusted by peristaltic pumps and valves, which were controlled by an electronic circuit and an Arduino microcontroller. Figure 3.2b shows a scheme of the flow-cell system. Figure 3.2c is a picture of the constructed prototype.

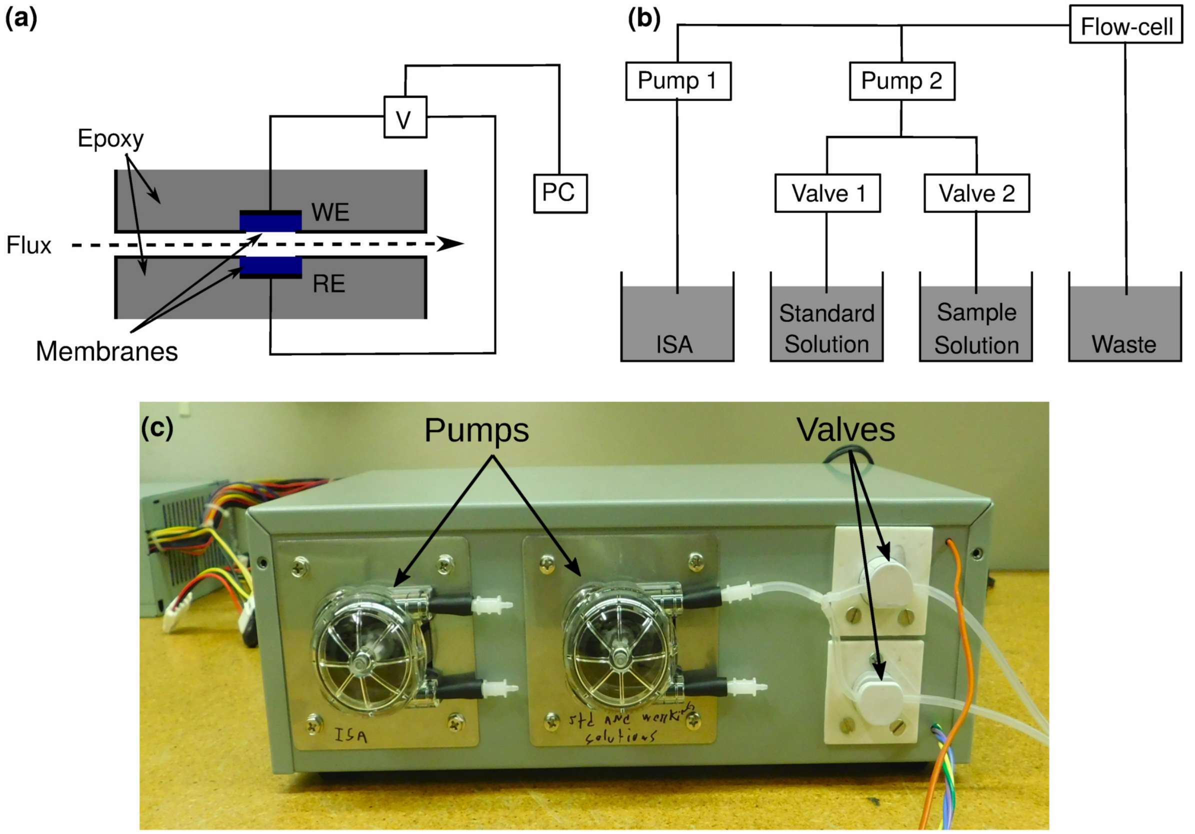

Figure 3.2: (a) a basic schematic diagram of a flow-cell with two electrode implanted in; (b) a schematic of the flow-cell system of the pumps and valves to control the solutions flux through the flow-cell assembly; (c) front picture of the constructed prototype.

The prototype worked in cycles as shown in Fig. 3.3a. As a first step the ISA (Ionic Strength Adjuster) solution was pumped alone through the flow-cell to provide a blank solution reading. After that a standard solution and ISA were pumped together through the flow-cell in a controlled flux, and the potential was read. These two reading points were used to calibrate the WE-RE assembly. Finally the sample and ISA solution were pumped together, and the concentration of Cl^- ion was determined. The ISA was pumped together with the standard and sample solutions to adjust the ionic strength of the final mixture. At the end the

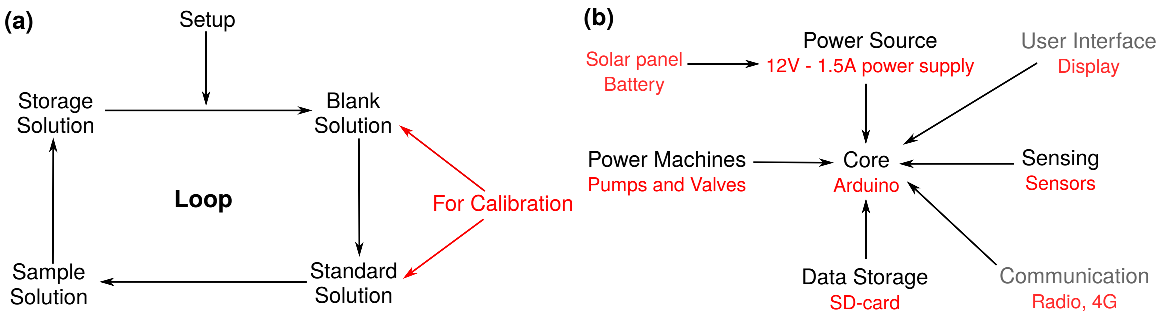

Figure 3.3: (a) A basic schematic of the prototype working cycle; (b) A schematic diagram of modules and possible future implementations.

standard solution was pumped alone to keep the sensors stored in this solution up to the next measurement cycle. The pumps and valves were turned off during the measurements to avoid any streaming potential generated by the flowing liquid and electrical noise the motors could generate. The time of each solution pumping, data acquisition and the wait time between each cycle were adjusted to achieve the best performance. Also, the solution consumption of the prototype in each cycle was very small allowing a plenty of measurement before the need of the replacement of the solutions.

The hardware of the flow-cell system was divided into modules, as shown in Fig. 3.3b, designed for an easy implementation and maintenance. The core module was an Arduino microcontroller. The system was powered by a 12-V DC charger; the power source module for this first generation prototype. In the future, a photovoltaic solar panel or a battery could be used as a power source, and the prototype could be able to work in remoted areas. The collected data were stored in an SD-card, which was the data storage module, for data analysis and data backup. In the future, the data could be transmitted to a data center by a radio communication module, which could be easily implemented to the prototype electronics. The power machine module was the electronics to operate the pumps and valves, and the sensing module was comprised of the WE and RE with an AD convertor.

3.2.3 Sensing Electrode Response Measurement

The responses of the sensing electrodes to Cl^- ions were measured with an NICO 2000 ELIT 8-Channel Ion Analyzer. The response curves were obtained in a two-electrode system immersed in a solution. A commercial BASI Ag/AgCl electrode was used as a RE, and a constructed sensing electrode was used as a WE. The solution was maintained at room temperature (25°C) and was magnetically stirred. The measurement started with the lowest concentrated solution (10^{-6} mol/L NaCl) to the highest one (10^{-1} mol/L NaCl), and the concentration were increased by adding in a preset amount of a high concentrated NaCl solution. To adjust the ionic strength, $NaNO_3$ was added to the analyzed solution (0.1 mol/L). Response slope and limit of detection (LoD) of each sensing electrode were measured accordingly to IUPAC recommendations [80].

