

Review of analytical techniques for the determination of lithium: From conventional to modern technique

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Received 19 May 2023,

Revised 25 July 2023,

Accepted 27 July 2023

Citation: Rohiman A., Setiyanto H., Saraswaty V., Amran M. B. (2023) Review of analytical techniques for the determination of lithium: From conventional to modern technique, *Mor. J. Chem.*, 11(4), 979-1012

Abstract: Renewable energy development and usage have spread around the world. This issue occurs as part of attempts to minimize the world's reliance on increasingly finite fossil resources. This has accelerated the transition from fossil-fuel cars to battery-powered electric vehicles. Lithium is a critical component of the battery. As a result, the worldwide usage of lithium will rise as the use of lithium batteries rises. Therefore, a quick and precise technique for identifying lithium is critical in exploration to fulfill the worldwide demand for lithium. Furthermore, a reliable lithium test for monitoring medicine doses for people with bipolar illness and areas contaminated with lithium battery waste is required. Thus, this research presents critical views on the literature addressing various lithium monitoring strategies. This work then examines the progress of lithium technology using conventional, spectroscopic, and electrochemical methods. Furthermore, bibliometric analysis is used to identify trends in the future usage of the desired technology. This leads to the creation of analytical equipment and portable systems for lithium detection in geological exploration, environmental, and medical domains.

Keywords: exploration, energy, lithium, sensor, spectroscopic, electrochemical method.

1. Introduction

The world's population is increasing rapidly. It is estimated that the population density will reach 769 people per km, and the total population will reach over 10 billion by 2025. As the impact, the need for fossil energy also increased (Bernasconi and Bernasconi, 2004, Weeks and Faiyetole, 2014). However, the production and exploration of fossil sources tend to be static and decreased, resulting in the awareness of the current global reliance on fossil fuels and driving the exploration of renewable energy sources (Widarsono, 2013, Weeks and Faiyetole, 2014, Bakhtiarvand Bakhtiari *et al.* 2021). Lithium has been identified as one of the most important metals in the energy industry to be used for energy storage and the transition to renewable energy due to its high reactivity (Abdollahzadeh *et al.*, 2022, Y. Ding *et al.*, 2019, Razmjou, Eshaghi, *et al.*, 2019). This metal has shown excellent performance as energy storage (batteries) for electronic equipment and instrument (Bakhtiarvand

Bakhtiari et al., 2021). More importantly, there is a rising requirement for the development of lithium as a battery for electric power vehicle propulsion, which is surely generating high market demand for lithium. It is also emphasized by the increment of the lithium market that is 700 times higher in the last decade (Ebensperger, Maxwell, and Moscoso, 2005, Natarajan and Aravindan, 2018, Guo, Zhang, and Tian, 2021, Cardoso-Fernandes *et al.*, 2020, Grosjean et al., 2012, Yokoi et al., 2021, Ni'mah et al., 2022). Lithium is commonly found in volcanic rocks and mineral sources. It is also reported that lithium is present in the bittern and brine (H. Aral and Vecchio-Sadus, 2019, Houk *et al.*, 1980, Date and Gray, 1985, Meermann and Nischwitz, 2018). However, the concentration of lithium in those resources may be varied. Thus, it is crucial to analyze the lithium concentration before exploiting these alternative resources. For this reason, an effective and efficient method to evaluate the lithium deposition in the rock as well as in the alternative resources is required.

Studies have shown the medical field also utilizes lithium for the treatment of bipolar disorder and to regulate protein kinase activity in the form of lithium carbonate (Hal Aral and Vecchio-Sadus, 2008, McKnight *et al.*, 2012). However, it was reported that several side effects, including neurological disorder, disruption of thyroid function, impaired kidney function, cardiovascular effects, and gastrointestinal symptoms occurs when an excess amount of lithium is exposed (U.S.EPA, 2008, Markowitz *et al.*, 2000, Kamenica *et al.*, 2017). Therefore, to avoid those side effect and monitor the effectiveness of medication using lithium, monitoring lithium levels in the blood and urine is necessary. An overabundance of lithium, particularly in regularly consumed river water and groundwater, can be hazardous to human health and the environment. For this reason, the drinking water threshold for lithium is determined as 60 ppb, while the amount of lithium allowed under the Health Based Screening Level is 10 ppb (Aragay *et al.*, 2011, Ouhammou *et al.*, 2016, Tondo *et al.*, 2019, Parchami *et al.*, 2020, Lindsey *et al.*, 2021). Therefore, to preserve environmental sustainability, a periodic evaluation of lithium levels in the environment, including wastewater runs-off, rivers, ponds, is urgently needed.

In this report, we reviewed several analytical techniques from conventional to modern techniques for the detection of lithium. Conventional techniques include gravimetric, titrimetric, flame testing, and colorimetric. Modern techniques apply to advanced instruments including X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Laser-Induced Breakdown Spectroscopy (LIBS), and sensor technology. For future insight, we also discuss the application of those techniques in mining exploration, environmental monitoring and health or medical evaluation.

