

Method Development for Estimation of Lithium



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By

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DEDICATION

TO

PROPHET MUHAMMAD (Peace Be Upon Him) and his Progeny

Blessing on whole Mankind

MY LOVING PARENTS

Whom

Prayers, love and guidance lightens my whole life

and are sources of inspiration for me

&

MY FAMILY

Without whom my life is incomplete

ACKNOWLEDGMENTS

In the name of Allah, the most Gracious, the most Merciful.

All praises thanks for **Allah Almighty**, who bestowed us with the heart to feel and brain to think, so that we know, what we don't indeed. He is the best knower, the wisest, peace and blessing of Allah be upon His **Holy Prophet Hazrat Muhammad (S.A.W.W) and his Progeny** which are the real role model for the mankind.

I feel highly indebted to my intellectual supervisor **Dr. Shaukat Ali** for his kind and affectionate attitude, guidance and keen interest throughout my research work. His support has been instrumental in my success, I appreciate his mentorship and the opportunity he has provided. Thank you for believing in me and pushing me to excel. His leadership has made significant impact on our teams' achievements. And I'm thankful for the trust he has placed in me and for his continued support.

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I dedicate my research work to my beloved and respectful father **Syed Mazhar Ali Shah** for his countless prayers, salutary advices and emboldening attitude that kept my spirit alive. I am unable to show my gratitude to my loving and encouraging **Mother, Brothers and Sister and my whole family**. They are symbol of love for me, prayers, support, and encouragement provided by my whole family.

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LIST OF ABBREVIATIONS

Li	Lithium
NiMH	Nickel metal hybrid
LIBs	Lithium-ion batteries
PEG	Polyethylene glycol
PAN	Polyacrylonitrile
XRD	X-ray Diffraction
AAS	Atomic Absorption Spectroscopy
GFAAS	Graphite Furnace AAS
PCGT	Pyrolytic-coated graphite tube
PTGT	Platform-type graphite tube
HDGT	High-density graphite tube
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LA-ICP-MS	Laser Ablation ICP-MS
ICCD	Intensified coupled charge device
LSPR	Localized Surface Plasmon Resonance
UV-Vis	Ultraviolet-visible
FTIR	Fourier transform infrared

DMSO	Dimethyl sulfoxide
ppm	Parts per million
ppb	Parts per billion
RSD	Relative standard deviation
TBP	Tributyl phosphate
LBH-AuNPs	Lithium borohydride gold nanoparticles
FAB	Fast atomic bombardment
AFM	Atomic force microscopy
SEM	Scanning electron microscopy
SEC	Spectroelectrochemical
TEGDME	Tetra-ethylene glycol dimethyl ether
DOD	Depth of discharge
MOF	Metal–organic framework
DFT	Density functional theory
LOD	Limit of detection
LOQ	Limit of Quantification
CV	Cyclic voltammetry
EDTA	Ethylenediaminetetraacetic acid
ICH	International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use

ABSTRACT

Over the past 10 years, there has been a notable growth in the demand for lithium (Li). The increasing use of Li in batteries, ceramics, and other chemical applications points to a growing need for Li in the near future. So there always need of new, cheaper, easy and robotic method development for the estimation of Li in different matrices. For the estimation of Li, several analytical methods, both traditional and contemporary, have been devised. These techniques are expensive and these may be available for only one or couple of matrices and have limitations. The goal of current research is to provide a novel, more dependable, robotic, inexpensive, and quick technique for determining Li from various sources. In current research UV/VIS Spectrophotometer was used for the spectroscopic determination of Li. Color was developed by reacting Li_2CO_3 with 3,4,5-Trihydroxybenzoic acid (Gallic acid). Method was developed by making different concentration ratios of Li_2CO_3 and Gallic acid. When the sample was subjected to a UV scan, its maximum absorbance was measured at 620 nm, which is the λ_{max} of the complex. Different method validation parameters including complex stability, precision, accuracy, LOQ, LOD and finally a calibration curve similarly, robustness parameters like effect of change in concentration, effect of change in pH and effect of change in temperature was performed according to ICH guidelines. A cheap, portable, robotic, fast and more reliable method was developed by using UV/Vis spectrophotometer. This method can be used for the estimation of Li in different samples.

CHAPTER 1

INTRODUCTION

The demand for Li has significantly increased during the last ten years. This surge is primarily attributed to the crucial role that Li plays in the development of various industrial products, with a particular emphasis on batteries used in electronic devices and electric vehicles. The expanding use of Li in these applications highlights its importance in powering modern technology and sustainable transportation [1]. New technologies often bring fresh and innovative approaches to how materials and energy are produced and used. These technologies are developing at an increasingly rapid pace, leading to the production of products that frequently involve the usage of rare and nonrenewable elements. Metals are mostly used in different applications such as panels, motors electric cars and in permanent magnets in maglev trains. Current research highlights the importance of materials in various cutting-edge applications [2]. As metals are used in very minute quantities but there has been a considerable flow in demand. That's why, it is very important to examine both their availability and the possibility of recovery [3, 4]. It is impossible to recover some rare metals from there concentrations so these metals have their limited availability in the nature [5].

The recovery of neodymium is impossible from its alloys because of very complicated process of making neodymium-iron-boron (Nd-Fe-B) magnets for computer hard drives, the reason is that, neodymium is first combined with oxygen to make a very stable compound. As a result, most neodymium is lost as waste, which creates problems for resource preservation and reducing the influence on the environment. For the management of electronic waste alternate materials and new recycling methods are being developed [6]. Due to fast advancements in technologies the need of the specific metals grows in considerable demand. But due to low availability of these metals these technologies do not use for a long time. The demand of metals increases due to advancements in technologies. For this effective resource management and long-lasting technologies are very necessary.

In spite of high shortage supply and potential substitutes for specific applications, Li is considered as economically important metal [7, 8]. Its primary economic significance arises from its utilization as a raw material for batteries

intended for portable electronic devices like laptops and cell phones. It also functions as a vital part of electric cars [9]. Li is a lightweight metal with great reduction capabilities that improves batteries with very high energy densities (usually more than 160 Wh/kg and 400 Wh/L). This represents an extensive improvement, surpassing conventional batteries by approximately 50% [10]. Li was first used as an industrial catalyst, an ingredient in glass formulations, and a hardening agent in products containing lead alloys. Presently, its most rapidly expanding market lies in secondary batteries, particularly LIBs. The surge in demand, because of electronic devices and electric vehicles, highlights the crucial role Li plays in modern technology. This shift signifies the evolution of Li from its earlier industrial uses to a key component in advanced energy storage systems, illustrating its changing role and significance in the market [11]. Between 2000 and 2007, the manufacturing of Li secondary batteries increased by almost 25% [12]. In early electric car models, for instance, nickel metal hybrid (NiMH) batteries are being replaced with Li-ion secondary batteries. This transition is driven by the superior energy densities of LIBs, leading to enhanced overall performance. The mass production of electric vehicles commenced around 2011–2012 and is projected to steadily increase by 3% to 10% from 2020 to 2025. This trend highlights the growing dominance of Li-ion technology in the electric vehicle sector, indicating a positive shift towards more efficient and compact energy storage solutions within the automotive industry [13].

Pegmatites are igneous rocks with a coarse grain size that are created when magma crystallizes at significant depths in the Earth's crust. At the moment, Greenbushes, Australia is one of the top countries for mining these pegmatite resources, which constitute the basis for Li extraction [14].

Shigar Valley serves as a route to second highest peak K-2 and is situated in Baltistan, Pakistan, some 32 kilometers northeast of Skardu (Figure 1.1). This valley is well-known for its jewels as well as its part in documenting regional tectonics. Shigar Valley is traversed by the Northern suture, which joins the Asian continent with the Kohistan-Ladakh Island arc. The valley is home to various types of pegmatites, some containing gemstones. To understand these formations better, it's essential to carefully map and study them based on field observations and petrographic studies.

Shigar Valley stands out not only for its gem treasures but also for its potential in helping to learn more about regional tectonics and geological processes [15].

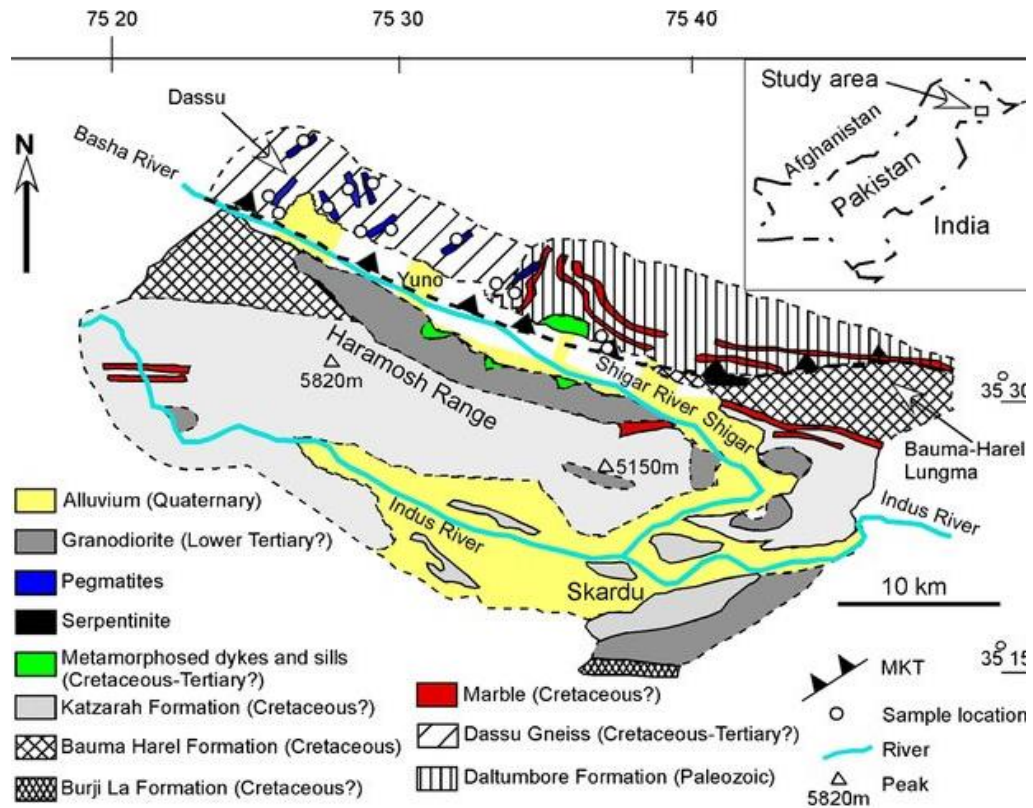


Figure 1.1 Location map of the Shigar valley, northern areas of Pakistan [16].

The chief sources of Li are brine lakes (also known as salars) and pegmatites. The Salars with the highest concentration are of Chile, Bolivia and Argentina. Salars of US and the Tibetan Plateau have minor concentration of Li [17]. Pegmatites are rocklike structures formed by the solidification of magma underground. Li is currently being extracted from pegmatites in Australia [14]. In addition, Li can be naturally extracted from clay and seawater [17, 18]. Li can be extracted from clay by various methods, such as lime-stone gypsum roasting, selective chlorination and leaching process [11]. Ion exchange resins, solvent extraction, co-precipitation, membrane processes, and absorption are some of the methods that may extract around 20% of Li from saltwater [19].

Process of obtaining Li from brine involves the lime soda evaporation method, resulting in Li carbonate (Li_2CO_3). This technique includes evaporating saline water for 1 to 1.5 year in ponds, utilizing solar energy. Significantly, Li is produced from

dry lakes by using solar energy which is the most economical and competitive method among various approaches [11]. Li is present in approximately 145 minerals, but it is primarily extracted from minerals like spodumene, lepidolite, petalite, amblygonite and eucryptite. Of them, spodumene is Li ore which contain about 8% pure Li oxide in its natural form. However, commercial ores typically have 1–3% Li oxide content. The concrete of spodumene is used to produce Li_2CO_3 and then Li metal. While Li_2CO_3 is economically preferred due to higher Li content, specific applications, like pharmaceuticals and plastics, still used to obtained Li metal. The selection depends on specific requirements within different industries [1]. Because of its various applications Li is produced in large quantities to meet the demand for production of Li compounds (Figure 1.2).

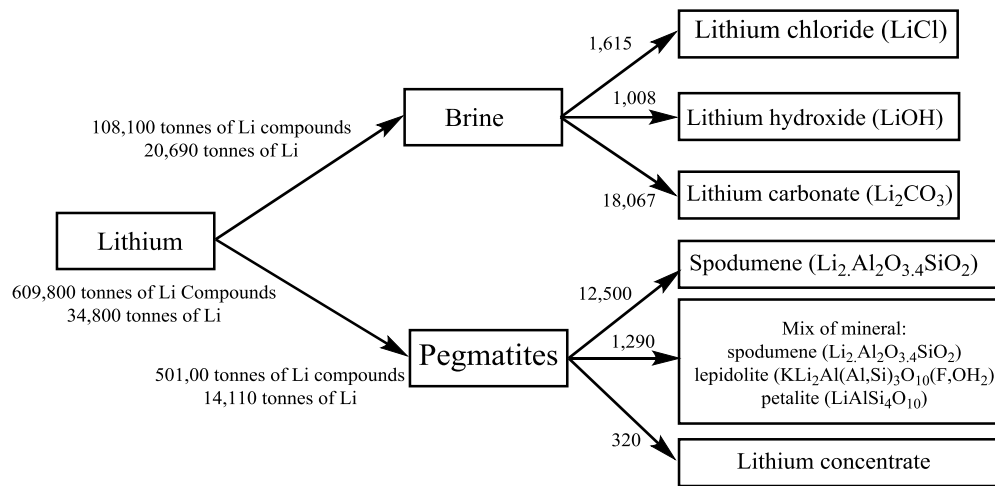


Figure 1.2 Li production from various sources in 2011 (in tons) [20].

Li_2CO_3 acts as the fundamental compound for the production of various Li-derived compounds, playing a crucial role in the creation of components like cathodes and electrolyte material used in Li-ion batteries (LIBs) [21]. Brine and spodumene are major sources for the Li production, resulting in Li_2CO_3 . This compound can be employed as directly or subjected to additional processing as needed [20, 22]. Industries like ceramics and glass used spodumene and Li_2CO_3 to decrease boiling points and improve resistance to thermal expansion. Li_2CO_3 undergoes additional processing to produce LiOH and LiCl. LiOH is used to make CO_2 absorber and Li_3PO_4 , LiOCl, Li_2O , Li_2O_2 and others. These derivatives serve various purposes, including catalysts, sanitation, neutron absorption and for making solutions for developing of photograph. LiCl is used in batteries as electrolyte. After further

processing, LiCl yields Li metal, LiH, and Li₃N, which are utilized in alloys, high-purity silane, and catalysts, respectively [11]. Li serves multiple dissipative functions, including its use in making greases, therapeutic and medicinal applications, as well as in cleaning air and sanitation (Figure 1.3).