3.3 Results and Discussion

3.3.1 GSS Electrodes

Figure 3.4 shows the responses of GSS electrodes to chloride ions. Before the first measurement all the electrodes were stored in 0.1 mol/L NaCl solution for 24 hours for membrane hydration. The responses to the first measurement are represented by black lines and squares. The red lines and circles are the responses 30 days after the first measurement. All the sensing electrodes were kept in 0.1 mol/L NaCl solution during this time. The GSS-C#6 electrode showed no response to chloride ions. The GSS-C#7 electrode exhibited an unexpected behavior after 30 days with an increasing potential when the solution changed from 0.01 to 0.1 mol/L Cl^-.

Table 3.2 summarizes the response slopes and LoDs of the GSS-C#4, GSS-C#5 and GSS-C#8 electrode. GSS-C#8 electrode had a slope two times higher than others and a LoD one order of magnitude higher in the measurement after 30 days. Moreover, it had the lowest drift in potential of approximately 20 mV when compared with other sensing electrodes, which was about 30 mV with GSS-C#5 electrode and 60 mV with GSS-C#4 electrode.

WE	Slope (mV/pCl$^-$)		LoD (mol/L)	
	First Measurement	After 30 days	First Measurement	After 30 days
GSS-C#4	6.9±0.1	8.6±0.2	$10^{-2.12\pm0.03}$	$10^{-2.27\pm0.03}$
GSS-C#5	7.9±0.2	6.1±0.3	$10^{-2.93\pm0.06}$	$10^{-2.46\pm0.09}$
GSS-C#8	13.8±0.5	11.5±0.8	$10^{-2.73\pm0.07}$	$10^{-3.8\pm0.3}$
GPS-C#4	11.6±0.5	5.9±0.3	$10^{-2.67\pm0.07}$	$10^{-2.37\pm0.07}$

Table 3.2: Glass Sensors electrochemical parameters.

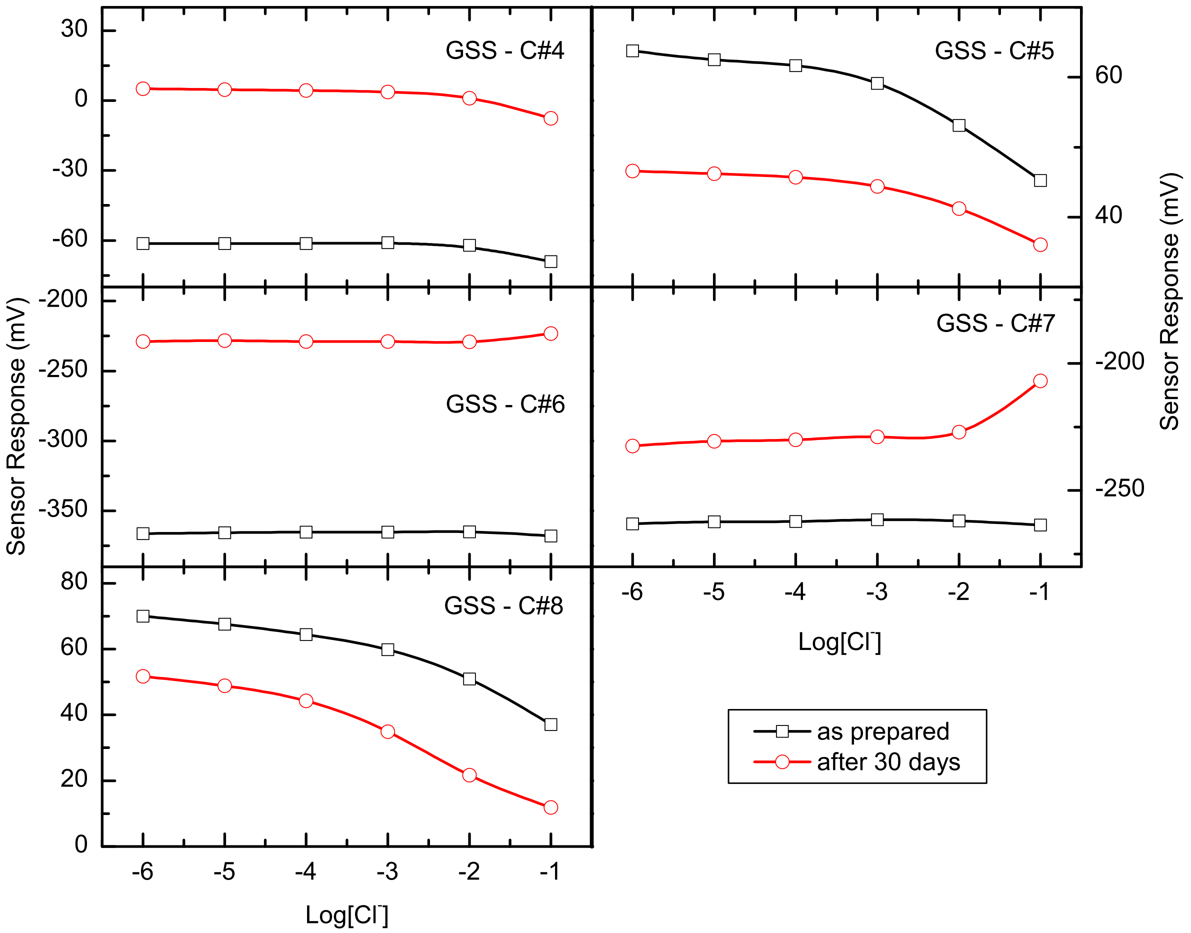

Figure 3.4: The response curves of the GSS electrodes to Cl^- ions. Black squares and lines are the response of the first measurement and red circles and lines are the response of the measurements done 30-days late.

3.3.2 GPS Electrodes

The response curves for the GPS electrodes are showed in Fig. 3.5. Only the GPS-C#4 electrode showed response to chloride ions. All the other electrodes showed no response and a high potential drift between the measurements. As shown in Table 3.2, the slope of GPS-C#4 was reduced by a factor of two after 30 days of the first measurement, though the LoD did not change. This could indicate a possible damage in the sensor membrane during the tests. When comparing GSS and GPS electrodes with the same glass composition of membranes, they exhibited different characteristics, such as response slope and LoD. The differences could