2. The classic lithium analysis technique

The classical technique is a chemical analysis method that includes the following features: (1) the instruments used are still simple, in the form of non-machine equipment, and do not use electricity; and (2) the science used in the analysis process is still related to stoichiometric chemical calculations.

2.1 Gravimetry

Lithium content can be quantified gravimetrically by the cold precipitation method. It is calculated as Lithium aluminate ($2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$) by reacting the sample with an excess amount of sodium aluminate in a basic environment (pH 12.6 -13.0). However, because of the time consuming, this method is less preferred (Jeffery et al., 1989). When done correctly, this procedure has the benefit of producing highly precise analytical data. In general, this approach is widely used to accurately calculate the atomic mass of several elements. Because the solvent temperature is insignificant, the gravimetric

approach is more accurate than the volumetric method. The temperature does not affect on the weight of the solvent. At the same time, gravimetric techniques can determine the result of a single element analysis on a single element or numerous elements. This approach does not require a series of conventional calculations, such as the use of calibration curves and low instrumental error. Then, possible sources of errors can be traced easily because the filtrate can be tested for complete precipitation and the precipitate can be examined for the presence of impurities. Unfortunately, this method takes a long time to get accurate results. Therefore, many researchers prefer other methods than this one.

2.2 Titrimetric

Titrimetry is a basic analytical method for determining metal analytes in materials. Chelating agents and titration endpoint indicators must be water-soluble since complexometric titrations are often performed in the aqueous phase. Ethylenediamine tetraacetic acid (EDTA) is a water-soluble chelating agent extensively employed in titrimetric metal analyte analysis. Eriochrome Black T and Murexide are extensively used as titration endpoint indicators. Conventional titration procedures for alkali metals like lithium are indirect and frequently rely on the precipitation of metal salts due to a lack of selective reagents. Furthermore, the number of competent complexometric chelating agents is still restricted since many reagents are insoluble in water. According to [Zhai \(2017\)](#), the new generation of titration reagents was effective in transitioning the titration process from a homogeneous phase to a heterogeneous phase ([Zhai et al., 2017](#)). Because of the utilization of nonpolar nanospheres, chelates and indicators are no longer confined to water-soluble chemicals. However, this approach is still confined to the use of ionophores, which only have a very high affinity for the analyte. As a result, the use of ionophore demonstrates a rather restricted titration capability.

[Zhai et al. \(2017\)](#) proposed employing solvent-based titration reagents to address these two constraints. The basic idea behind this heterogeneous titration is to dissolve all of the hydrophobic recognition components in a dichloromethane (CH_2Cl_2) solvent containing an ionophore to retain a high affinity for the analyte ion. NaTFPB and potassium ionophore one are mixed in a combination of CH_2Cl_2 and CHI stock solution to be used for potassium titration. Meanwhile, for lithium titration, KTFPB and lithium ionophore VIII are dissolved in a CH_2Cl_2 and CHI solution combination. The endpoint of the titration is then determined using a digital camera and paired with an automated titration setting. The potassium content in human serum has been precisely established to be $0.438 \times 10^{-2} \pm 0.10 \times 10^{-3} \text{ mol/dm}^3$. These results outperform atomic emission spectroscopy at $0.447 \times 10^{-2} \pm 0.20 \times 10^{-3} \text{ mol/dm}^3$. In terms of lithium target ion analysis, lithium selective ionophore reagents can withstand extremely high KCl concentrations, with a predicted inaccuracy of 1.1% for 10^{-1} M KCl . However, because of its low selectivity, the approach cannot sustain high Na^+ concentrations ([Zhai et al., 2017](#)). As a result, this approach is not suited for accurate and affordable lithium in serum analysis. As a result, various changes to the technique or reagents must be considered in order to get more effective and efficient procedures.

Titrimetric analysis has the benefit of being quicker than complicated gravimetric procedures. This procedure improves accuracy by reducing material loss during pouring, filtering, settling, and weighing. The precision of the glassware used to measure solutions, such as pipettes and burettes, might, however, be a restriction of the titration technique. Although glassware can be calibrated, it is not always perfectly precise. Human error can also restrict the titration procedure, particularly in estimating the endpoint of the titration.

2.3 Flame test

The flame test is a basic qualitative analytical technique used to determine the presence of metal ions based on each element's emission spectrum characteristics. In this test, a sample of an element or compound is introduced into a colorless flame and the color of the ensuing flame is observed. The atoms in the sample evaporate and, as a result of the heat, produce light when placed in a flame. Bulk samples produce light as well, but owing to interference from other components or the matrix, the light is not suitable for qualitative examination. Because bulk samples produce light mostly owing to the mobility of their atoms, the spectrum is broad and includes a wide range of colors. Only electron transitions between atomic energy levels may cause the emission of separated sample atoms in a flame.