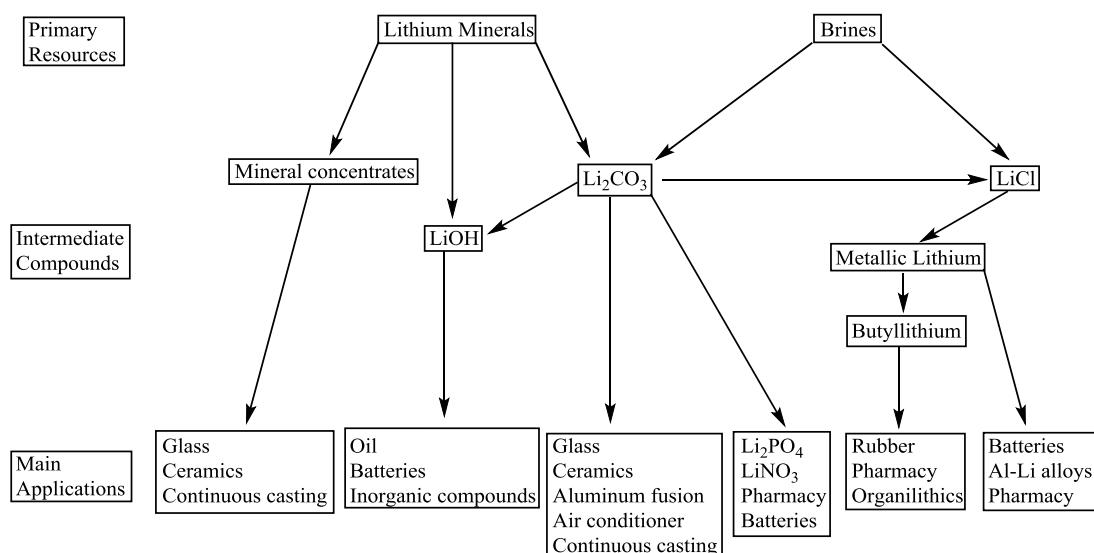


Figure 1.3 Resources and applications of Li [17]

The most significant market expansion for Li has been observed in its application in rechargeable batteries, surpassing growth in other sectors [23]. Different active material combinations that affect battery performance can be set in LIBs. These batteries fall into two broad categories: primary (single-use) and secondary (rechargeable). Primary batteries employ metallic Li as the anode and Li salt combined with an organic solvent as the electrolyte. Common Li primary batteries use cathodes made of minerals such as SO₂, FeS₂, MnO₂, and SOCl₂ [24]. Primary batteries, available in button and cylindrical shapes, are commonly employed in small devices. Similarly, in secondary batteries, graphite act as anode, metallic oxides of Li are the cathode, and an electrolyte made of diluted Li salt in an organic solvent is the electrolyte. Li-ion and Li-poly are the two types of Li secondary batteries that are most often used [23]. Unlike conventional Li batteries, which employ a Li salt as the electrolyte, Li polymer batteries use polymers such as polyethylene glycol (PEG) and polyacrylonitrile (PAN). These polymer batteries are commonly used in various applications, including Wireless tools, Movable computers, telephones, video cameras, tablets, and electric vehicles.

Li has diverse applications, ranging from its use in glass and ceramics to pharmaceuticals. Percentage usage of Li in different areas shown in Figure 1.4.

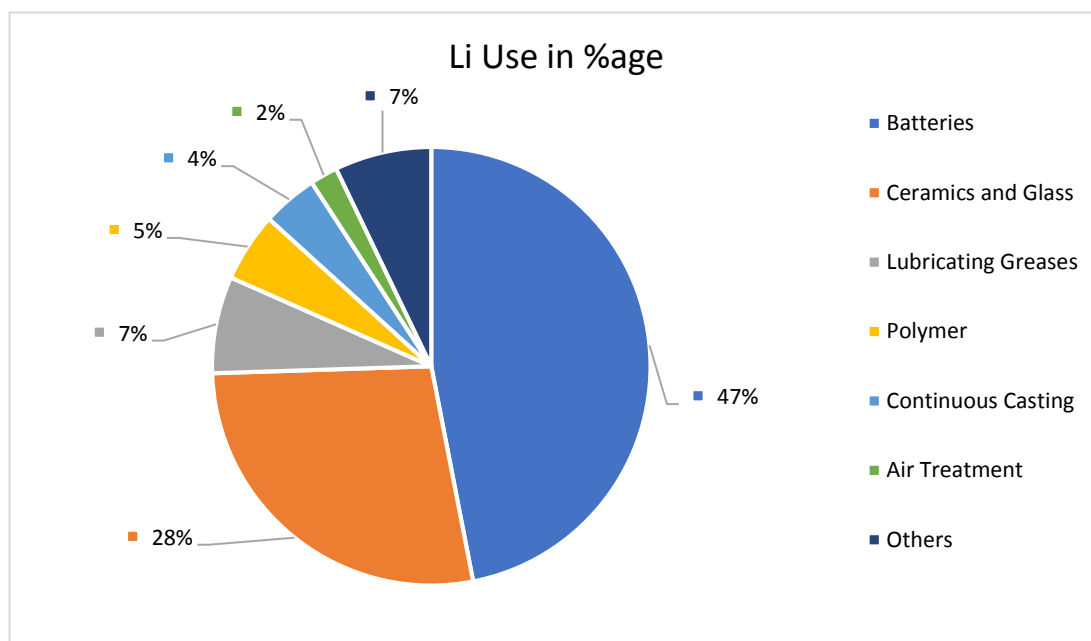


Figure 1.4 Diagram of Li usage proportions [25].

Until 2005, the main utilization of Li was in glass and ceramics [26]. However, since that time, LiBs have emerged as a dominant application, particularly contributing to the progress of the electronic and green industries. Among various applications, LiBs are witnessing the most substantial growth and are about to play an increasingly pivotal role in the Li industry (Figure 1.4). Projections suggest an expected growth rate of 10% for Li_2CO_3 and 14.5% for LiOH until 2025 [27], given their crucial roles as raw materials for LiBs. In 2016, prices for Li_2CO_3 were described to range between 10 thousand US\$ and 16 thousand US\$, while LiOH prices varied from 14 thousand US\$ to 20 thousand US\$ [28].

For the purpose of estimating Li, several analytical procedures, both classical and modern, have been devised. For instance, the cold precipitation method of assessing Li content involves measuring it using gravimetry. In order to create Li aluminate ($2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$), the sample must react with an excess of sodium aluminate in a basic environment (keeping the pH range of 12.6 - 13.0). However, a significant drawback of this approach is its extended time requirement to achieve accurate results. As a result, numerous researchers prefer exploring alternative methods [29].

Scientists proposed a solution to address challenges by introducing solvent-based titration reagents. Dissolving hydrophobic recognition components in an ionophore-containing dichloromethane (CH_2Cl_2) solvent to provide a strong affinity for the analyte ion is the fundamental idea behind this heterogeneous titration technique. In contrast to complex gravimetric procedures, titrimetric analysis offers a quicker method. In the process of pouring, filtering, settling, and weighing, this method reduces material loss, which increases accuracy. Though there are options for calibration, the accuracy of glassware such as pipettes and burettes may restrict the titration method. Moreover, human error, especially in determining the titration endpoint, can affect the accuracy of the procedure [30].

Researcher mentions that Li makes a non-luminous Bunsen flame appear dark crimson, though this color can be hard to see if there's too much sodium salt. Spectrophotometers, which display a red line at 671 nm in wavelength, can be used to quantify the quantity of Li. However, this method isn't ideal for quickly and accurately checking Li levels in the field because it lacks the needed portability and precision [31].

Colorimetric analysis is a way to figure out how much of a chemical is in a liquid by using color. Scientists came up with an easy method to measure the amount of Li in human blood using a paper device with no need to separate the blood plasma. Li concentrations as low as 0.054 mM may be detect with this technique. For this color test, it is best to utilize a paper device because it is inexpensive, lightweight, disposable, and suitable for biological materials. It's also made to be simple and easy for anyone to use. However, it's important to know that this method can't be used for substances without color. A unique chemical that changes color when it adheres to the target is required to address this. However, certain substances may provide false positives because they form stable compounds with the target [32].

Since it is a non-destructive tool, Xray Diffraction (XRD) is a difficult tool to use to evaluate Li. This method is a method for a complete analysis of Li content, it is a qualitative and quantitative method; it does not destroy the sample. Bragg's hypothesis basically gives a basis to the XRD analysis, which states that the path difference of the Xray diffraction beam will be a multiple of the wavelength. This principle has a formula of $n\lambda = d\sin\theta$, where d is the distance between planes, λ is the

X-ray wavelength, n is an integer. Nevertheless, the effectiveness of XRD characterization has its drawbacks; especially mineral analysis. Identification of mineral phases with the same diffracted peak is often ambiguous. Size of crystals is another constraint. XRD is very accurate with larger crystallization structures but can be quite inaccurate in small crystallization structures. Hence, small structures with small amounts could go unnoticed during XRD measurements and be said to be wrong findings. One drawback of this approach is that, unlike bulk mineral components, it does not provide a precise way to identify minerals in bulk natural samples. The challenge is to overcome these challenges and reduce the error in the XRD analysis, which requires an advanced and more sophisticated approach. It might involve improving data interpretation techniques or using complementary methods to reinforce the results so as to have a more comprehensive knowledge of Li composition across various samples. [33].

Atomic Absorption Spectroscopy (AAS) is a widely used method for identifying metallic elements in samples [34]. The technique involves the observation that the metal atoms absorb light at a given wavelength. By deriving the fundamental idea of AAS from the Beer Lambert law a connection between substance concentration and the amount of light it will absorb. Now note that this law is only for "free atoms" which means atoms not bound to any other elements. But in real samples the atoms are generally bound to other elements to form molecules. There are two types of AAS instruments: flame AAS and Graphite Furnace AAS (GFAAS). Depending on how the atomization is carried out, the choice will then be up to them [35-37]. At GFAAS graphite cylinders are used for measurements and of course the type of graphite employed affects the analysis outcome. The three types of graphite tubes currently in use include the platform type graphite tube (PTGT), high density graphite tube (HDGT) and pyrolytic coated graphite tube (PCGT). There are some types of YBC used for for example, HDGT is useful for elements with low atomization temperatures and where a high sample concentration exists. When performing GFAAS analysis of metals, one always pretreats test samples. It can include extraction, precipitation, membrane filtration processes or even ion exchange chromatography. [38, 39]. These pre-treatments help ensure accurate and reliable measurement results.

AAS is a widely used analytical method, but ICP-OES, which has excellent detection limits, is very commonly used. They use high temperature Argon plasma for ionizing the sample for the evaluation of main and trace elements associated with geological, medical, and environmental studies. The apparatus of an ICP-OES usually includes an optical spectrometer, RF generator, nebulizer, spray chamber, sample injector and ICP torch. Argon plasma is inductively connected to the sample injection, and the sample is introduced by such an injection device. The latter is in this plasma, the sample becomes atomized, ionized and excited. [40]. Analysis depends on the photons that are emitted after an electron returns from an excited energy level to a lower one. This occurrence, often referred to as atomic or ionic emission, is recorded by a detector that has optical components that discern between emission wavelengths according to the characteristics of each analyte element [41, 42]. The detector then measures the emission signal intensity at various wavelengths. ICP-OES is well-known for its speed, linearity, acceptability for a wide concentration range, and capacity to carry out simultaneous elemental analysis at part per billion (ppb) level, despite the requirement for previous sample dissolving. Nevertheless, as Tyler (2001) points out, ICP-OES has several difficulties, such as ionization, matrix effects, and spectrum interference. When a species' wavelength is comparable to the analyte's, spectral interference takes place. For the detection of Li, common wavelengths include 460.29 nm, 610.35 nm, and 670.78 nm [43-47]. It's essential to highlight that while ICP-OES is a powerful analytical tool, it comes with higher operating and maintenance costs compared to AAS.

Among the most sensitive analytical methods for determining tiny amounts of various elements, especially in liquid samples, is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Additionally, it may be directly used using Laser Ablation ICP-MS (LA-ICP-MS) to solid materials [48-50]. When comparing ICP-MS apparatus to optical emission spectrometry, the technical advancement in this method enables steady analysis with significantly lower detection limits. [51-53]. However, despite its capabilities, ICP-MS comes with certain drawbacks. The cost of standard reference materials is high, and the operating and maintenance expenses are also elevated compared to AAS and ICP-OES. Furthermore, ICP-MS is not suitable for in situ research or real-time field analysis. Low-energy pulsed lasers, typically with tens to hundreds of millijoules per pulse, are used in an analytical technique known as Laser-

Induced Breakdown Spectroscopy (LIBS). A little amount of the sample—which might be in the form of a solid, liquid, gas, or aerosol—is vaporized by this laser using a focus lens. Using this method, microplasma is produced. The light that the plasma generates is then collected by an optical wire and directed toward a spectrometer. Inside the spectrometer, light is dispersed by excited atoms, ions, and simple molecules in the plasma.

The emission signal is recorded and examined using the intensified coupled charge device (ICCD) detection system. The information is digitalized by this technology, which also shows the outcomes. With a somewhat lower spatial resolution of around 6 to 8 micrometers, LIBS offers a direct way for quantifying Li, but at a lower detection limit of about 5 ppm. Li at trace element levels in minerals may now be properly identified thanks to a major development in Li analysis made possible by LIBS. Moreover, the LIBS approach is versatile enough to detect other trace elements [54].

Scientist conducted a study using a remote sensing method to detect Li, particularly in exploration target areas, especially those located in remote regions. This approach proves useful for characterizing various deposit types, with a specific focus on pegmatite minerals, which are known to contain Li. The study introduces an innovative methodology capable of identifying spectral indications associated with Li-containing pegmatites. A remote sensing algorithm is employed to discern changes in the light spectrum related to pegmatite features. Yet, there is a limitation to this method. As Sentinel-2 lacks a thermal band, the ability to disambiguate Li-containing pegmatites with RGB alone is prevented. Both limitations discussed here result from the particular spectral characteristics of Li-containing pegmatites as reflected by the Sentinel-2 Remote Sensing Platform. [55].