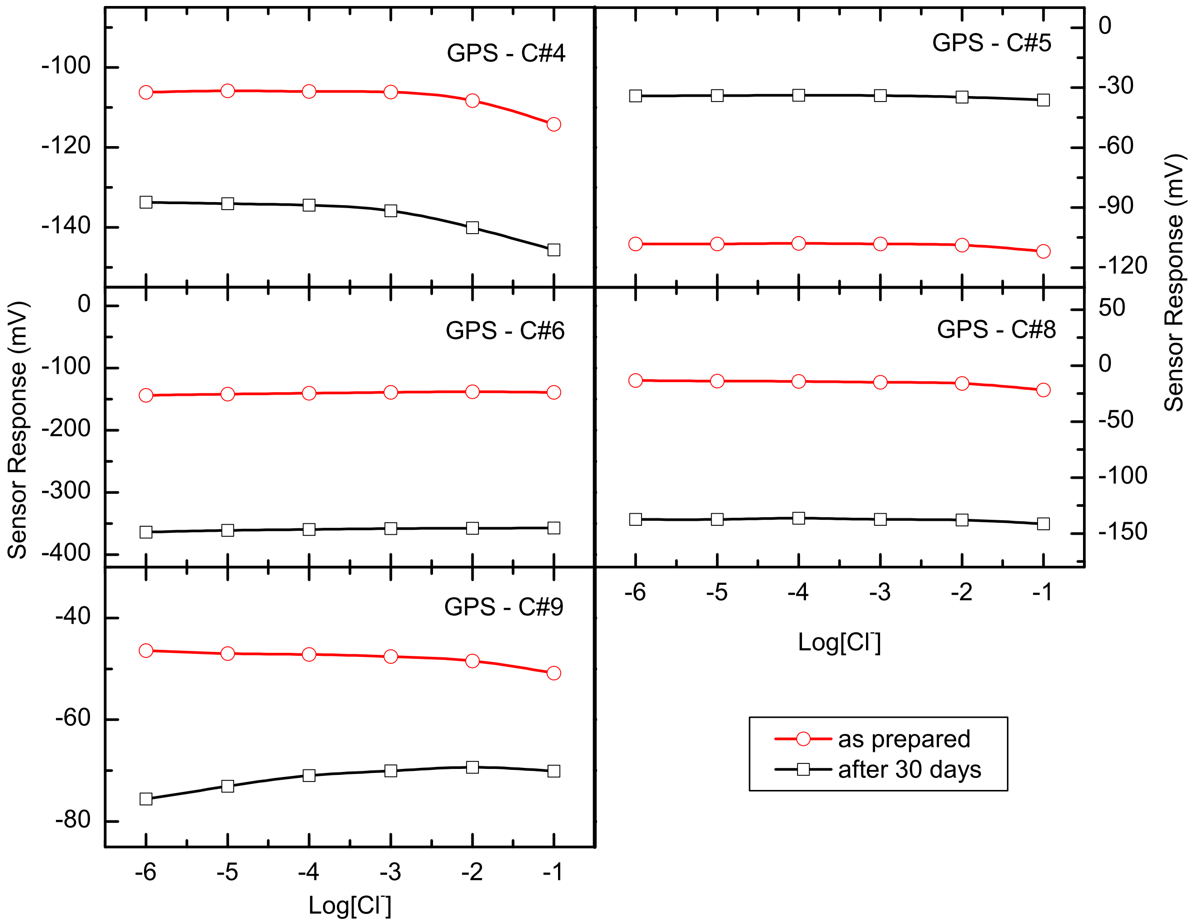

Figure 3.5: The response curves of GPS electrodes to chloride ions. Black squares and lines are the response of the first measurement and red circles and lines are the response of the measurements done 30-days late.

be attributed to different sensor fabrication methods.

3.3.3 Sensor Prototype

As shown in Table 3.2, the GSS-C#8 electrode was more stable compared with the GPS-C#4 one. In the first measurement, both electrodes showed almost the same response slope and LoD. However, after 30 days, the response slope of the GPS-C#4 electrode was much lower than that of the GSS-C#8 electrode. Also, among all the electrodes, GSS-C#8 electrode showed the best slope and was therefore selected as a WE in the sensor prototype. The response

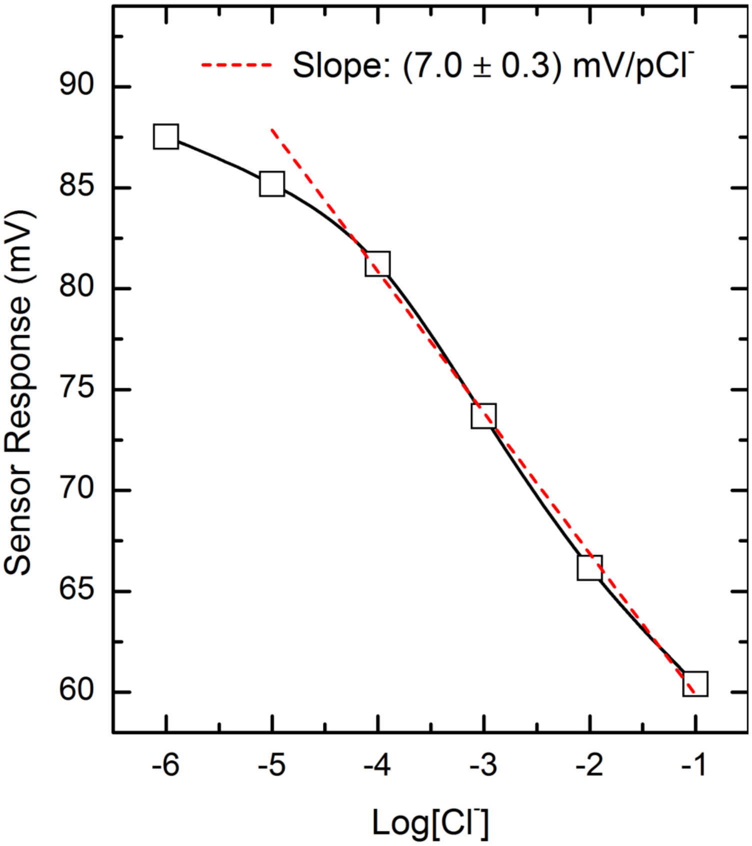

Figure 3.6: The response of the sensor prototype to chloride ion concentration.

of the sensor prototype is shown in Fig. 3.6. Its slope was 7 mV/pCl$^-$ and showed a linear range of up to 4 orders of magnitude as well. The sensor prototype could work in a remote area for the measurement of salinity in mining wastewater.

3.4 Conclusions

We used 6 different chalcogenide glass compositions and 2 different construction methods to develop 10 sensing electrodes, and their responses to chloride ions were evaluated. The response slope and detection limits were determined for the GSS-C#4, GSS-C#5, GSS-C#8 and GPS-C#4 electrodes, which were able to show response to Cl$^-$ ions. Other electrodes showed no response. The GSS-C#8 electrodes showed the best performance and was employed as a working electrode in a constructed sensor prototype, which showed a response with a slope of 7 mV/pCl$^-$ and a linear range of up to 4 orders of magnitude of Cl$^-$ concentration. This prototype could be used for long-term Cl$^-$ monitoring in remote areas.

Chapter 4

Conclusion and future work

We have developed chalcogenide glasses ISEs sensors with sensitivity to Cl^- ions. The research is innovative and opens up new possibilities for applications in this field. Six different chalcogenide glass compositions based on As_2S_3-Ag_2S-AgX (X = Cl or Br) were synthesized and applied as sensitive membranes. The samples produced in this work were the first chalcogenide glasses ever produced in the Laboratory of Glass Synthesis at the Department of Physics of UEM, opening new research directions to our research group. Many sensors were produced at National Research Council Canada and at least three showed sensitivity to Cl^- ions. The best one (GSS-C#8) was paired together with a solid contact reference electrode in a flow-cell as part of a prototype for remote monitoring. The prototype working cycles were configured and the slope of the flow-cell assembly was around 7 mV/pCl^- with a linear range of up to 4 orders of magnitude of Cl^- concentration.