A technology for detecting Li by a calorimetric or luminescent method was devised. The main objective of this approach is finding signal variations that correlate with the Li content of a particular sample. This method uses optical approach, which is advantageous with the advantages such as rapid detection, easy maintenance, and without the requirement of electrodes for sample analysis. In order to manipulate the optical properties Spectro-photochemical based sensors are used. Again, these techniques involve forming complex compounds and using nanoparticles.

Nanoparticle's analogy is compared with chromophores that have same refractive index of surroundings. LSPR frequency of the precious metal nanoparticles is highly dependent on the local environment, including the solvent refractive index. However, there is an interesting remaining issue in creating optically based Li sensors for in vivo and in situ applications. The factors that make this difficult involve the reversibility of the sensor, the reaction speed, and keeping high sensor stability over a broad temperature range. Small ionic radius and high charge density for Li cations results in shallowness of selectivity to alkaline cation interference and the challenge in coordination. Furthermore, our challenge is to synthesize ligands or complex compounds as they are difficult and time consuming to synthesize [56].

Electrochemical method is a precise technique for quantifying different substances in solution according to electrical principle. It is advantageous because this method is inexpensive, fast, accurate, and highly selective [57]. There are four components which are essential to potentiometry, a voltage meter, a salt bridge circuit, reference electrode and working electrode. They have been using more often and paper based sensors have been being utilized in many industries such as geological research, pharmaceuticals and medical [58, 59]. Voltammetry, on the other hand, is a commonly used analytical method in industries including mining, environmental research, and medicine. With this technique, the working electrode's current is tracked in proportion to the potential. Voltammetry is a useful tool for assessing both organic and inorganic species because of its remarkable sensitivity over a broad concentration range [60, 61].

The development of analytical techniques based on voltammetry and potentiometry has been prompted by the unique characteristics of Li metal, including its low density, high theoretical specific capacity, and redox potential. These methods assess different electrical properties in connection to chemical properties (reaction or concentration), such as potential, current, charge, and conductivity [62-66]. The fact that this technique has mostly been studied and developed for identifying Li in saliva is remarkable, despite these developments, indicating a restriction in its present area of use.

Table 1.1 Simplified comparison between different analytical methods for the estimation of Li [67].

Analytical Technique	Method Used	Benefits	Limitations
<i>Conventional Methods</i>			
Gravimetry	Precipitation	Precise method, no temperature effect.	Impurities in precipitation, slow.
Titrimetry	Complexometric Titrations	Fast, accurate, less waste.	Calibration error, human error.
Colorimetry	Absorption of light	Low cost, easy.	Low range, costly when making colored samples, manual, use color sample.
<i>Modern Methods</i>			
Spectrofluorimetry	Emission of light	Highly sensitive and specific, large linearity.	pH sensitive, auto-fluorescence, toxic to biological media
ICP-MS	Ionization of sample and separation by charge to mass ratio	Measure multi-elements at same time, better than ICP-OES, low detection limits.	Spectral interference, very costly, can't be used in situ or in real-time analysis.
ICP-OES	Ionic emission	Higher detection limits than AAS, fast, linear, high resolution, wide concentration range.	Spectral interference, matrix effect, ionization, expensive than AAS.
Thermal Ionization Mass Spectrometry	Thermal ionization and separation by charge to mass ratio	Precise, use low energy, near 100% emission of ions, easy automated lower mass fractionation.	Require pure solution, limited to element having less than three isotopes, mass fractionation continuously change.
AAS	Absorption of light	High sensitivity, low sample consumption.	Low atomization efficiency and sensitivity, evaporation of water into sample.
XRF	Inner electron transition	Fast, non-destructive, low running cost.	Interference, matrix effect, uncertainty, noise.
XRD	X-ray scattering	Direct sampling, non-destructive.	low image quality, invisible to amorphous solids

The above-mentioned techniques are expensive and these may be available for only one or couple of matrices and have limitations. The purpose of this study is to develop a new, cheaper, robotic, fast and more reliable method for the determination of Li from different sources. In this research we use UV-Vis Spectrophotometer for the spectroscopic determination of Li.

Ultraviolet-visible spectroscopy is a scientific technique that focuses on understanding how matter interacts with electromagnetic radiation within a specific range. This range, known as the ultraviolet-visible (UV-Vis) region, spans from 10 to 380 nanometers (nm) in the electromagnetic spectrum. Additionally, there's a segment called vacuum ultraviolet (VUV), which includes the range of 10–200 nm. It is essential to remember that measurements in a vacuum are the only way the VUV range is investigated. Conversely, the visible (Vis) portion of the spectrum has wavelengths ranging from 380 to 750 nm. The conclusion of this work is that the study by UV-Vis spectroscopy of materials' interaction with electromagnetic radiation in the visible and ultraviolet spectra is invaluable for study characteristics of many substances. Extremely important UV-Vis spectroscopy is about exciting the outside electrons of atoms to form the molecule. The process is also called 'electronic spectroscopy'. In UV-Vis measurements, there are three main modes: photoluminescence (fluorescence, phosphorescence); transmittance; reflectance. The measurements are made in transmittance and reflectance modes with respect to a standard material. With the reference it is very clear that the recorded data is accurate. Similarly, when we are measuring photoluminescence in terms of fluorescence and phosphorescence as such measurements, these can be treated as absolute. Therefore, these acquisitions do not require a reference material. Such an approach is flexible and precise for the study of the molecules' behavior in the presence of the UV—Vis radiation [68].

This study reports the difficulties faced by current methods of estimating Li. These methods have issues like accuracy problems, inefficiencies, and challenges in meeting new technological needs. The study aims to improve the dependability and usefulness of Li estimation techniques, especially considering the fast changes happening in energy storage and related industries.

AIM AND OBJECTIVES

Aim and objectives of the study are given below:

- Novel method development for estimating of Li.
- Encompass the improvement of accuracy, precision, and overall efficiency in the measurement of Li content.
- This involves a comprehensive exploration of analytical techniques, the finetuning of methodologies, and the rigorous validation of these methods.
- The overarching objective is to surmount challenges inherent to Li analysis.

CHAPTER 2

LITERATURE REVIEW

Using a technique called slow evaporation, Priya et al., (2009) has been able to grow single crystals of Li sulfate monohydrate — crystals with the ability to interact with light in special ways, (non-linear optical activity). After growing the crystal, it looked very clear and transparent and had a size of $14 \times 8 \times 5$ mm³. I measured a bit more than 1 cm or 0.4 inch long, at which point it was about 4 weeks. First, they grew the crystal and then subjected it to various tests to learn more about what it was made of. The crystal's response was investigated in regard to the different light wavelengths using FTIR. Also, they did thermal analysis (TG/DTA) to find how the crystal behaves on heating. In addition, they used UV-Vis analysis to determine how the crystal absorbs light, and studied its mechanical, and dielectric properties. They did some calculations that helped them to further understand the crystal's behavior and determine its band gap energy. It is an indication of how easy it is for electrons to move around in the crystal. Polarizability was also attempted to be calculated through a method known as Penn analysis. This allows them to see how the crystal reacts to current. They related Penn analysis results then compared with the ones obtained using conventional methods and recorded these in a table for easy reference [69].

Stewart and Newman (2007) have been interested in that kind of knowledge of how Li battery electrolytes flow in solutions for improving battery performance. For this, they used a process known as restricted diffusion with minor modifications. Instead of using difficult techniques, they used a methodology referred to as UV-Vis absorption, it is easier and less vulnerable to mistakes caused due to other reactions also occurring at the same time. What they discovered is that the more the concentration of the electrolyte drops, the less effectively it was able to move through the solution. The relationship was used in mathematical equations. For example, they demonstrate that in acetonitrile as the electrolyte diffusion coefficient decreases by the formula for the diffusion coefficient. As in ethylene carbonate/diethyl carbonate they noticed a decrease in the diffusion coefficient. As long as the diffusion coefficient of the substance is greater than 10^{-6} cm²/s, this method can be used to study any liquid solution that can be detected using ultraviolet or visible light. However, it makes it

easier to grasp how things move throughout solutions which is handy for a number of scientific and innovative projects — especially in battery technology [70].

According to He et al., (2020), one particular problem that Li-sulfur (Li-S) batteries face is poor performance and subsequently low durability and this can be improved if you know precisely what happens inside a working Li-S battery at the fundamental stage of reactions. This study came up with a new way to see what is going on in these batteries as these batteries work. The cell is a special one that couples UV Vis spectroscopy with electrochemistry. The electrode in this cell is a common one composed of the elements sulfur and carbon. By achieving this setup, it made their identification of the different chemicals that work in the battery operation clear, more so with the liquid chemicals that take place in the discharging stage of the battery. What they discovered was a new S_3^{2-} type of sulfur compound. It turns out that they actually manage to find it at a particular stage of its discharge cycle in a not surprising quantity. This S_3^{2-} happened upon reduction of another sulfur compound, S_4^{2-} . They checked this by studying UV-Vis spectra change over battery operation and charge transfer amount. Additionally, their observations while the battery operated also offered insights as to which sulfur compounds were more stable under certain conditions and at what point does the battery limit how fast it can discharge. Finally, taking into account the observations and previous research, they proposed a likely way that S_8 molecules were transformed into other Li_2S_2/Li_2S compounds during the battery operation. This process proposed will help us to better understand how these batteries work and if possible improve them in the future [71].

According to research conducted by Zou and Lu (2016), design of electrolytes with optimal battery performance demands knowledge of how different solvents influence redox processes in Li-S batteries. In this work, the redox processes in Li-S batteries under various solvent conditions are studied by means of operando UV-Vis spectroscopy. Their results indicate that the redox reactions in solvents with large donor numbers like dimethyl sulfoxide (DMSO), contain many electrochemical and chemical processes such as the formation of sulphur polysulfides intermediates. Among them, S_3^- is the most prevalent and reliable intermediate. In contrast, solvents of low donor number (such as 1,3 dioxolane:1,2 dimethoxyethane) predominantly give the main intermediate as S_4^{2-} . As these initial polysulfide intermediates are stable

(unstable), the rate at which polysulfides undergo disproportionation, dissociation and recombination processes influences the rate of reactions of the individual Li-S battery reactions separately. In illustration, they showed that dimethylformamide is a better stabilizer of S_3 , is less polarising in Li-S than DMSO, and as anticipated, there is no S_4 contribution. This work demonstrates that Li-S reactions care different solvents, highlighting the significance of polysulfide stability in the ability to increase efficiency of Li-S batteries [72].

Patel and Dominko (2014) has applied UV-Vis spectroscopy to examine how Li-sulfur batteries behave, both qualitatively and quantitatively. To do this, they used catholytes made from specific combinations of Li and sulfur that they prepared in the lab. By doing this, they can create calibration curves for two different kinds of electrolytes used in these batteries. By analyzing the UV-Vis spectra, first-order derivatives show five distinct peak positions in both types of electrolytes. During tests while the batteries are running (operando measurements), Between 650 and 400 nm in wavelength, they observed slow shifts in the UV-Vis spectra. The derived peak positions detected with catholytes are consistent with those obtained from operando measurements. Through recalculating normalized UV-Vis spectra reflections acquired during operando mode, we can monitor the development of polysulfides and track their concentrations. This helps to see how the movement of polysulfides differs between the two electrolytes and how these differences might be linked to changes in the battery's capacity over time [73].

Gulino and his fellows (2014) has found out that quartz substrates were first treated with a chemical called $4\text{-ClCH}_2\text{C}_6\text{H}_4\text{SiCl}_3$. Then, they were mixed with another substance called Pyridylazo-calix[4]arene. This mixing resulted in a special material where a layer of a substance that can sense color, called a chromogenic sensing agent, was attached firmly to the quartz surface. This unique layer on the quartz was studied structurally using X-ray photoelectron spectroscopy. They also used another method called UV-Vis spectroscopy to understand how well this layer could detect Li ions. It is interesting that the layer, a good capture of Li ions was found even in small amount of Li ions present as few parts per million sample. Even when there are other ions, such as sodium ions, in similar amounts as the chloride ions, this was still true. The result of this study is that we can make a special layer on a solid

surface that is sensitive at the same time for Li ions and almost any other ions present at the same time. This could be used to make devices which must be able to detect Li ions with specific accuracy [74].

In the study by Dubois et al., (1988), Li polysulfides in liquid ammonia solutions were investigated and are described using two methods: UV-Vis spectrophotometry and Raman spectroscopy. This showed that the least reduced polysulfide, S_6^{2-} , is in equilibrium with the other radical, S_3^{3-} . It is seen that temperature has large effect on this equilibrium since the constant of 4.3×10^{-3} M at 293 K. They also observed a slight change in S_6^{2-} , which appeared in S_4N^- . Additionally, S_4^{2-} was confirmed in the solution and it also undergoes a change as manifested by S_3^{3-} . These shifts in S_4^{2-} are based on the amount of measured S_3^{3-} and the constant used for this shift is about 10^{-6} M. On top of that, they also found another compound derived from the solution, S_2^{2-} , which does not dissolve much. In addition, they considered the presence of S_5^{2-} in solution [75].

Gracia *et al.*, (1997) has developed a highly accurate method for detecting Li. It works by mixing Li ions with a substance called 1,4-dihydroxyanthraquinone, also known as Quinizarin. This reaction happens in a solution containing mostly dimethylsulfoxide, along with some sodium hydroxide and sodium carbonate. As a result of this reaction, the solution turns into a bluish-violet color with a specific wavelength of light at 601 nm. This color remains stable for a period ranging from 30 minutes to 2.5 hours. The response surface approach technique was employed to ensure that the sodium hydroxide and quinizarin concentrations were appropriate. This method involves conducting experiments in a particular order, known as sequential experimental Doehlert designs. The good news is that this method follows Beer's law, which means it gives reliable results. It can detect Li concentrations ranging from 14 to 250 ppb in both water and serum samples. When measuring 100 ppb of Li, the errors in the results, known as relative standard deviation (RSD), are just 4.0% in water and 3.9% in serum. This method has been successfully used to measure the levels of Li in medications and human blood without needing to remove proteins [76].

Tabata and his colleagues (1998) have synthesized and developed a water-soluble porphyrin, designated as Octabromo-tetrakis(sulfonatophenyl)porphyrin; $H_2obtpps^{4-}$), specifically for the precise recognition of Li ions in aqueous solutions.