Further development in this area could be achieved with the preparation of glasses with different compositions, and improved synthesis method, allowing the use of ISEs to detect other ions. Nowadays this process is quite delicate because the glass fusion is performed inside evacuated quartz ampoules. In this process, the thermal regimes should be carefully set up to avoid a quick pressure increase inside the ampoule, which can cause its explosion. With the preparation of new glasses, new sensors could be developed and assembled together with the Cl^- device in a sensor array. By applying adequate mathematical methods for the signal processing it is possible to develop an Electronic Tongue device. This would allow the simultaneous detection of a large number of pollutants with the same prototype, increasing thus its precision.

Appendix A

Chalcogenide Glass Synthesis

To prepare the samples listed in Table 3.1 firstly the arsenic trisulphide (As_2S_3) was synthesized from the high pure elements arsenic (As - 99.999 %) and sulphur (S - 99.999 %). They were proportionally weighted, totaling 10 grams of sample, mixed and vacuum ($\approx 10^{-4}$ torr) sealed in quartz ampoules, as can be seen in figure A.1. The ampoule was heated up to 500°C with a heating rate of 2°C/min in a rocking furnace. After 3 hours in that temperature the ampoule was then heated up to 600°C with a heating rate of 1°C/min and stayed for 8 hours. Finally, the temperature was elevated up to 800°C with a heating rate of 1°C/min. After 6-8 hours in that temperature the ampoule was air quenched at room temperature to form the desired glass. Along all the time the rocking furnace was periodically moving to homogenize the chemicals during the fusion process. The rocking furnace can be seen in figure A.2.

Figure A.1: Quartz ampoule.

The As_2S_3 was pulverized and proportionally mixed with the silver sulphide (Ag_2S) and silver chloride (AgCl) compounds (samples C#4, C#5 and C#6) or mixed with the silver sulphide (Ag_2S) and silver bromide (AgBr) compounds (samples C#7, C#8 and C#9), totaling 5

Figure A.2: Rocking furnace.

grams of sample. The reagents were then sealed in quartz ampoules under vacuum ($\approx 10^{-4}$ torr) and the ampoules were heated up to 920°C with a heating rate of 3°C/min in a rocking furnace. After 10 hours in that temperature the ampoules were quenched in water at room temperature to form the desired glasses. The obtained glass samples were then annealed at 100°C for 4 hours to remove the stress generated during the quenching process. Finally the ampoules were carefully broken to remove the glass samples.

Bibliography

[1] Total natural resources rents (% of GDP). `https://data.worldbank.org/indicator/NY.GDP.TOTL.RT.ZS?end=2016&start=1970&view=chart`. [Online; accessed June 8^{th} 2018].

[2] G. Walser. Economic impact of world mining. `http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/33/032/33032900.pdf`. [Online; accessed June 8^{th} 2018].

[3] J. P. S. Silva. Impactos ambientais causados por mineração. *Revista espaço da Sophia*, 1:1–13, 2007.

[4] T. Hezard, G. Durand, M. Rakib, P. Viers, S. Roy, N. Guigues, M. Brach, J.P. Heitzmann, P. Eberle, and F. Bellouard. Metal on-line voltammetric analyzer for on-site monitoring of iron speciation in acid mine drainage waters: Development and characterization. *Electroanalysis*, 21:1401–1410, 2009.

[5] C.N. Mulligan, R.N. Yong, and B.F. Gibbs. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering geology*, 60:193–207, 2001.

[6] A. Jang, Z. Zou, K.K. Lee, C.H. Ahn, and P.L. Bishop. State-of-the-art lab chip sensors for environmental water monitoring. *Measurement Science and Technology*, 22:032001, 2011.

[7] B.S. Caruso, T.J. Cox, R.L. Runkel, M.L. Velleux, K.E. Bencala, D.K. Nordstrom, P.Y. Julien, B.A. Butler, C.N. Alpers, and A. Marion. Metals fate and transport modelling in streams and watersheds: state of the science and USEPA workshop review. *Hydrological processes*, 22:4011–4021, 2008.

[8] D. Fortin, B. Davis, G. Southam, and T.J. Beveridge. Biogeochemical phenomena induced by bacteria within sulfidic mine tailings. *Journal of industrial Microbiology*, 14:178–185, 1995.

[9] Environmental Law Alliance Worldwide. Guidebook for evaluating mining project EIAs. *Environmental Law Alliance Worldwide, Eugene, Oregon*, 2010.

[10] `https://www.samarco.com/rompimento-de-fundao/`. [Online; accessed June 8^{th} 2018].

[11] Pre-feasibility report of ESI water working group. Technical report, Canada Mining Innovation Council, 2014.

[12] P.H. Gleick. Water resources. *Encyclopedia of climate and weather*, 2:817–823, 1996.

[13] P. Gardolinski, G. Hanrahan, E.P. Achterberg, M. Gledhill, A.D. Tappin, W.A. House, and P.J. Worsfold. Comparison of sample storage protocols for the determination of nutrients in natural waters. *Water Research*, 35:3670–3678, 2001.

[14] M. Essi and A. Pradel. Micro-electrode for copper ion detection in solution. *Chalcogenide Lett.*, 8:15–23, 2011.

[15] V.K. Gupta, M.R. Ganjali, P. Norouzi, H. Khani, A. Nayak, and S. Agarwal. Electrochemical analysis of some toxic metals by ion-selective electrodes. *Crit. Rev. Anal. Chem.*, 41:282–313, 2011.

[16] G. Hanrahan, D.G. Patil, and J. Wang. Electrochemical sensors for environmental monitoring: design, development and applications. *Journal of Environmental Monitoring*, 6:657–664, 2004.

[17] A. Bratov, N. Abramova, and A. Ipatov. Recent trends in potentiometric sensor arrays - a review. *Anal. Chim. Acta*, 678:149–159, 2010.

[18] A. Legin, Y. Vlasov, A. Rudnitskaya, and E Bychkov. Cross-sensitivity of chalcogenide glass sensors in solutions of heavy metal ions. *Sens. Actuators B*, 34:456–461, 1996.

[19] V. Vassilev and S. Boychevea. Chemical sensors with chalcogenide glassy membranes. *Talanta*, 67:20–27, 2005.

[20] R. Agrawal and R. Gupta. Superionic solid: composite electrolyte phase–an overview. *J. Mater. Sci.*, 34:1131–1162, 1999.

[21] Y. Mourzina, J. Schubert, W. Zander, A. Legin, Y. Vlasov, H. Lüth, and M.J. Schöning. Development of multisensor systems based on chalcogenide thin film chemical sensors for the simultaneous multicomponent analysis of metal ions in complex solutions. *Electrochim. acta*, 47:251–258, 2001.

[22] Y. Mourzina, T. Yoshinobu, J. Schubert, H. Lüth, H. Iwasaki, and M.J. Schöning. Ion-selective light-addressable potentiometric sensor (LAPS) with chalcogenide thin film prepared by pulsed laser deposition. *Sens. Actuators B*, 80:136–140, 2001.

[23] Y. Vlasov and E. Bychkov. Ion-selective chalcogenide glass electrodes. *Ion-Sel. electrode Rev.*, 9:5–93, 1987.

[24] A. Wróblewski, W.and Dybko, E. Malinowska, and Z. Brzózka. Towards advanced chemical microsensors - an overview. *Talanta*, 63:33–39, 2004.

[25] Y. Vlasov. New solid-state ion-selective electrodes-sensors for chemical analysis of solutions. *Fresenius Z. Anal. Chem.*, 335:92–99, 1989.

[26] A. Legin, A. Rudnitskaya, and Y. Vlasov. Electronic tongues: sensors, systems, applications. *Sens. Update*, 10:143–188, 2002.

[27] Y. Vlasov, A. Legin, A. Rudnitskaya, A. D'Amico, and C. Di Natale. Electronic tongue - new analytical tool for liquid analysis on the basis of non-specific sensors and methods of pattern recognition. *Sens. Actuators B*, 65:235–236, 2000.

[28] A. Legin, A. Rudnitskaya, Y. Vlasov, C. Di Natale, and A. D'Amico. The features of the electronic tongue in comparison with the characteristics of the discrete ion-selective sensors. *Sens. Actuators B*, 58:464–468, 1999.

[29] A. Legin, A. Rudnitskaya, Y. Vlasov, C. Di Natale, E. Mazzone, and A. D'Amico. Application of electronic tongue for quantitative analysis of mineral water and wine. *Electroanalysis*, 11:814–820, 1999.

[30] S. Baldacci, T. Matsuno, K. Toko, R. Stella, and D. De Rossi. Discrimination of wine using taste and smell sensors. *Sens. Mater.*, 10:185–200, 1998.

[31] A. Legin, A. Rudnitskaya, L. Lvova, Y. Vlasov, C. Di Natale, and A. D'amico. Evaluation of Italian wine by the electronic tongue: recognition, quantitative analysis and correlation with human sensory perception. *Anal. Chim. Acta*, 484:33–44, 2003.

[32] A.M.S. Costa, I. Delgadillo, and A. Rudnitskaya. Detection of copper, lead, cadmium and iron in wine using electronic tongue sensor system. *Talanta*, 129:63–71, 2014.

[33] A. Legin, A. Rudnitskaya, Y. Vlasov, C. Di Natale, F. Davide, and A. D'Amico. Tasting of beverages using an electronic tongue. *Sens. Actuators B*, 44:291–296, 1997.

[34] A. Legin, A. Rudnitskaya, Vlasov. Y., C. Di Natale, E. Mazzone, and A. D'Amico. Application of electronic tongue for qualitative and quantitative analysis of complex liquid media. *Sens. Actuators B*, 65:232–234, 2000.

[35] F. Winquist, C. Krantz-Rülcker, P. Wide, and I. Lundström. Monitoring of freshness of milk by an electronic tongue on the basis of voltammetry. *Meas. Sci. Technol.*, 9:1937, 1998.

[36] C. Di Natale, R. Paolesse, A. Macagnano, A. Mantini, A. D'Amico, A. Legin, L. Lvova, A. Rudnitskaya, and Y. Vlasov. Electronic nose and electronic tongue integration for improved classification of clinical and food samples. *Sens. Actuators B*, 64:15–21, 2000.

[37] H. Yamada, Y. Mizota, K. Toko, and T. Doi. Highly sensitive discrimination of taste of milk with homogenization treatment using a taste sensor. *Mater. Sci. Eng. C*, 5:41–45, 1997.

[38] L.A. Dias, A.M. Peres, A.C.A. Veloso, F.S. Reis, M. Vilas-Boas, and A.A.S.C. Machado. An electronic tongue taste evaluation: Identification of goat milk adulteration with bovine milk. *Sens. Actuators B*, 136:209–217, 2009.

[39] F. Winquist, P. Wide, and I. Lundström. An electronic tongue based on voltammetry. *Anal. Chim. Acta*, 357:21–31, 1997.

[40] Y. Sasaki, Y. Kanai, H. Uchida, and T. Katsube. Highly sensitive taste sensor with a new differential LAPS method. *Sens. Actuators B*, 25:819–822, 1995.

[41] K. Beullens, P. Mészáros, S. Vermeir, D. Kirsanov, A. Legin, S. Buysens, N. Cap, B.M. Nicolai, and J. Lammertyn. Analysis of tomato taste using two types of electronic tongues. *Sens. Actuators B*, 131:10–17, 2008.

[42] A. Legin, A. Rudnitskaya, D. Clapham, B. Seleznev, K. Lord, and Y. Vlasov. Electronic tongue for pharmaceutical analytics: quantification of tastes and masking effects. *Anal. Bioanal. Chem.*, 380:36–45, 2004.

[43] K. Woertz, C. Tissen, P. Kleinebudde, and J. Breitkreutz. Taste sensing systems (electronic tongues) for pharmaceutical applications. *Int. J. Pharm.*, 417:256–271, 2011.

[44] J.K. Lorenz, J.P. Reo, O. Hendl, J.H. Worthington, and V.D. Petrossian. Evaluation of a taste sensor instrument (electronic tongue) for use in formulation development. *Int. J. Pharm.*, 367:65–72, 2009.

[45] A. Radu, T. Radu, C. Mcgraw, P. Dillingham, S. Anastasova-Ivanova, and D. Diamond. Ion selective electrodes in environmental analysis. *J. Serb. Chem. Soc.*, 78:1729, 2013.

[46] C. Krantz-Rülcker, M. Stenberg, F. Winquist, and I. Lundström. Electronic tongues for environmental monitoring based on sensor arrays and pattern recognition: a review. *Anal. chim. acta*, 426:217–226, 2001.

[47] C. Zuliani and D. Diamond. Opportunities and challenges of using ion-selective electrodes in environmental monitoring and wearable sensors. *Electrochim. Acta*, 84:29–34, 2012.

[48] S. Zhuiykov. Solid-state sensors monitoring parameters of water quality for the next generation of wireless sensor networks. *Sens. Actuators B*, 161:1–20, 2012.

[49] P. Namour, M. Lepot, and N. Jaffrezic-Renault. Recent trends in monitoring of European water framework directive priority substances using micro-sensors: a 2007-2009 review. *Sensors*, 10:7947–7978, 2010.

[50] M. Cuartero and E. Bakker. Environmental water analysis with membrane electrodes. *Curr. Opin. Electrochem.*, 3:97–105, 2017.

[51] G.A. Crespo. Recent advances in ion-selective membrane electrodes for in situ environmental water analysis. *Electrochim. Acta*, 245:1023–1034, 2017.

[52] N. Pankratova, G.A. Crespo, M.G. Afshar, M.C. Crespi, S. Jeanneret, T. Cherubini, M. Tercier-Waeber, F. Pomati, and E. Bakker. Potentiometric sensing array for monitoring aquatic systems. *Environ. Sci.: Process. Impacts*, 17:906–914, 2015.

[53] T.S. Light. Industrial use and applications of ion selective electrodes. *J. Chem. Educ.*, 74:171–177, 1997.

[54] I. Yaroshenko, D. Kirsanov, L. Kartsova, A. Sidorova, I. Borisova, and A. Legin. Determination of urine ionic composition with potentiometric multisensor system. *Talanta*, 131:556–561, 2015.

[55] L. Van de Velde, E. d'Angremont, and W. Olthuis. Solid contact potassium selective electrodes for biomedical applications-a review. *Talanta*, 160:56–65, 2016.

[56] A. Lewenstam. Routines and challenges in clinical application of electrochemical ion-sensors. *Electroanalysis*, 26:1171–1181, 2014.

[57] W. Gao, S. Emaminejad, H.Y.Y. Nyein, S. Challa, K. Chen, A. Peck, H.M. Fahad, H. Ota, H. Shiraki, D. Kiriya, D. Lien, G.A. Brooks, R.W. Davis, and A. Javey. Fully integrated wearable sensor arrays for multiplexed in situ perspiration analysis. *Nature*, 529:509–514, 2016.