This porphyrin has something called octabromo groups in it, which make it less likely to react with other substances by pulling electrons away. This unique feature allows the porphyrin to interact specifically with Li ions when the water is slightly basic. This interaction results in the construction of a Li complex, accompanied by a shift in the absorption peaks, observed at 490.5 nm (with a molar absorptivity of 5.31) and 734 nm (with a molar absorptivity of 4.36). The process is not hampered, notably, by sodium and potassium ions, which are frequently found in water. For the process combining Li ions and the porphyrin, the equilibrium constant was found to be 10^{8.80}. Li-ion concentrations in aqueous solutions might be precisely determined with the help of these discoveries. Using a solution of Magnesium EDTA, the interference from transition and heavy metal ions was successfully reduced. Using a blank solution as a reference, the concentration of Li ions was measured spectrophotometrically at 490 nm. The reduction of transition and heavy metal ion interference was accomplished. Spectrophotometric measurements of the concentration of Li ions were made at 490 nm using a blank solution as a reference. A calibration curve showed linearity between 0.007 and 0.7 mg cm⁻³ of Li(I), resulting in a correlation value of 0.967. This technique made it easier to find Li ions in aqueous solutions at concentrations lower than parts per million. Li content analysis of human serum and seawater samples was used to confirm its applicability [77].

Ferric chloride is necessary for things like giving nutrients and being part of ores, however Liu *et al.*, (2006) have claimed that scientists still do not fully understand how it functions in hydrothermal solutions and hypersaline brines. Only room temperature and low chloride concentrations are covered by the experimental data available today. This study aimed to fill in some gaps by doing experiments using a method called UV-Vis spectrophotometry. We looked at how ferric chloride behaves in solutions with chloride concentrations as high as 15 m (which is really salty) and temperatures ranging from 25 to 90°C. The solutions include several forms of ferric chloride complexes, according to a qualitative examination of the UV-Vis spectra. FeCl₄-containing complexes become more prevalent as chloride concentration rises, with FeCl₄⁻ containing solutions having the highest chloride concentration at 25°C and having more ligands than the average. The intricate geometry between FeCl₂⁺ and FeCl₃(aq) is significantly altered, as evidenced by XANES and UV-Vis spectra. Another technique called EXAFS confirmed that as the chloride concentration goes

up, more chloride atoms stick to the iron atom, giving it an octahedral shape. $\text{FeCl}_3(\text{aq})$ may vary in form, depending on the data, whereas FeCl_4^- is most certainly tetrahedral. Although the Fe–Cl distances in the EXAFS data are comparable, they indicate a tetrahedral geometry for FeCl_4^- , especially at 90°C. EXAFS findings indicate that $\text{FeCl}_3(\text{aq})$ might exist as a trigonal bipyramidal or a mixture of eight and four corner forms at ambient temperature. Results obtained from UV data at room temperature for three ferric chloride complexes show good agreement with prior research' formation constants. Hematite solubility appears to be far larger than previously thought, according to calculations extrapolated to 300°C, and even in solutions with trace amount chloride concentrations, higher order complexes $\text{FeCl}_3(\text{aq})$ and FeCl_4^- play an important role at rising temperatures. Yet, limitations in current experimental methodologies and extrapolation methods, together with an insufficient knowledge of activity–composition correlations in concentrated electrolytes, restrict the precision of these features. Nonetheless, the incorporation of higher order complexes into computational models of ore transport and deposition enhances the qualitative forecast of iron behavior in hydrothermal and hypersaline environments [78].

Enneffati and his fellows (2019) has synthesized sodium Li orthovanadates using the traditional ceramic method. The structure, phase purity and content of the compounds were investigated using a diversity of methods, including X-ray powder diffraction, IR spectroscopy, EDS, SEM, and AFM. Using ellipsometric and ultra-visible spectroscopies encompassing a spectrum range of 200 to 800 nm, the optical characteristics of complexes were studied at ambient temperature. The coefficient of reflection of the pellets was high, exceeding 80% in the visible band. Within the $[\text{VO}_4]^{3-}$ groups found in the orthovanadate compounds, charge transference from the oxygen ligands to the central vanadium atom was responsible for the UV–Vis absorption bands seen in the spectra. When $x = 0.5, 1$, optical permitted direct transitions for $\text{Na}_x\text{Li}_{1-x}\text{CdVO}_4$ are present, which were calculated using the Kubelka–Munk function. Cauchy model was used to examine the photosensitive characteristics of specimens by spectroscopical ellipsometry measurements [79].

Zhou *et al.*, (2013) investigated the structural characterization of complexes generated by tributyl phosphate (TBP), Li^+ , and ferric chloride in an organic extraction

solvent using the continuous variation technique in combination with UV–visible, Raman, and infrared spectroscopy. The evidence from many spectroscopic tests verified the existence of FeCl_4^- in the solution. Furthermore, it was noted that LiFeCl_4 is created when Li^+ and FeCl_3 combine. It was discovered that many complexes occur when Li^+ is extracted from an aqueous solution using the continuous variation approach. Using a curve-fitting technique, the IR spectra of the organic solvent obtained after various cations were extracted were analyzed in order to establish the coordination mode of the complex. The outcomes showed that the cation and TBP extractant worked together to create high molecular weight organic cations. It was discovered that an ion association process involving the organic cation and the tetrachloroferrate(III) anion was responsible for the selective recovery of Li^+ . The planar and stereo structures of the complexes produced during the extraction were reported, and the structural formulae were validated [80].

McCarrick and his coworkers (1993) have conducted an investigation on three new chromogenic calix[4]arene tetra-esters containing nitrophenol residues. These compounds show significant changes in their UV–Vis absorbance spectra when they form complexes with metal ions. When they added Li or sodium metals to these compounds in a liquid, the liquid changed from clear to yellow. The more metal they added, the stronger the yellow color became. These compounds preferred to stick to Li more than sodium. However, the color change only happened when a base was also present. They also found that these compounds could move metal ions from water into a different liquid (butan-1-ol) that had been made basic. This transfer caused the color of the liquid to change from clear to yellow. This color change went back to clear over time, and how fast it went back depended on how oily the compound was. Researchers looked into these compounds for use in sensors. Ongoing research is focusing on these and similar chromogenic systems, as well as integrating these ligands into fiber optic sensors [81].

Shi *et al.*, (2016) has proposed that separation of Li ions from magnesium ions remains a significant challenge. The method of extracting Li ions from a magnesium (II)-containing salts and putting it into a generally used ionic liquid ($[\text{C}_4\text{mim}][\text{NTf}_2]$) by using tri-n-butyl phosphate (TBP), a neutral phosphorus compound, was investigated in this study. In this work, the extraction behavior of Li ions was

examined and the influence of such many other parameters, such as phase ratio, ionic liquid quantity, and Salt Lake brine acidity was examined as well. Under ideal operation conditions, the efficiency of extracting only Li ions was found to be 92.37%, suggesting that new lithium-ion extraction system is highly efficient for recovering Li ions. We determined the thermodynamic restrictions for the Li ion extraction reaction by thermodynamics research. It was found that the extracted species have 1:1 metal to ligand in the complex using the slope analysis approach. Similarly, they also investigated FTIR and UV-Vis spectroscopy to describe further the nature of the extracted species [82].

In fact, Nayaka et al., (2019) has carried out an environmentally friendly route for recovering metal ions on used LIBs using a hydrometallurgical leaching method. First, in physical processes the researchers dismembered and disaggregated the spent LIBs so that a powder was obtained. Such as ascorbic acid, adipic acid, and nitrilotriacetic acid, organic acids were used to leach this powder, because they decompose easily. The reductive complexing mechanism was employed with about 6 hours to accomplish the leaching process. The researchers then evaluated the leaching efficiency using 'cubic rate law' plots and calculated rate constant (k) of li and cobalt ions dissolution. Leaching was also performed under UV-Vis spectra analysis to verify formation of Co(III)–to Co(II)–citrate. Both morphological and structural alterations of the cathode materials before and after leaching were described using SEM and XRD. The Li and cobalt amounts in the leachate were measured using AAS. In particular, the researchers observed that ascorbic acid increased the leaching effectiveness in solution of adipic acid, as this water-soluble reagent acted as an active reducing reagent, but that the leaching rate was not improved in solution of nitrilotriacetic acid. In this paper, a viable method to long term recovery of precious metals from used LIBs is presented [83].

Agrell et al., (2003) considered a deliberate degradation of the dye sensitized solar cell components to determine the failure processes in this device. This was concentrated on a dye adsorbed onto a nanostructured TiO₂ film. UV and IR spectroscopy was applied to monitor the dye in various circumstance including: air exposure, increase temperature, visual and UV radiation, electrolyte immersion, and presence of water in the electrolyte. Research indicates that the thiocyanate ligand is

lost upon exposure to air, to temperatures up to or exceeding 135°C, when an electrolyte becomes immersed in water, and also possibly UV radiation. However, interestingly, in air, the degradation of the SCN^- ligand was accelerated under visual light. Analysis of functioning electrodes submerged in the electrolyte or of damaged solar cells showed changes in the absorption peak associated with the thiocyanate ion ligand such as widening and blue shifting, and relative intensity decrease. One known failure mechanism is the removal of the electrolyte and thiocyanate ion ligand from the dye. In addition, as the electrolyte contains 5 vol. % water, the SCN^- ligand exchanges with water and/or hydroxide ion. While under visual illumination, the conversation between ligand and SCN^- and the water and/or hydroxide were accelerated [84].

According to Agarwal et al., (2014) this chemical, Li borohydride, provides a fast way to make small particles of gold. Stable at different pH levels, these particles were called Li borohydride gold nanoparticles (LBH-AuNPs). Then they made the particles even more useful indeed by adding two kinds of molecules that glow: FITC and lysine. These particles were also good at keeping the two types of molecules attached. In the process, they used FITC's glowing properties and lysine, plus who knows what gold particles themselves do, to produce a method for detecting collagen, a protein typified by rat tails. As they become less collagen this indicates that these particles may have been very useful in counting collagen. In the range of 2 to 10 $\mu\text{g ml}^{-1}$, their success in their use as probes for sensitive fluorometric analysis of rat tail collagen was shown through their linear relationship with the reappearance of FITC and lysine fluorescence [85].

Using an aqueous solution of Li hydroxide and cyanuric chloride, Ponnuvel and colleagues (2021) synthesized a polymeric complex called poly[hexa- μ -aqua-diaquatetra- μ -cyanurato-tetraLi] $[\text{Li}_4(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_4(\text{H}_2\text{O})_7]_n$ at ambient temperature. In the triclinic space group P1, it crystallizes. There is two separate Li^+ cations in the asymmetric unit. Trigonal-bipyramidal geometry is deformed in one of them, Li1. Li1 is coordinated by oxygen to three water molecules, two of which are in axial locations and the third of which is in an equatorial position, and two cyanurate anions that are located equatorially. Interestingly, in this compound, one water molecule sits between two Li atoms (Li1), and another water molecule links one of the Li1 atoms to a

different Li atom (Li2). The distance between the Li1 atoms is about 3.037 Å, while the distance between Li1 and Li2 is about 3.438 Å. Li2 is encircled by a slightly compressed tetrahedron formed by three water molecules and an oxygen atom from a cyanuric anion. The structure is held together by a network of hydrogen bonds between different parts of the molecule. The compound was also analyzed using infrared and UV-Vis light, as well as thermal analysis [86].

Sánchez-Vergara et al. (2012) made semiconducting thin films using $C_{32}H_{16}Li_2N_8$ as precursor material and using organic ligands anthraflavic acid and 2,6-diaminoanthraquinone, which are grown on quartz substrates as well as on crystalline silicon wafers. Characterization of the produced films using a series of characterization techniques including rapid atomic bombardment (FAB^+) mass and FTIR spectroscopies, UV-Vis spectroscopies was performed. Surface morphology were evaluated by SEM and AFM. The electrical behavior of the films exhibited typical semiconductor characteristics with conductivities approximately at $10^{-6} \text{ S cm}^{-1}$ across different temperatures, with the highest conductivity observed in the thin film derived from the bidentate amine precursor. A strong band was discovered between 2.3 and 2.43 eV, which was attributed to non-direct transitions. The optical band gap values, as calculated by Tauc and Cody studies based on absorption coefficients, were about 1.5 eV. A lower Tauc optical gap was found for thicker films, mostly because the thickness of the film affected the bend in the Tauc plot and affected the calculation of the optical gap. Yet, it was discovered that there is very no correlation between film thickness and the Cody optical gap [87].

Gold nanoparticle surface engineering has been used by Obare *et al.*, (2002) to develop a novel approach for the detection of Li^+ ions in water. This detection is critical to many industries, including industry and medical. Using a ligand called 1,10-phenanthroline, which binds selectively to Li^+ , 4 nm gold particles are modified in this manner. Gold nanoparticles aggregate as a result of this ligand's interaction with Li^+ , which creates a complex with a ratio of two ligands to one metal ion. The extinction spectrum of the nanoparticles varies as a result of this aggregation, obviously changing their hue. Li^+ ion detection in water is made reliable by this optical shift. The presence of Li^+ can be identified by looking for red-shifts in the extinction spectra or enhanced optical density at a wavelength that is considerably displaced from the initial

maximum. In order to achieve lower detection limits, smaller gold nanoparticles are preferred over bigger ones since they require less Li^+ to assemble. A JEOL TEM-100CXII running at 80 kV was used to analyze gold nanoparticles. Utilizing an AMT Kodak Mega-plus digital camera and its software, sizing was made easier. 1 mL of the nanoparticle solution was evaporated onto former coated copper grids at 25°C in order to prepare samples for electron microscopy. Using a Cary 500 Scan UV-Vis-NIR spectrophotometer, the extinction spectra of liquids containing nanoparticles were acquired. This system is capable of effectively detecting Li^+ concentrations within the range of approximately 10-100 mM. Similar strategies can be employed to develop detection systems for other target substances by designing selective ligands capable of forming complexes with the analytes in a 2:1 ligand/analyte ratio [88].