[58] G. Lisak, T. Arnebrant, T. Ruzgas, and J. Bobacka. Textile-based sampling for potentiometric determination of ions. *Anal. Chim. Acta*, 877:71–79, 2015.

[59] A. Cazalé, W. Sant, F. Ginot, J.C. Launay, G. Savourey, F. Revol-Cavalier, J.M. Lagarde, D. Heinry, J. Launay, and P. Temple-Boyer. Physiological stress monitoring using sodium ion potentiometric microsensors for sweat analysis. *Sens. Actuators B*, 225:1–9, 2016.

[60] F. Haber and Z. Klemensiewicz. Über elektrische phasengrenzkräfte. *Z. Phys. Chem.*, 67:385–431, 1909.

[61] Y. Vlasov, A. Legin, and A. Rudnitskaya. Electronic tongue: chemical sensor systems for analysis of aquatic media. *Russ. J. Gen. Chem.*, 78:2532–2544, 2008.

[62] R. Tomova, G. Spasov, R. Stoycheva-Topalova, and A. Buroff. Copper-doped vacuum evaporated chalcogenide layers as sensitive ion-selective membranes. *J. Non-Cryst. Solids*, 266:985–988, 2000.

[63] J. Hu, A. Stein, and P. Bühlmann. Rational design of all-solid-state ion-selective electrodes and reference electrodes. *Tr. Anal. Chem.*, 76:102–114, 2016.

[64] C.T. Baker and J. Trachtenberg. *U. S. Off. Saline Water Res. Dev. Prog. Rep.*, 469:35, 1969.

[65] C.T. Baker and J. Trachtenberg. Ion selective electrochemical sensors-fe^{3+}, cu^{2+}. *J. Electrochem. Soc.*, 118:571–576, 1971.

[66] C.E. Koenig and E.W. Graber. Reinvestigation of a ferric ion-selective electrode based on the chalcogenide glass $Fe_xSe_{60}Ge_{28}Sb_{12}$ (x=1-10). *Electroanalysis*, 7:1090–1094, 1995.

[67] P. Ciosek and W. Wróblewski. Sensor arrays for liquid sensing - electronic tongue systems. *Analyst*, 132:963–978, 2007.

[68] M. del Valle. Sensor arrays and electronic tongue systems. *Int. J. Electrochem*, 2012:1–11, 2012.

[69] T. Yusuke and T. Kiyoshi. Electronic tongues - a review. *IEEE Sens. J.*, 13:3001–3011, 2013.

[70] L. Li, H. Yin, Y. Wang, J. Zheng, H. Zeng, and G. Chen. A chalcohalide glass/alloy based Ag^+ ion-selective electrode with nanomolar detection limit. *Sci. Rep.*, 7:16752, 2017.

[71] S. Boycheva, V. Vassilev, and Z. Ivanova. On the glass formation in the semiconducting-Se-ZnTe, Se-Se-ZnSe and -ZnTe-ZnSe systems. *J. Phys. D*, 32:529–532, 1999.

[72] Z. Ivanova, E. Cernoskova, V. Vassilev, and S. Boycheva. Thermomechanical and structural characterization of $GeSe_2$-Sb_2Se_3-ZnSe glasses. *Mater. Lett.*, 57:1025–1028, 2003.

[73] A. Piarristeguy, J.M. Conde Garrido, M.A. Ureña, M. Fontana, and B. Arcondo. Conductivity percolation transition of $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses. *J. Non-Cryst. Solids*, 353:3314–3317, 2007.

[74] J.M. Conde Garrido, M.A. Ureña, and B. Arcondo. Ion selective electrodes based on chalcogenide glasses. *J. Alloys Compd.*, 495:356–359, 2010.

[75] J. Bobacka, A. Ivaska, and A. Lewenstam. Potentiometric ion sensors. *Chem. Rev.*, 108:329–351, 2008.

[76] E. Guggenheim. The conceptions of electrical potential difference between two phases and the individual activities of ions. *J. Phys. Chem.*, 33:842–849, 1929.

[77] B. Nicolsky. Theory of the glass electrode. *Acta Physicochim. URSS*, 7:597, 1937.

[78] F. Conti and G. Eisenman. The non-steady-state membrane potential of ion exchangers with fixed sites. *Biophys. J.*, 5:247–256, 1965.

[79] F. Conti and G. Eisenman. The steady-state properties of ion exchange membranes with fixed sites. *Biophys. J.*, 5:511–530, 1965.

[80] R.P. Buck and E. Lindner. Recommendations for nomenclature of ionselective electrodes (iupac recommendations 1994). *Pure Appl. Chem.*, 66:2527–2536, 1994.

[81] Y. Vlasov, Y. Ermolenko, A. Legin, A. Rudnitskaya, and V. Kolodnikov. Chemical sensors and their systems. *J. Anal. Chem.*, 65:880–898, 2010.

[82] Y. Vlasov and E. Bychkov. Sodium ion-selective chalcogenide glass electrodes. *Anal. Lett.*, 22:1125–1144, 1989.

[83] Y. Vlasov, E. Bychkov, and A. Medvedev. Copper ion-selective chalcogenide glass electrodes: analytical characteristics and sensing mechanism. *Anal. Chim. Acta*, 185:137–158, 1986.

[84] M. Maric, M. Sohail, and R. De Marco. A near edge x-ray absorption fine structure (NEXAFS) study of the response mechanism of the iron (III) chalcogenide glass membrane ion-selective electrode. *Electrochem. Commun.*, 41:27–30, 2014.

[85] Y. Vlasov, E. Bychkov, and B. Seleznev. Silver ion sensors based on Ag-As-Se-Te glasses I. Ionic sensitivity and bulk membrane transport. *Sens. Actuators B*, 2:23–31, 1990.

[86] Y. Vlasov, A. Legin, and D. Baidakov. Chalcogenide films prepared by chemical deposition. *Zh. Prikl. Khim.*, 69:1436–1441, 1996.

[87] T. Seiyama. *Chemical Sensor Technology*. Elsevier Science Ltd, 1989.

[88] E. Bychkov, M. Bruns, H. Klewe-Nebenius, G. Pfennig, W. Hofmman, and H. Ache. Cu^{2+}-selective thin films for chemical microsensors based on sputtered copper-arsenic-selenium glass. *Sens. Actuators B*, 25:733–736, 1995.

[89] M.J. Schöning, Y. Mourzina, J. Shubert, W. Zander, A. Legin, Y. Vlasov, and H. Lüth. Pulsed laser deposition - an innovative technique for preparing inorganic thin films. *Electroanalysis*, 13:727–732, 2001.

[90] M. Frumar, B. Frumarova, P. Nemec, T. Wagner, J. Jedelsky, and M. Hrdlicka. Thin chalcogenide films prepared by pulsed laser deposition - new amorphous materials applicable in optoelectronics and chemical sensors. *J. Non-Cryst Solids*, 352:544–561, 2006.

[91] A. Guessous, J. Sarradin, P. Papet, K. Elkacemi, S. Belcadi, A. Pradel, and M. Ribes. Chemical microsensors based on chalcogenide glasses for the detection of cadmium ions in solution. *Sens. Actuators B*, 53:13–18, 1998.