In a spectroelectrochemical study, Usov and his colleagues (2012) has employed a simple and reliable method for optical properties investigation of a metal–organic basis showing redox activity. This technique was used to create the framework and investigated the optical characteristics of the framework in various redox states for first time. Comparison with earlier measurements in solution showed that the DPNI ligand can be reduced to its mono- and dianion forms. This approach of simply needing a very little amount of the substance being examined and a low quantity of electrolyte is one of many benefits of this approach. Moreover, this also makes use of an external diffuse reflectance probe that is commercially available. In contrast, compact material should have absorption bands to the UV/Vis-NIR part of the electromagnetic spectrum depending on the material's redox state in order to support this approach. Despite this drawback, the SEC cell's use for measuring the redox states of moisture and air sensitive metalorganic frameworks may increase. This approach can also be used to evaluate the electrical characteristics of solid materials and a redox active metal organic frameworks. [89].

Cañas et al., (2014) has explored the mechanism of sulfur reduction during the reaction of Li–S battery through the analysis of UV–Vis spectroscopy results combined with other characterization methods besides a theoretical model. The UV-Vis absorption experiments were made possible thanks to the experimental configuration under an argon environment. Specific absorption bands (λ_{max}) for S and Li_2S were obtained using tetra-ethylene glycol dimethyl ether (TEGDME) of 265 nm

and 255 nm respectively. Decrease in the value of λ_{max} at the UV region indicates reduction in the polysulfide order by the presence of reference polysulfide solution. This decreasing trend showed that the decrease of polysulfides in an electrolyte is gradual and constant over the range of 25% to 75% depth of discharge (DOD). At changed DOD levels, absorption bands at 425 and 615 nm were observed in the electrolyte as well as the reference polysulfide solutions. They studied semi quantitatively changes in the concentration of these species and these bands were identified to be the distinct bands of S_4^{2-} and S^{3-} . Computer simulations as well as electrochemical impedance spectroscopy showed good agreement with the fact that polysulfides were at the maximum concentration around 37% DOD ($450 \text{ Ah}\cdot\text{kgS}^{-1}$) [90].

The synthesis of many salt complexes obtained from Manganese (III) Schiff base cubane cluster by Gibney *et al.*, (1996) represents the first quantifiable enquiry of the cation and anion preferences within metal-crowns. Each salt complex is formed via a simple one-step synthesis that produces 2:1 metal:metallacrown complexes with sodium and potassium ions and 1:1 metal:metallacrown adducts with Li. The experiments showed that these molecules prefer to bind to certain ions more than others: they like Li ions the most, then sodium ions, and then potassium ions. For negative ions, they prefer chloride ions the most, then bromide ions, trifluoroacetate ions, fluoride ions, and finally triiodide ions. The shape of these molecules was compared to other similar molecules, showing they are quite similar in structure. Tests confirmed that when these molecules are mixed with certain salts, the salts stay together with the molecules even when they dissolve. These molecules also don't easily exchange parts in certain liquids. This study helps to understand how these molecules interact with different ions, which is important for their use in various applications. These studies are essential in demonstrating the physical resemblances between metallacrowns and crown ethers, providing the groundwork for investigating their functional parallels. The confirmed structural stability of metallacrowns reinforces the idea of employing them as selective agents for cations and anions, as well as nano-molecular frameworks for assembling supramolecular systems. The diverse options for ring metal, structural pattern, ligand arrangement, ligand donor characteristics, and bound salts strongly demonstrate the synthetic versatility of

metallacrowns in the deliberate crafting of nano-molecular inorganic recognition agents [91].

McKervey *et al.*, (1992) has suggested that two novel chromogenic calix[4]arene tetra-esters featuring nitrophenol residues exhibit a remarkable preference for cations, causing a noticeable shift in absorption maximum from the ultraviolet to the visible spectrum when a base is introduced along with Li ions, and to a lesser extent, sodium ions. The solution turns from colorless to yellow with the addition of the metal salt, with the strength of the color directly according to the concentration. These chromo-ionophores hold significant promise for future applications in the development of optical sensors and colorimetric reagents for detecting these ions, especially in bodily fluids. While the selectivity demonstrated for Li compared to sodium falls slightly short of ideal levels for Li detection in blood (around 150), the absence of response to potassium ions suggests that ligand 7, in particular, might prove useful for detecting sodium in the absence of Li [92].

Giovinazzo and Zemke (2013) have aim to detect trace amounts of Li ions in water samples using silver nanoparticles. Li finds applications in various medications, LIBs, and is even considered for use as a supplement in drinking water. While Li ions are known for their mood-altering effects, they can also disrupt thyroid function. Therefore, it is essential to keep an eye on the Li^+ content in water solutions to avoid related problems. Silver nitrate is reduced with NaBH_4 in this study to create silver nanoparticles. The nanoparticles are capped with a particular ligand, 3,4-dimethoxythiophenol, which makes it easier for Li^+ ions to bind. UV-Vis spectroscopy may be used to examine the discernible color shift that results from the two nanoparticles that these ions bind to aggregating in solution. As shown by tracking the absorbance spectrum over time, the present approach calls for an incubation duration of 60 minutes. Determining these ligand-capped nanoparticles' selectivity and detection limit is the goal of ongoing research [93].

Through the solvothermal interaction of Li^+ with a carefully crafted organic ligand Kim *et al.*, (2013) created a luminous Li metal–organic framework (MOF). When this Li-based MOF is in the solid form, it exhibits a notable color shift coupled with luminescence quenching, indicating that it may detect explosive aromatic chemicals with nitro groups, or explosophores. Strong connections between the

electron-deficient nitrobenzene and the aromatic structures of the electron-rich CPMA2-molecules are demonstrated by single-crystal-to-single-crystal transformations, which assist to elucidate the specific detection locations. In conclusion, the effective synthesis of a luminous three-dimensional Li-based MOF was made possible by the introduction of H₂CPMA, an expertly designed ditopic organic ligand that gives MOFs luminescent features. With noticeable color shifts and luminescence quenching in the solid state, this MOF demonstrates the selective finding of explosive nitroaromatic chemicals. Direct proof of the interaction sites inside the MOF was given by using single-crystal XRD of the MOF containing nitroaromatic chemicals. This modification of the MOF's electrical structure is explained by the strong interactions it has with the chemicals contained. The construction of MOFs as sensors is made possible by these results, which deepen our understanding and allow for the customization of certain interaction sites with analytes [94].

Kim and Koo (2022) have discussed the critical need for effective Li detection methods due to Li's scarcity and its importance in various applications. They highlighted the current challenges, noting the lack of Li-sensing compounds that are both highly selective and easy to synthesize. In order to tackle this, the scientists created a unique chemical that can identify Li ions in organic solvents by observing variations in fluorescence and absorbance. The compound they created was a modified form of naphthalene, where they attached a specific molecule called 1-aza-12-crown-4. This modification was achieved through a single-step process using commercially available 1-bromonaphthalene and a technique called Buchwald–Hartwig amination. They also synthesized two similar compounds, labeled 2 and 3, with slight structural variations for comparison. When they tested their compounds with Li ions, they found that compound 1 showed a significant change in its absorption and fluorescence spectra, making it an effective Li detector. In contrast, compounds 2 and 3 showed minimal changes, indicating that they were not as suitable for Li detection. Further analysis using ¹H NMR titration and density functional theory (DFT) calculations confirmed that Li binds specifically to the 1-aza-12-crown-4 part of the compound. The researchers also determined the limit of detection (LOD) for their compound to be 21 μM, demonstrating its sensitivity to Li. Importantly, their compound showed selectivity for Li over other alkali metals like sodium, potassium, and cesium. This

selectivity was attributed to the unique structure of the compound, which allowed it to specifically bind with Li ions. Overall, Kim and Koo's study provides valuable insights into the design of effective Li sensors, offering a promising approach for future developments in this field [95].

Kim and Koo (2024) have proposed a new method for detecting Li ions using ^{19}F NMR spectroscopy, utilizing fluorinated naphthalene compounds. A monofluorinated naphthalene unit and a crown ether aza-12-crown-4 combine to form these compounds. By using Buchwald-Hartwig amination, FNC12 and FNC15 were synthesized. Li bound to FNC12, and the absorption spectra changed, suggesting a shorter conjugation duration. Rapid equilibrium of metal-ligand interactions is suggested by the alterations in chemical characteristics and peak widening observed in the ^{19}F NMR spectra of FNC12 and Li. Comparable findings were observed in ^1H NMR spectra. ^{19}F NMR spectroscopy was used to measure the stability constant (K_s) and limit of detection (LOD), which were found to be $17\ \mu\text{M}$ and $50\ \text{M}^{-1}$, respectively. Stability constants (K_s) were found to be around $4000\ \text{M}^{-1}$ and $2000\ \text{M}^{-1}$, respectively. FNC15, which was first discovered to bind selectively to sodium, was also found to bind to Li, demonstrating a greater affinity than sodium under the studied circumstances. In addition, the study looked at how water affects senses. The novel Li sensing technique presented in this study makes use of UV-Vis and ^{19}F NMR spectroscopy, and it may have wide-ranging field applications [96].

Aza-crown naphthalene di-imide was synthesized by Hangarge *et al.*, (2017) who also investigated the material's characteristics as a colorimetric and fluorescence sensor. By binding to Li^+ instead of bigger monovalent cations which contains the aza-12-crown-4 part, exhibits selectivity. Specifically, optical changes in response to monovalent Li^+ ions are made possible by the sensor's chemical stability owing to the crown-ether and the associated NDI fluorophore. They confirmed the sensor's selective and complex attachment to Li^+ ions, with a LOD of $5.0\ \mu\text{M}$, using UV-Vis absorption, fluorescence, cyclic voltammetry (CV), ^1H NMR, and visual inspection. The recovery of the sensor by basic centrifugation was made possible by the reversible binding of Li^+ ions by ligand that was noticed following the addition of EDTA. This implies that biological sensing devices may employ it. In order to assess Li^+ concentrations in biological systems and get insight into the function of Li^+ in illnesses

such as manic-depressive disorder, complex molecules have potential as reversible fluorescent probes. To detect distinct cations in water and biological systems, the researchers are presently examining the usage of water-soluble NDI derivatives with diverse aza-crown ether receptors [97].

Sheikh and his fellows (2022) have highlighted the historical importance of Li as a primary treatment for bipolar disorder, a role it has played since the mid-20th century. They underlined that because Li has a limited therapeutic range, it is vital to closely check blood levels. Concentrations exceeding 1.2 mmol/L can lead to toxicity and potentially life-threatening complications. Presently, atomic absorption spectrometry, flame emission photometry, and traditional ion-selective electrodes are among the techniques employed by researchers to measure Li levels in clinical settings. On the other hand, they pointed out that these procedures are laborious and need regular blood tests, which may cause patients discomfort and deter them from remaining in therapy. Moreover, these techniques require specialized personnel and expensive equipment, limiting their widespread use. Given these challenges, the researchers emphasized the urgent need to develop cost-effective and user-friendly devices for decentralized monitoring of Li levels. Their study aimed to review the existing literature on Li monitoring techniques comprehensively. They hoped to identify new opportunities and strategies that could facilitate the development of automatic and point-of-care analytical devices for determining Li levels, making monitoring more accessible and convenient for patients [98].

Pseudocalixarene macrocyclic L2 is produced in high yield via a [2 + 2] condensation reaction between Chrysazin diester and 2-hydroxy-1,3-diaminopropane in ethanol, according to research by Yao *et al.*, (2021). A slightly smaller [1 + 1] macrocycle, L1, is formed when L2 is heated to 200 °C in DMSO. All non-hydrogen atoms, with the exception of one carbon from 2-hydroxy-1,3-diaminopropane, are coplanar, according to the crystal structure of L1. As demonstrated by their CV and ¹H NMR spectra, L2 may interact with a variety of cations, including alkaline, alkaline-earth, cations (chloride), but L1 exhibits significant inertness. Significant alterations in the UV–Vis spectra and ¹H NMR are seen in the presence of Cu²⁺, Fe³⁺, and Al³⁺ when the L2:M ratio is 1:2. The chromogenic reaction to monovalent cations demonstrates the critical role anions play in the cation binding process. L2 reacts 1:1

with TBAOH in DMSO and produces a 2:3 complex with bases. Additionally, L2 has a high Li loading capacity and interacts with LiOH in a 1:4 stoichiometry. In the presence of 4.0 equivalents of LiOH, the reaction is second-order and has a half-life of almost half an hour for 0.25 mM L2. Changes in color and NMR spectra show that L2 may interact with TBAF in addition to hydroxide to create 1:1 host–guest complexes. Essential to note is that TBAOH shifts $E_p(II)$ more negatively with bulky cations, whereas $E_p(II)$ changes to positive values with other cations. By binding hydroxide and fluoride salt, L2 functions as an ion pair acceptor and triggers chromogenic reactions [99].

Solvent extraction (SX) with a hydroxyl-functionalized ionic liquid, namely [HEMIM][NTf₂], in conjunction with a neutral ligand, trialkylphosphine oxides, as the extractants, has been developed by Yang *et al.*, (2019) as a method for Li recovery from alkaline brine. To find out how different extraction parameters affected the effectiveness of Li extraction, they looked at a number of factors, including the ionic liquid concentration, extraction time, phase ratio, pH of the aqueous phase, and mole ratio of sodium to Li. They were able to extract more than 93% Li in a single run under ideal circumstances. Ion exchange was shown to be the primary governing factor of the extraction process of Li, which was investigated via the use of experimental techniques and UV–Vis spectroscopic characterisation. Cyanex923, Li⁺, and [NTf₂]-formed a complex with a 2:1:1 ratio, according to analysis performed using the slope technique. The spontaneous character of the Li extraction process was shown by thermodynamic studies. Li recovery from alkaline brine appears to have great promise using the [OHEMIM][NTf₂]-Cyanex923 extraction technique [100].

According to Aleksanyan *et al.*, (2013), phosphorylated salicylaldimines may interact with Li and scandium hexamethyldisilazides directly or through a methylene unit, producing complexes in high yields. A zinc (II) complex was generated by treating the methylene-linked derivative with Et₂Zn and 1,10-phenanthroline. This complex featured a bidentate coordination mechanism. IR spectroscopy and, in certain cases, XRD studies were used to confirm complex structures. Although the temperature-dependent vapor pressures of the ligands and complexes were determined by the Knudsen effusion technique, the thermal characteristics of compounds 1a, b, and 4b were examined using DSC. Crystal-to-gas phase transitions were characterized

by estimated thermodynamic parameters. Room-temperature THF solution containing these complexes demonstrated modest photoluminescence, and low-to-moderate intensity green light was emitted by unoptimized three-layer OLEDs based on 2a, b, and 3a, b [101].

CHAPTER 3

MATERIAL AND METHODS

3.1 APPARATUS

Graduated pipettes ranging from 2 mL to 25 mL, measuring flasks ranging from 10 mL to 200 mL, wash bottles, beakers, butter papers, spatula and stirrer were employed. All samples were analyzed at room temperature.

3.2 INSTRUMENTATION AND SPECTROSCOPIC CONDITIONS

A UV-VIS spectrophotometer (Shimadzu-UV1900i) was used to measure the absorbance. All the parameters of spectrophotometer were controlled by Lab solutions software. Water bath was used for heating the sample and sonicator was used for mixing of sample. A pH meter (Mettler Toledo). Micro-balance (Mettler Toledo) was used for the measurement of weights. All samples were analyzed at wavelength of 620 nm. Developed method was validated for parameters like precision, accuracy, linearity as described in International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH) guidelines [102].

3.3 REAGENTS

For the experimental work Li_2CO_3 is used as the Li standard. Li itself does not give any absorbance with UV-Vis spectrometer so it is necessary to develop a color by reacting it with a compound which make complex with Li metal. For the development of the color an organic compound named 3,4,5-Trihydroxy benzoic acid (Gallic acid) was used (formula shown in Figure 3.1). All reagents were of analytical grade and distilled water was used.

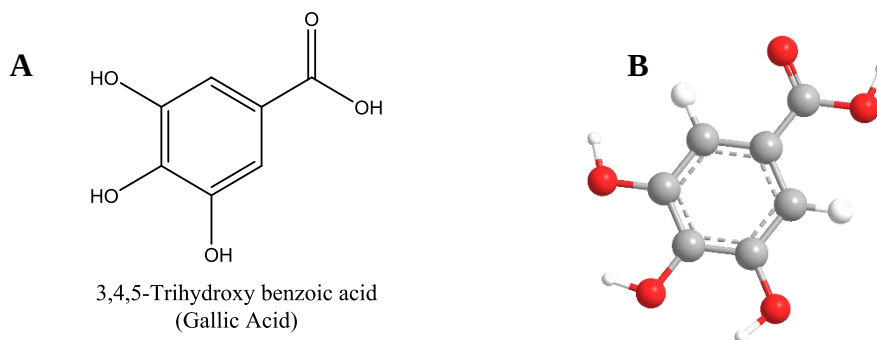


Figure 3.1 Formula of Gallic acid (**A**) structural formula (**B**) 3D formula.

3.4 METHOD DEVELOPMENT

3.4.1 PREPARATION OF STOCK AND STANDARD SOLUTIONS

First challenge for the development of the method was to select a suitable concentration of the reagents which gave best absorbance with spectrophotometer. For this purpose, hit and trial method was used. Solutions of different concentrations was made by adding Li and coloring agent both with same and different ratios. Best ratio of the reagents was obtained at 100:100. To obtain this 100 mg of each Li_2CO_3 and gallic acid was added to 100 mL volumetric flask and made volume up to the mark with distilled water (1 mg/mL). 0.5 mL of 0.5M NaOH was added to stock solution. Then 5 mL of this solution was added to 20 mL volumetric flask and made the volume with distilled water to obtain required dilution 0.25 mg/mL.

3.4.2 MEASUREMENT OF λ_{MAX}

λ_{max} of the sample was measured from the standard solution obtained from the standard solution (0.5 mg/mL). After connecting the Lab solution software with UV-Vis spectrophotometer the blank (distilled water) was placed in cuvettes to perform baseline and autozero. After autozero one of the cuvettes was filled by the standard solution. After placing the cuvette in spectrophotometer, the scan was obtained between 800 nm to 190 nm and then clear graph was obtained between 800 nm to 500 nm.

3.5 METHOD VALIDATION

The Innovated procedure was validated for linearity range, precision, accuracy, limit of detection (LOD) and limit of quantification (LOQ) and Robustness parameters as per ICH guidelines [102].

3.5.1 LINEARITY (CALIBRATION CURVE)

The absorption of the complex shows the linearity in the absorption. 10 absorption values on different concentrations ranging from 20% to 200% at the λ_{max} of 620 nm were obtained. The calibration curve was constructed by plotting absorbance v/s. concentrations. The linear regression equation was $y = mx + c$ and R^2 was obtained.

3.5.2 LIMIT OF DETECTION AND LIMITS OF QUANTIFICATION

The absorption values obtained from the UV-Vis spectrophotometer which were used to calculate the LOD and LOQ. For this purpose, ICH guideline was used to calculate LOD and LOQ. LOD and LOQ was calculated by the STEYX method [103-105]. For measurement of LOQ formula $3.3 \times (\text{STEYX}/\text{Slope})$ was used and LOQ was calculated by $10 \times (\text{STEYX}/\text{Slope})$. All the data obtained from LOD and LOQ calculations was shown in Table 4.4 and 4.5.

3.5.3 PRECISION

The degree of agreement between several measurements made from several samplings of the same homogenous sample under particular circumstances is what determines how precise an analytical process is. The repeatability, intra-day, inter-day, and reproducibility of this procedure were assessed in order to determine its accuracy. Precision was assessed by repeatedly measuring the absorbance of the complex (0.25 mg/mL) in 3 replicates ($n = 3$) without altering the parameters of the proposed method. The %RSD was calculated to quantify precision from the formula given below. All the formulas are used in excel sheet and then drawn into the word file.

$$\%RSD = (\text{Standard deviation}/\text{Average absorption}) \times 100$$

3.5.4 ACCURACY

Accuracy was evaluated by the pre-quantified sample preparation at three different concentration levels 60%, 100%, and 140%. Each concentration was analyzed three times.

3.5.5 SPECIFICITY

Specificity in the context of a method, especially in analytical chemistry or research, refers to the ability of the method to accurately and precisely measure a particular substance or analyte in the presence of other components, such as impurities, degradants or matrix components. Specificity is an important parameter during the validation of an analytical method. It's tested by analyzing samples with known potential interferences and confirming that the method still accurately measures the target analyte. Because in this method 3 components were used; water, Li_2CO_3 and gallic acid so their specificity graphs were plotted at 800 nm to 190 nm.

3.6 ROBUSTNESS OF THE METHOD

For the measurement of the robustness of the method there are several parameters. In this paper three parameters were discussed to verify the robustness of the method.

3.6.1 EFFECT OF CHANGE OF λ_{MAX}

The first parameter discussed in this section was to measure absorption of the standard solution at different λ_{max} . The changing criteria of λ_{max} was ± 2 . For the measurement of the effect of λ_{max} was assessed by repeatedly measuring the absorbance of the standard solution (0.5 mg/mL) in 3 replicates (n=3) by altering the λ_{max} at two ranges 618 nm and 622 nm.

3.6.2 EFFECT OF pH CHANGE

pH of the solution having concentration of 0.25 mg/mL was measured at room temperature by pH meter (METTLER TELDO). Then pH of the solution was measured at different pH. The pH of the standard solution was decreased by adding 0.5N HCl and the pH of the standard solution was increased by adding 0.5N NaOH. The absorbance of solution at different concentrations was measured by UV-Vis spectrophotometer.

3.6.3 EFFECT OF TEMPERATURE CHANGE

The sample (0.25 mg/mL) was analyzed at different temperature to measure the absorbance of the solution at different temperature. Spectrophotometer was used for the measurement of the absorption at different temperatures of 23°C, 25°C and 27°C. Water bath was used to attain temperature at different degrees.

3.6.4 EFFECT OF COLOR PRODUCING REAGENT

To measure the effect of color producing reagent different solutions having fix amount of Li and increasing concentration of gallic acid was made. For these 2 sets of solutions was made in which concentration of Li was kept fix by 50 mg and 25 mg respectively but the concentration of gallic acid was increased by different ratios.

3.7 VALIDITY ON COMMERCIAL SAMPLE

After development of the method, this method was applied on the commercial sample of 150 ppm of ACS grade. With commercial sample different parameters was performed and compared the results with the developed complex.

CHAPTER 4

RESULTS

4.1 ABSORPTION SPECTRUM OF COLORED COMPLEX

Without any heating, 3,4,5-Trihydroxy benzoic acid (Gallic acid) combines with Li_2CO_3 to produce an olive-green color complex, the absorption maximum of which, under ideal circumstances, is at 620 nm at absorbance 1.4280. Graph of λ_{max} with peak pick point shown in Figure 4.1.

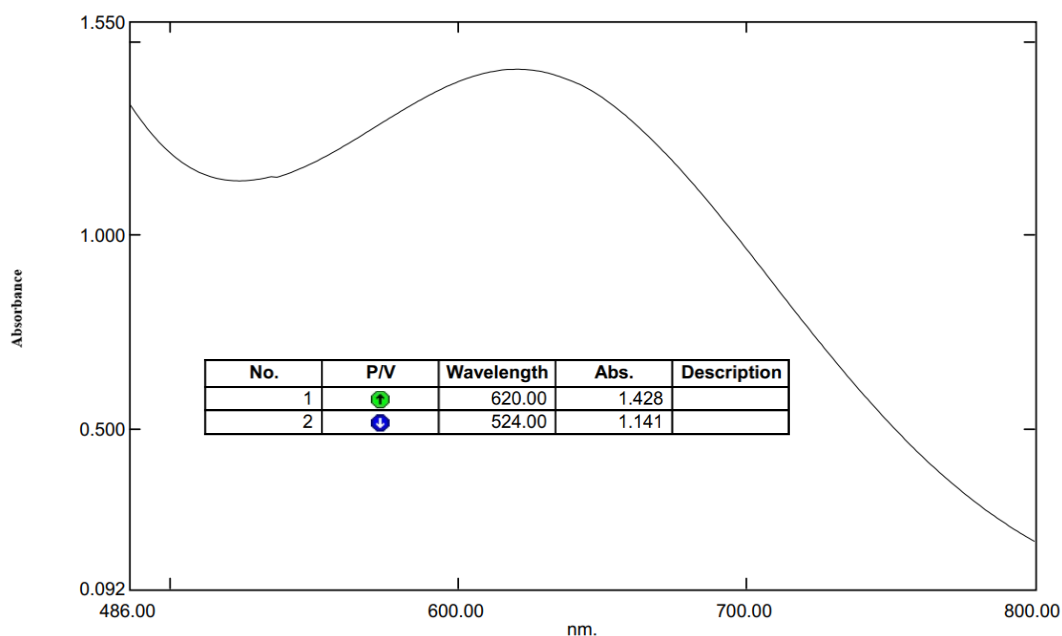


Figure 4.1 Absorption spectra of complex.

4.2 METHOD VALIDATION

4.2.1 LINEARITY (CALIBRATION CURVE)

A 5-point calibration curve was constructed in a concentration range of 60% to 140% for linearity. The absorbance of complex was plotted against its concentration and linear least square regression analysis was performed. Accurately measured stock solution of colored complex (1 mg/mL) were transferred to a series of 20 mL of volumetric flasks to make 5 solutions from 60% to 140% as shown in Figure 4.2. For making 60% solution, 3 mL of stock solution taken in 20 mL volumetric flask

and made the volume with distilled water to obtain solution of 0.15 mg/mL (150 ppm). Similarly, solutions of 200 ppm, 250 ppm, 300 ppm and 350 ppm were obtained. The absorbance was measured (n=3) at 620nm. The calibration curve was constructed by plotting absorbance v/s. concentrations. The linear regression equation was $y = 0.0022x + (-0.0003)$ and $R^2 = 0.9999$). Absorbance of each sample is shown in Table 4.1. and the linearity graph was shown in Figure 4.3.

Table 4.1 Absorption of the sample at different concentrations.

Sr. No.	Conc. in mg/mL	Conc. (%)	$\lambda_{\max}$	Absorbance
1	0.15 (150 ppm)	60%	620 nm	0.3330
2	0.2 (200 ppm)	80%	620 nm	0.4488
3	0.25 (250 ppm)	100% (Std)	620 nm	0.554
4	0.3 (300 ppm)	120%	620 nm	0.6671
5	0.35 (350 ppm)	140%	620 nm	0.7809

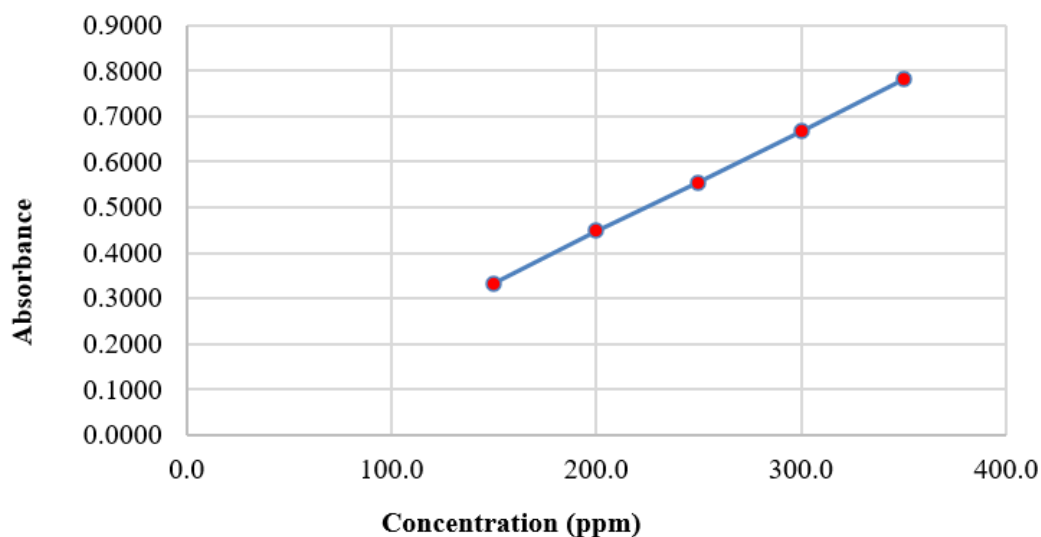


Figure 4.2 Calibration curve of Li-Gallic acid complex.

Table 4.2 calculation of linearity parameters.

Sr. No.	Absorbance (Y)	Concentration ppm (X)	Linest ($y = mx + b$)
1	0.3330	150	0.3
2	0.4488	200	0.4
3	0.5540	250	0.6
4	0.6671	300	0.7
5	0.7809	350	0.8
Correlation co-efficient			0.9999
Y-Intercept (b)			-0.0003
% Y-Intercept			-0.0523
Slope (m)			0.0022
Linest equation		$y = 0.0022x + (-0.0003)$	

4.2.2 EFFECT OF COLOR PRODUCING REAGENT

The color developing reagent was 3,4,5-Trihydroxy benzoic acid, also known as gallic acid. To measure the effect of color producing reagent different solutions having fix amount of Li and increasing concentration of gallic acid was made. It was observed that the color intensity of the complex increased with increase of the concentration of the gallic acid as shown in Figure 4.2, indicating that the complex was stable and that an increase in the concentration of reagent (mL) caused an increase in absorbance.