[92] M.J. Schöning and J.P. Kloock. About 20 years of silicon-based thin-film sensors with chalcogenide glass materials for heavy metal analysis: Technological aspects of fabrication and miniaturization. *Electroanalysis*, 19:2029–2038, 2007.

[93] Y. Vlasov. Sensor R&D in the former soviet union. *Sens. Actuators B*, 15:6–15, 1993.

[94] J.M. Conde Garrido, J. Silveyra, and M. Ureña. Multi-ion and pH sensitivity of AgGeSe ion selective electrodes. *J. Phys. Chem. Sol.*, 89:115–119, 2016.

[95] Y. Vlasov, B. Bychkov, B. Seleznev, and M. Miloshova. Ion-implanted chalcogenide glasses as membrane materials for solid-state chemical sensors. *Sens. Actuators B*, 7:501–504, 1992.

[96] Y. Vlasov, L.N. Moskvin, E. Bychkov, and D.V. Golikov. Silver bromide based chalcogenide glassy-crystalline ion-selective electrodes. *Analyst*, 114:185–190, 1989.

[97] N. Tohge and M. Tanaka. Chalcogenide glass electrodes sensitive to heavy metal ions. *J. Non-Cryst. Solids*, 80:550–556, 1986.

[98] V. Vassilev, M. Radonova, and S. Boycheva. Cd (II)-ion-selective electrode based on chalcogenide glasses. *J. Non-Cryst. Solids*, 355:2365–2369, 2009.

[99] M. Miloshova, M. Kassem, and E. Bychkov. Chalcogenide glass chemical sensor for cadmium detection in industrial environment. *ECS Trans.*, 50:357–362, 2013.

[100] M. Essi. Chemical sensor for the determination of toxic species in solution. *Chalcogenide Lett.*, 8:25–31, 2011.

[101] M. Essi. Characterization of cadmium (II) selective electrode based on chalcogenide glass. *Chalcogenide Lett.*, 8:341–347, 2011.

[102] A. Legin, E. Bychkov, and Y. Vlasov. Analytical applications of chalcogenide glass chemical sensors in environmental monitoring and process control. *Sens. Actuators B*, 24:309–311, 1995.

[103] R. Jasinki and J. Trachtenberg. A chalcogenide glass electrode sensitive to cupric ions. *J. Electrochem. Soc.*, 121:363–370, 1974.

[104] A. Owen. Chalcogenide glasses as ion-selective materials for solid-state electrochemical sensors. *J. Non-Cryst. Sol.*, 35:999–1004, 1980.

[105] M. Essi. Chalcogenide sensors for copper (II) detection in polluted waters. *Chalcogenide Lett.*, 8:103–110, 2011.

[106] S.P. Awasthi, N.S. Shenoy, and T.P. Radhakrishnan. Copper ion-selective electrode based on a chalcogenide glass membrane. *Analyst*, 119:1361–1362, 1994.

[107] C. Cali, D. Foix, G. Taillades, E. Siebert, D. Gonbeau, A. Pradel, and M. Ribes. Copper (II) selective electrode based on chalcogenide materials: study of the membrane/solution interface with electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy. *Mater. Sci. Eng. C*, 21:3–8, 2002.

[108] Y. Vlasov, E. Bychkov, and A. Legin. Chalcogenide glass chemical sensors: research and analytical applications. *Talanta*, 41:1059–1063, 1994.

[109] R. Jasinki and J. Trachtenberg. Evaluation of the ferric ion sensitive chalcogenide glass electrode. *J. Electrochem. Soc.*, 120:1169–1174, 1973.

[110] Y. Vlasov, Y. Mourzina, A. Legin, Y. Ermolenko, J. Schubert, M.J. Schöning, and H. Lüth. Solid-state thin-film sensors based on chalcogenide materials obtained by planar technology and pulsed laser deposition. *Russ. J. Appl. Chem.*, 75:351–356, 2002.

[111] C Bohnke, J. Malugani, A. Saida, and G. Robert. Conductivite electrique et selectivite ionique des verres $AgPO_3$-MI_2 et $AgAsS_2$-MI_2 avec M=Pb,Hg. *Electrochim. Acta*, 26:1137–1142, 1981.

[112] V. Vassilev, K. Tomova, and S. Boycheva. Pb (II)-ion-selective electrodes based on chalcogenide glasses. *J. Non-Cryst. Sol.*, 353:2779–2784, 2007.

[113] M. Miloshova, B. Seleznev, and E. Bychkov. Chalcogenide glass chemical sensors for determination of thallium in natural and wastewater. *Sens. Actuators B*, 19:373–375, 1994.

[114] D. Kalyagin, I. Ermolenko, Y.and Alekseev, E. Bychkov, S. Krotov, N. Melnikova, I. Murin, and Y. Vlasov. Ag_2S-As_2S_3-TlI chalcogenide glasses as perspective material for solid-state chemical sensors. *Russ. J. Appl. Chem.*, 87:1044–1048, 2014.

[115] Y. Ermolenko, D. Kalyagin, I. Alekseev, E. Bychkov, V. Kolodnikov, N. Melnikova, I. Murin, Y. Mourzina, and Y. Vlasov. New membrane material for thallium (I)-selective sensors based on arsenic sulfide glasses. *Sens. Actuators B*, 207:940–944, 2015.

[116] V. Vassilev, S. Hadjinikolova, and S. Boycheva. Zn (II)-ion-selective electrodes based on $GeSe_2$-Sb_2Se_3-ZnSe glasses. *Sens. Actuators B*, 106:401–406, 2005.

[117] S. Boycheva, V. Vassilev, and Z. Ivanova. A Zn(II) ion-selective electrode based on chalcogenide As_2Se_3-Sb_2Se_3-ZnSe and $GeSe_2$-ZnSeâĂŞZnTe glasses. *J. Appl. Electrochem.*, 32:281–285, 2002.

[118] R. Tomova, J. Assa, R. Stoycheva-Topalova, and A. Buroff. As_2S_3 and AgI thin layers as ion sensitive membranes. *J. Non-Cryst. Sol.*, 260:195–198, 1999.

[119] R. Tomova, R. Stoycheva-Topalova, and A. Buroff. Ion-selective membranes based on chalcogenide glasses. *J. Optoeletron. Adv. Mater.*, 7:1399–1406, 2005.

[120] M.J. Schöening, J. Schubert, W. Zander, M. Mueller-Veggian, A. Legin, Y. Vlasov, P. Kordos, and H. Lüth. Pulsed-laser deposition as a novel preparation technique for chemical microsensors. In *Chemical Microsensors and Applications II*, volume 3857, pages 124–135. International Society for Optics and Photonics, 1999.

[121] J. Schubert, M.J. Schöning, C. Schmidt, M. Siegert, W. Zander, P. Kordos, H. Lüth, A. Legin, Y. Mourzina, and B. Seleznev. Chalcogenide-based thin film sensors prepared by pulsed laser deposition technique. *Appl. Phys. A*, 69:S803–S805, 1999.

[122] M.J. Schöning, C. Schmidt, J. Schubert, W. Zander, S. Mesters, P. Kordos, H. Lüth, A. Legin, B. Seleznev, and Y. Vlasov. Thin film sensors on the basis of chalcogenide glass materials prepared by pulsed laser deposition technique. *Sens. Actuators B*, 68:254–259, 2000.

[123] H. Spelthahn, D. Kirsanov, A. Legin, T. Osterrath, J. Schubert, W. Zander, and M.J. Schöning. Development of a thin-film sensor array for analytical monitoring of heavy metals in aqueous solutions. *Physica Status Solidi A*, 209:885–891, 2012.

[124] J. Salardenne, J. Morcos, M. Ait Allal, and J. Portier. New ISFET sensitive membranes. *Sens. Actuators B*, 1:385–389, 1990.

[125] J. Schubert, M.J. Schöning, Y. Mourzina, A. Legin, Y. Vlasov, W. Zander, and H. Lüth. Multicomponent thin films for electrochemical sensor applications prepared by pulsed laser deposition. *Sens. Actuators B*, 76:327–330, 2001.

[126] J.P. Kloock, Y. Mourzina, J. Schubert, and M.J. Schöning. A first step towards a microfabricated thin-film sensor array on the basis of chalcogenide glass materials. *Sensors*, 2:356–365, 2002.

[127] J.P. Kloock, Y. Mourzina, Y. Ermolenko, T. Doll, J. Schuberth, and M.J. Schöning. Inorganic thin-film sensor membranes with PLD-prepared chalcogenide glasses: challenges and implementation. *Sensors*, 4:156–162, 2004.

[128] J.P. Kloock, L. Moreno, A. Bratov, S. Huachupoma, J. Xu, T. Wagner, T. Yoshinobu, Y. Ermolenko, Y. Vlasov, and M.J. Schöning. PLD-prepared cadmium sensors based on chalcogenide glasses - ISFET, LAPS and μISE semiconductor structures. *Sens. Actuators B*, 118:149–155, 2006.

[129] Y. Mourzina, M.J. Schöning, J. Schubert, W. Zander, A. Legin, Y. Vlasov, and H. Lüth. Copper, cadmium and thallium thin film sensors based on chalcogenide glasses. *Anal. Chim. Acta*, 433:103–110, 2001.

[130] M. Turek, W. Heiden, S. Guo, A. Riesen, J. Schubert, W. Zander, P. Krüger, M. Keusgen, and M.J. Schöning. Simultaneous detection of cyanide and heavy metals for environmental analysis by means of μISEs. *Physica Status Solidi A*, 207:817–823, 2010.

[131] Y. Tarantov, Y. Vlasov, Y. Mesentsev, and Y. Averyanov. Physical and chemical processes in ISFETs with chalcogenide membranes. *Sens. Actuators B*, 1:390–394, 1990.

[132] M. Bruns, H. Klewe-Nebenius, G. Pfennig, E. Bychkov, and H. Ache. Production and surface analytical characterization of various chalcogenide glass thin films for analytical microdevices. *Surf. Coat. Technol.*, 97:707–712, 1997.

[133] G. Taillades, O. Valls, A. Bratov, C. Dominguez, A. Pradel, and M. Ribes. ISE and ISFET microsensors based on a sensitive chalcogenide glass for copper ion detection in solution. *Sens. Actuatros B*, 59:123–127, 1999.

[134] A. Pradel, O. Valls, C. Cali, G. Taillades, A. Bratov, C. Dominguez, and M. Ribes. Chalcogenide glasses as sensitive membranes for the detection of ions in solution. *J. Optoecletron. Adv. Mater.*, 3:641–648, 2001.

[135] J. Hüller, M. Pham, T. Vopel, and J. Albrecht. Ion-beam modification of ISFET membranes for copper ion detection. *Sens. Actuators B*, 24:225–227, 1995.

[136] R. Tomova, G. Spasov, R. Stoycheva-Topalova, and A. Buroff. Cu-ion-selective membranes based on chalcogenide glasses. *Sens. Actuators B*, 103:277–283, 2004.

[137] A. Guessous, P. Papet, J. Sarradin, and M. Ribes. Thin films of chalcogenide glass as sensitive membranes for the detection of mercuric ions in solution. *Sens. Actuators B*, 24:296–299, 1995.

[138] M. Miloshova, E. Bychkov, V. Tsegelnik, V. Strykanov, H. Klewe-Nebenius, M. Bruns, W. Hoffmann, P. Papet, J. Sarradin, and A. Pradel. Tracer and surface spectroscopy studies of sensitivity mechanism of mercury ion chalcogenide glass sensors. *Sens. Actuators B*, 57:171–178, 1999.

[139] R. Tomova, R. Stoycheva-Topalova, and A. Buroff. Thin-film sensors based on evaporated chalcogenide glasses. *J. Mater. Sci.: Mater. Electron.*, 14:843–845, 2003.

[140] Y. Mourzina, M.J. Schöning, J. Schubert, W. Zander, A. Legin, Y. Vlasov, P. Kordos, and H. Lüth. A new thin-film Pb microsensor based on chalcogenide glasses. *Sens. Actuators B*, 71:13–18, 2000.

[141] Y. Vlasov, E. Bychkov, and A. Legin. Mechanism studies on lead ion-selective chalcogenide glass sensors. *Sens. Actuators B*, 10:55–60, 1992.

[142] Y. Vlasov, E. Bychkov, B. Seleznev, E. Zhilinskaya, and I. Licholit. Ni-implanted vitreous electrolyte $AgAsS_2$: ECR, ionic and electronic conductivity. *Solid state ionics*, 45:1–7, 1991.

[143] A. Legin, E. Bychkov, and Y. Vlasov. Thin-layer chemical sensors based on chemically deposited and modified chalcogenide glasses. *Sens. Actuators B*, 15:184–187, 1993.

[144] M. Inês G.S. Almeida, R.W. Cattrall, and S.D. Kolev. Polymer inclusion membranes (PIMs) in chemical analysis - a review. *Anal. Chim. Acta*, 987:1–14, 2017.

[145] E. Bakker and E. Pretsch. Potentiometric sensors for trace-level analysis. *Tr. Anal. Chem.*, 24:199–207, 2005.

[146] I.A. Pechenkina and K.N. Mikhelson. Materials for the ionophore-based membranes for ion-selective electrodes: problems and achievements. *Russ. J. Electrochem.*, 51:93–102, 2015.

[147] R.D. Johnson and L.G. Bachas. Ionophore-based ion-selective potentiometric and optical sensors. *Anal. Bioanal. Chem.*, 376:328–341, 2003.

[148] K.N. Mikhelson. *Ion-selective electrodes*, volume 81. Springer Science & Business Media, 2013.

[149] J.M. Conde Garrido, F. Macoretta, M.A. Ureña, and B. Arcondo. Application of Ag-Ge-Se based chalcogenide glasses on ion-selective electrodes. *J. Non-Cryst. Solids*, 355:2079–2082, 2009.

[150] L.M. Moretto and K. Kalcher. *Environmental Analysis by Electrochemical Sensors and Biosensors*, volume 2. Springer Science & Business Media, 2015.

[151] R. De Marco, G. Clarke, and B. Pejcic. Ion-selective electrode potentiometry in environmental analysis. *Electroanalysis*, 19:1987–2001, 2007.

[152] M. Václavíková, K. Vitale, G.P. Gallios, and L. Ivanicová. *Water treatment technologies for the removal of high-toxity pollutants*. Springer, 2009.

[153] L. Li, H. Yin, Y. Wang, J. Zheng, H. Zeng, and G. Chen. Study on crystallization behavior of novel silver chloride based chalcogenide glasses. *J. Alloys Compd.*, 706:48–55, 2017.