4.2.3 PRECISION

For the precision three sample solutions of concentration of 0.25 mg/mL were prepared. Precision was assessed by repeatedly measuring the absorbance of the

complex (0.25 mg/mL) in 3 replicates ($n = 3$) without altering the parameters of the proposed method ($\lambda_{\max} = 620 \text{ nm}$). The %RSD was also calculated to quantify precision as shown in Table 4.3. %RSD was calculated by the following formula.

Table 4.3 Absorption of the Standard (0.25 mg/mL).

Sr. No.	Concentration	$\lambda_{\max}$	Absorbance
1	0.25 mg/mL (250ppm)	620 nm	0.6154
2	0.25 mg/mL (250ppm)	620 nm	0.6100
3	0.25 mg/mL (250ppm)	620 nm	0.6074
Average			0.6109
Standard deviation			0.0041
RSD			0.67

4.2.4 ACCURACY

For the measurement of accuracy, samples were prepared of three different concentration levels 60%, 100%, and 140%. Each concentration was analyzed three times as shown in Table 4.4.

Table 4.4 Absorption of the sample at three concentrations (60% - 100% -140%).

Concentration	Sr. No.	$\lambda_{\max}$	Absorbance
60%	1	620 nm	0.3527
	2	620 nm	0.3551
	3	620 nm	0.3530
100%	1	620 nm	0.7430
	2	620 nm	0.7443

	3	620 nm	0.7422
140%	1	620 nm	0.8692
	2	620 nm	0.8706
	3	620 nm	0.8672

4.2.5 MEASUREMENT OF LOD AND LOQ

The ICH guideline outlines several methods for determining detection and quantification limits, (1) including visual evaluation, (2) signal-to-noise ratio, (3) the use of the standard deviation of the response along with the slope of the calibration curve and (4) the standard error of the predicted y-values in the regression of range-Y (dependent data) on range-X (independent data) also called STEYX Function. In this study, the LOD and LOQ were determined (Table 4.5,4.6) using the Fourth method [106]. STEYX can be calculated by using following excel formula.

STEYX = STEYX(dependent data range y-axis, independent data range x-axis).

Table 4.5 Measurement of LOD by absorbance and concentration values.

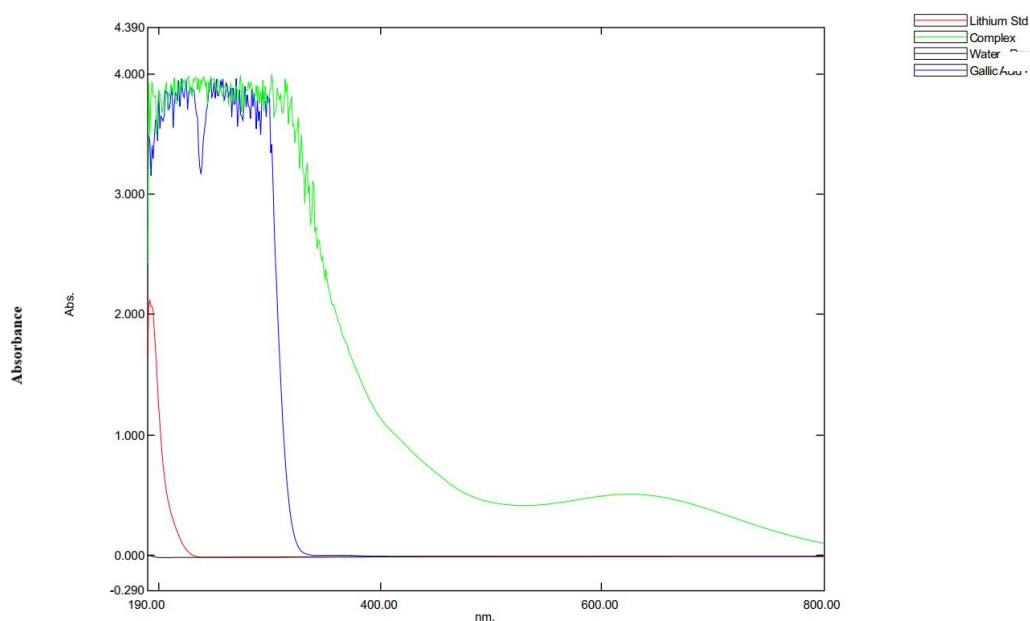
Sr. No.	Absorbance (Y)	Concentration ppm (X)
1	0.3330	150
2	0.4488	200
3	0.5540	250
4	0.6671	300
5	0.7809	350
Slope (m)		0.0022
STEYX		0.00279

Table 4.6 Measurement of LOQ by absorbance and concentration values.

Sr. No.	Absorbance (Y)	Concentration ppm (X)
1	0.3330	150
2	0.4488	200
3	0.5540	250
4	0.6671	300
5	0.7809	350
Slope (m)		0.0022
STEYX		0.00279
LOQ		12.5

4.2.6 SPECIFICITY

To run specificity, water, Li_2CO_3 and gallic acid was used. Distilled water, separate solution of Li_2CO_3 and gallic acid and complex was prepared (0.25 mg/mL) as shown in Figure 4.4. The overlay graph of specificity shown in Figure 4.5.

**Figure 4.3** Overlay graph showing graph of different solutions.

4.3 ROBUSTNESS OF THE METHOD

4.3.1 EFFECT OF λ_{MAX} CHANGE

One of the parameters for validating the robustness of the method was to take absorption values at different λ_{max} . These values are taken at ± 2 of original λ_{max} . because the original λ_{max} is 620 nm therefor, repeatedly measure absorbance of standard solution (0.25 mg/mL) in 3 replicates (n=3) at 618 nm and 622 nm each. %RSD was also calculated from the values as shown in Tables 4.7 and 4.8.

Table 4.7 Absorbance of the complex (0.25 mg/mL) at 618 nm.

Sr. No.	Absorbance
1	0.6256
2	0.6258
3	0.6260
Average	0.6258
STD	0.0002
RSD	0.03

Table 4.8 Absorbance of the complex (0.25 mg/mL) at 622 nm.

Sr. No.	Absorbance
1	0.6317
2	0.6318
3	0.6320
Average	0.6318
STD	0.0002
RSD	0.02

4.3.2 EFFECT OF pH CHANGE

When Li_2CO_3 was mixed with Gallic Acid (0.25 mg/mL) without the addition of NaOH or HCl, the pH was 6.6. To check the change of pH two solution of complex (0.25 mg/mL) was prepared in 20 mL volumetric flask. pH of the solution was changed by ± 3 as per ICH guidelines. 0.5M acidic solution of HCl and 0.5M solution of NaOH was prepared. 0.5 ml of each solution was added to solution. It was observed that by addition of acid solution the absorbance of the sample decreased and by addition of NaOH the absorbance of the solution increased as shown in Figure 4.6. It was also observed that the color of the complex disappeared by adding three drops of H_2SO_4 .

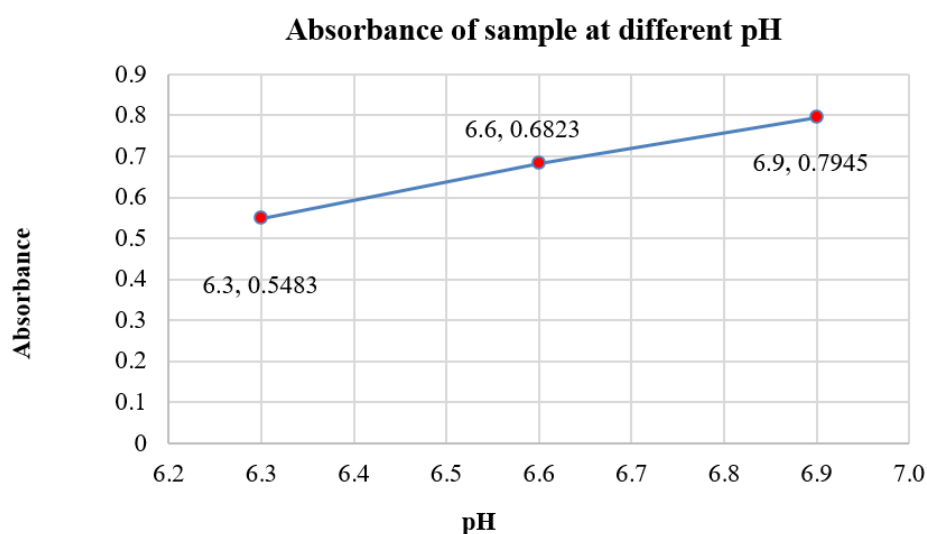


Figure 4.4 Effect of pH on formation of color complex.

4.3.3 EFFECT OF TEMPERATURE CHANGE

The effect of temperature is shown in Figure 4.7. The color develops at room temperature. Absorption of the standard solution was observed at different temperatures ranging from 23°C to 27°C as per ICH guidelines. As the temperature increases the absorption of the standard solution goes on decreasing.

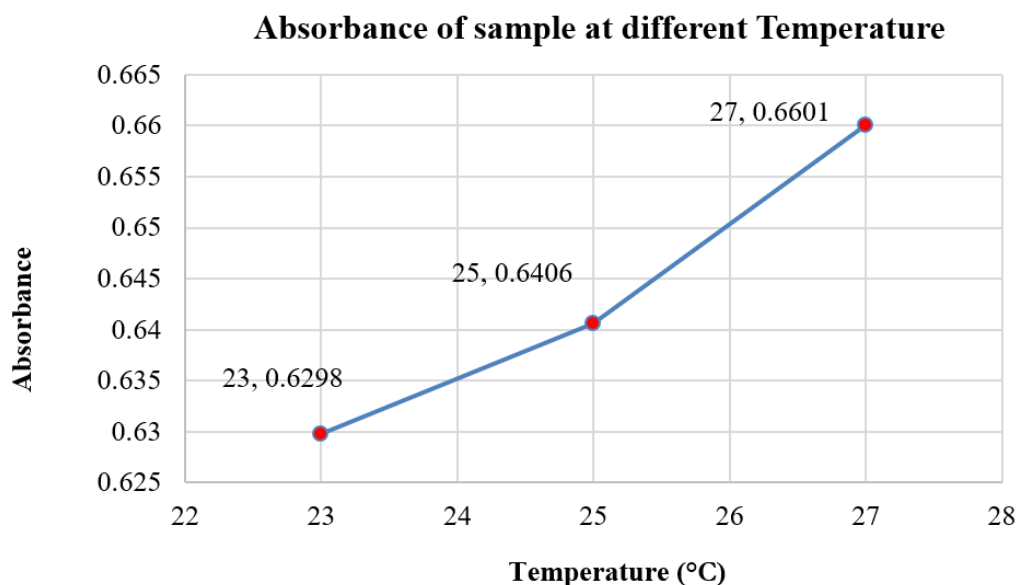


Figure 4.5 Effect of Temperature on stability of color complex.

4.4 VALIDITY ON COMMERCIAL SAMPLE

Because the commercial sample was of 150 ppm so 150 ppm solution of gallic acid was prepared. For this, 100 mg of gallic acid was taken in 100 mL of volumetric flask and made the volume with distilled water (1 mg/mL). 3 mL of this solution was added to 10 mL volumetric flask and made volume with water (0.15 mg/mL or 150ppm). Then 3 mL of gallic acid and 3 mL of commercial sample was taken in flask (0.075 mg/mL). Light olive-green color was developed as the concentration of the complex was very low. linearity table and calibration curve are shown in Table 4.9, 4.10 and Figure 4.8 respectively.

Table 4.9 Absorption of the commercial sample at different concentrations.

Sr. No.	Conc. in mg/mL	Conc. (%)	$\lambda_{\max}$	Absorbance
1	0.025 (25ppm)	60%	620 nm	0.2812
2	0.05 (50ppm)	80%	620 nm	0.4376
3	0.075 (75ppm)	100% (Std)	620 nm	0.5167
4	0.1 (100ppm)	120%	620 nm	0.6835
5	0.125 (125ppm)	140%	620 nm	0.8322

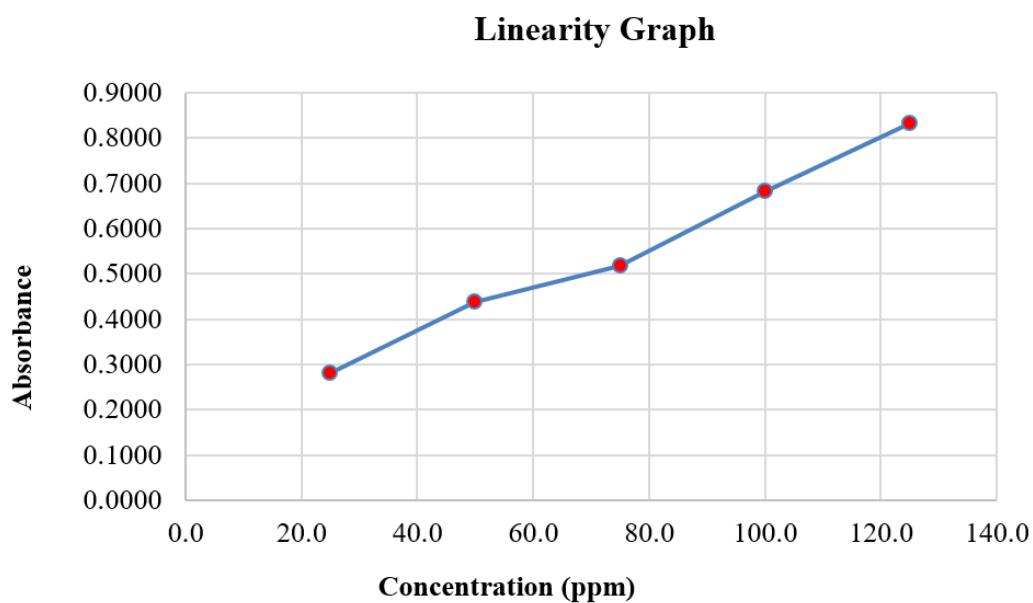


Figure 4.6 Calibration curve of complex of commercial sample.

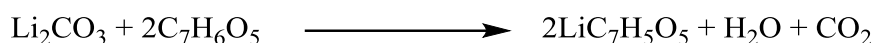
Table 4.10 Calculation of linearity parameters.

Sr. No.	Absorbance (Y)	Concentration ppm (X)	Linest ($y = mx + b$)
1	0.2812	25	0.3
2	0.4376	50	0.4
3	0.5167	75	0.6
4	0.6835	100	0.7
5	0.8322	125	0.8
Correlation co-efficient			0.9952
Y-Intercept (b)			0.1459
% Y-Intercept			28.2311
Slope (m)			0.0054
Linest equation		$y = 0.0054x + (0.1459)$	

CHAPTER 5

DISCUSSION

A novel method for the estimation of the Li was developed by using UV-Vis spectrophotometer. For this purpose, Li_2CO_3 was used as a Li standard and 3,4,5-trihydroxybenzoic acid (gallic acid) was used as a coloring reagent. When Li_2CO_3 and gallic acid are allowed to react with each other in the presence of water first light-yellow color appears which changes into brownish yellow and then light green to olive-green color. This color change indicates the complexation chemistry of the gallic acid with Li. When lithium carbonate (Li_2CO_3) reacts with gallic acid ($\text{C}_7\text{H}_6\text{O}_5$), the reaction typically involves the neutralization of the carbonate by the acidic protons of the gallic acid, leading to the formation of lithium gallate and carbon dioxide.



Lithium carbonate dissociates in water to form lithium ions (Li^+) and carbonate ions (CO_3^{2-}). Gallic acid, being a weak acid, donates protons (H^+) to the carbonate ions (CO_3^{2-}). This neutralizes the carbonate, forming carbonic acid (H_2CO_3), which quickly decomposes into carbon dioxide (CO_2) and water (H_2O). The lithium ions (Li^+) then associate with the deprotonated form of gallic acid (gallate anion, $\text{C}_7\text{H}_5\text{O}_5^-$) to form lithium gallate ($\text{LiC}_7\text{H}_5\text{O}_5$).

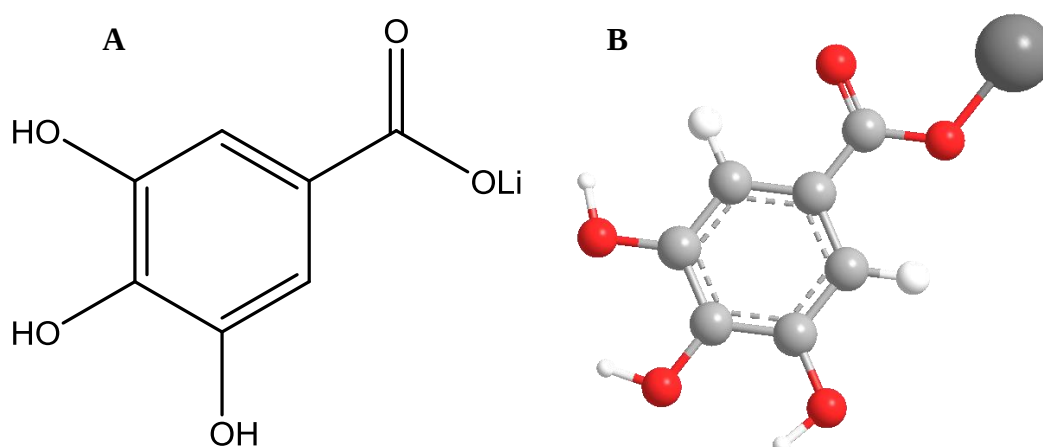


Figure 5.1 Structure of Lithium Gallate (A) Structural formula (B) 3D structure.

5.1 STRUCTURE PREDICTION

Gallic acid contains three hydroxyl groups and one carboxyl group on its benzene ring. These functional groups can act as a ligand, binding sites for the Li metal by a process known as chelation. In this process the Li ion formed coordinate bond with oxygen atoms present in it. Structure prediction of the complex are shown in figure 5.1. The color change during the chemical reaction is due to the result in a shift in the absorbance spectrum of the solution. The color of the complex produced depends upon the pH, temperature and the concentration of the gallic acid used. The carboxyl group ($-\text{COOH}$) of gallic acid can deprotonate to form a carboxylate anion ($-\text{COO}^-$), which can coordinate with the lithium ion. The hydroxyl groups ($-\text{OH}$) on the benzene ring, especially those in the ortho position relative to the carboxyl group, can also participate in coordination with lithium, though typically weaker than the carboxylate interaction. In a simple 1:1 complex, the lithium ion may coordinate primarily with the carboxylate group of one gallic acid molecule. If excess gallic acid is present (1:2), the lithium ion may coordinate with two gallic acid molecules, potentially through the carboxylate groups and/or hydroxyl groups.

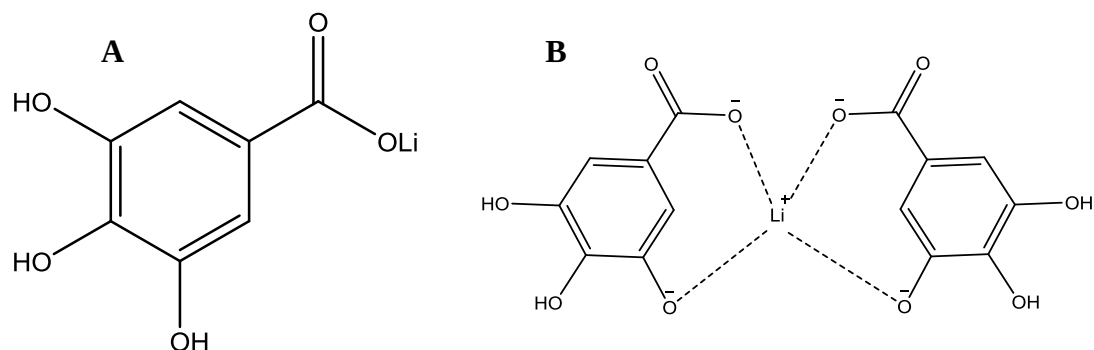


Figure 5.2 Structure prediction of Li-Gallic acid complex. **(A)** 1:1 **(B)** 1:2.

5.2 METHOD DEVELOPMENT

After the development of the color the next step is to make a suitable solution for all the parameters which were being discussed in the thesis. For this, hit and trail method was used. Firstly, solutions of different ratios of Li_2CO_3 and gallic acid were prepared. For this, 6 solutions were prepared in which concentration of Li was kept constant. The ratios for the gallic and Li_2CO_3 were 5:50, 10:50, 20:50, 10:25, 20:25 and 25:25 respectively. It was observed that when different ratio of both reagents were used then

there was a peak of gallic acid but at same ratio of both reagents no peak of gallic acid was observed. Which indicates that at same ratio all the gallic acid were converted into complex remaining no gallic acid behind. So, it was decided to select the solution having same ratio. Next step was to select a more suitable solution having same ratio of both reagents. For this, 5 solution of same ratios having ratios of Li and gallic acid 5:5, up to 50:50 and 100:100, 200:200 respectively. It was observed that as ratio of the reagents increased the peak get cleared. So, it was decided to made more concentrated solution like 100:100 and 200:200 of 0.5 mg/mL concentration. For this, 5 mL of 100:100 solution was taken to 10 mL volumetric flask and made the volume with water to get 0.5 mg/mL solution. Similarly, for 200:200 5 mL sample was added to 20 mL flask (0.5 mg/mL). At 100:100 ratio the peak was maximum (overly graph of ratio 50:50, 100:100, 200:200 having 0.5 mg/mL concentration are shown in Figure 5.3). It was observed that when 0.5 mL of 0.5M NaOH was added to the solution the peak gets cleared and when added H₂SO₄ then color was disappeared. All concentrations were observed at 620 nm which is the λ_{max} of the complex.

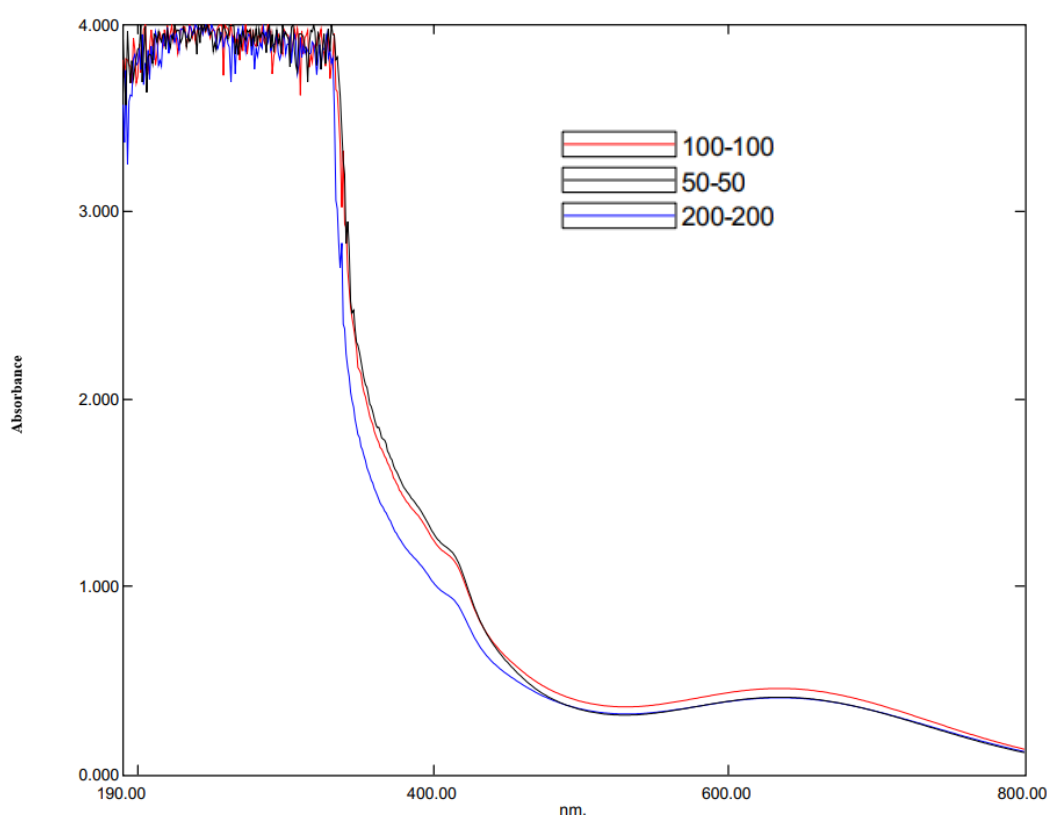


Figure 5.3 Overlay graph of complex at same ratio with 0.5M NaOH.

5.3 METHOD VALIDATION

All the parameters of the method validation were measured accordance with ICH guidelines at wavelength range of 620nm. The first parameter which was discussed was calibration curve (linearity). It shows that how much values are linear with each other. To assess linearity, 5 different concentration solutions were prepared, ranging from 60% to 140%. The linearity of the absorbance was observed by its R^2 . The closer the R^2 is to one, the more perfect the linearity will be. In this method the R^2 was observed at 0.9999 and slope was observed at 0.0022. The results indicate that as per correlation coefficient the linearity of the complex was validated. The stock solution was prepared by adding 100 mg of Li_2CO_3 and 100 mg of gallic acid into 100 ml volumetric flask which was further diluted to obtained 0.25 mg/mL solution. When the amount of the gallic acid was increased symmetrically then the absorption measured for each concentration gives a linear graph showing that the gradual increase in concentration of the gallic acid will gives the gradual increase in absorbance. The intensity of the color increased as the concentration of the gallic acid increased. Another parameter for method validation discussed in this thesis was precision, which was assessed by repeatedly measuring the absorbance of the complex in three replicates. %RSD was also calculated for the precision which was observed as 0.67. As the %RSD value is less than 2 so the method is said to be précised. Accuracy of the method was measured by preparing three solutions of different concentration one of minimum concentration (60%) one of middle concentration (100%) and one higher concentration (140%). The absorbance of the solutions of the different concentration shown in Table 4.4. the results shows that the mean of all values as different concentration is close to the three values so it was indicated that the method is accurate. The LOD and LOQ of the standard solution was calculated by the STEYX method on excel. The results of accuracy indicates that LOD and LOQ value depends upon the concentration of the solution. The LOD and LOQ for this method is 4.13 and 12.5 respectively.

5.4 ROBUSTNESS OF THE METHOD

For the robustness of the method three parameters were used as per ICH guidelines. The first parameter which was discuss is effect of change of λ_{max} . The λ_{max}

was changed at ± 2 of original $\lambda_{\max}$ as ICH criteria. The absorbance at different $\lambda_{\max}$ shows there is no significant change in the absorbance so it indicated that the method is robust. Similarly, the sample was taken at different pH and temperature values. The results shows that the absorbance of the sample increases with increase of pH and temperature of vice versa.

5.5 VALIDITY ON COMMERCIAL SAMPLE

The commercial sample of 150ppm which was used was of analytical grade. It gave light olive-green color with 150ppm solution of gallic acid showing that complex was formed. 5-point linearity was performed by making three solutions of 60% to 140% at 620 nm. Results shows that the absorbance of the commercial sample was very close to the standard complex. R^2 value was 0.9952 and lineest equation was $y = 0.0054x + (0.1459)$ The correlation coefficient (R^2) results showed that the method may be applicable on Li samples and an excellent method for determination of Li from 0.05 mg/mL to 3 mg/mL.

CHAPTER 6

CONCLUSION

Considering the demand of Li in near future, it is necessary to develop a technique that investigates Li in different matrices. A novel method for the estimation of Li was developed by using UV-Vis spectrophotometer. A new complex was made by reacting Li_2CO_3 and 3,4,5-trihydroxybenzoic acid (gallic acid). This complex has olive green color and λ_{max} of 620 nm. Method was developed by preparing most suitable concentration ratio of both Li_2CO_3 and 3,4,5-trihydroxybenzoic acid (gallic acid). Method was validated by discussing all the parameters like complex stability, precision, accuracy, LOQ, LOD and finally a calibration curve similarly, robustness parameters like effect of change in concentration, effect of change in pH and effect of change in temperature according to ICH guidelines. All the results shows that method is validated and can be used for the estimation of Li in its samples. Further investigation is needed.

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Report:Novel Method Development for Estimation of Lithium (Syed Asim Abbas Zaidi)

ORIGINALITY REPORT

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