According to [Svehla \(1997\)](#), lithium imparts a dark crimson hue to a non-luminous Bunsen flame. However, the presence of excessive levels of sodium salt can occasionally obscure the hue. Quantitative data may be acquired by utilizing a spectroscope with a spectrum consisting of a red line at a wavelength of 671 nm ([Svehla, 1997](#)). As a result, this approach is unsuitable for quick, precise, portable, and in-field monitoring of lithium concentration.

2.4 Colorimetric

Colorimetric is a method of determining the concentration of a chemical element of a compound in a solution with the aid of a colour reagent. [Komatsu \(2020\)](#), have developed a facile and simple colorimetric measurement of Lithium content from human blood samples by using a paper-based device without blood plasma separation. This method estimated the LOD of lithium content from the blood sample as 0.054 mM. The advantages of using a paper-based device for a colorimetric evaluation are inexpensive, good portability, disposability, and biological compatibility. Furthermore, by using this technique a simple and user-friendly was achieved ([Komatsu et al., 2020](#)).

The colorimetric approach has various benefits over other methods, including low cost, easy apparatus, and the ability to identify qualitatively or semi-qualitatively with the naked eye. Colorimetry, on the other hand, is often less sensitive. Colorimetry, however, has limits. Because the appropriate range is generally only a few milligrams per liter, the sample must be diluted or occasionally concentrated before meaningful measurements may be taken. To get the best results, the colorimetric approach necessitates the use of equipment known as a colorimeter. Unfortunately, these colorimeters are relatively costly and cannot automatically choose certain wavelengths since they must first set the proper range of measurement parameters.

The technology cannot then be used to analyze colorless substances. As a result, a chelating agent that can emit a specific color when it binds to the target ion is required. However, certain chemicals have properties that might lead to incorrect test findings owing to the stability of the complex compounds created with the target ion. Furthermore, because smartphone cameras have less resolution than digital cameras, they produce less accurate findings when analyzing variations in concentration based on the color density of the target ion-chelating complex molecule.

3. Modern Lithium analysis technique

The modern technique is a chemical analysis method with the following characteristics: (1) the instruments employed are pretty complicated, in the form of machines that utilize electric current as a source of energy; and (2) the science employed in the analysis process is frequently associated with atomic physics, resistivity, conductivity, waves, and so on.

3.1 Lithium Analysis by Spectrochemical Approaches

The evolution of methodologies and technological improvements in elemental analysis in geochemistry, medicine, and the environment over the last several decades has resulted in considerable decreases in detection limits for both elemental concentration and isotope ratio studies. The requirement to examine smaller samples has increased the development of sample preparation technologies as well as the demand for dependable analytical instruments. These advancements have encouraged further instrumental innovations in sample ionization, signal analysis processing, robust detection approaches, and low detection limits. We propose to just provide a quick summary of the analytical techniques that have been widely employed in geological, medicinal, and environmental research in recent decades. Analytical techniques are an area that is always evolving, with new methods, tools, and applications providing more assistance for understanding geological processes, medical and environmental monitoring, and other sectors. Here are a few spectrophotometers that are commonly used for elemental measurements of lithium, main elements, and trace elements in rocks and other materials.

3.1.1 Stationary instrumentation in the Laboratory

3.1.1.1 XRD

XRD is a powerful instrument for evaluating lithium. By using this method, no sample destruction is required. More importantly, the qualitative and quantitative data on lithium content can be observed. The principle of XRD evaluation is based on Bragg's theory that the difference in the path of the X-ray diffraction beam must be a multiple of the wavelength, the formula $n\lambda = d\sin\theta$ is used, where n is an integer, whereas λ is the wavelength of the X-ray, d is the distance between the planes, and θ is the diffraction angle (Fultz and James, 2013).

The XRD analysis generates a diffractogram, an arrangement of lines or peaks with varying intensities and precise locations based on the examined substance. Because each crystalline phase has its own diffractogram arrangement, it may be utilized as a fingerprint in identification tests. The appropriateness of the produced crystal structure is determined by matching each peak on the diffractogram at a certain angle value of 2θ and d from the study with a standard mineral database to gain information on the orientation of the crystal planes. If all of the crystal plane orientations are correctly recognized, the crystal structure certainly conforms.

A qualitative evaluation of lithium by XRD can be established by the existence of a peak at position 2θ in the range of 15° to 70° for spodumene minerals (Tian et al., 2019). The peaks characterize the phase, size, shape, and fingerprint of spodumene. In general, lithium may be found in minerals such as spodumene, amblygonite, pegmatite, and zinnwaldite. Ulitzka (2017), described an approach for quantitative measurement of the element lithium found in spodumene ore utilizing XRD with the "Whole Pattern Profile Fitting" (WPPF) method included in the PDXL program, allowing the proportion of each mineral to be estimated exactly. Thus, the mineral composition may be determined by a quantitative examination of ore samples (Ulitzka, Chai, and Narbery, 2017). Meanwhile, the amount of lithium in a geological material may be calculated using stoichiometric ratios (Pöllmann and König, 2021, Mubarak et al., 2021).

According to Ulitzka et al. (2017), the presence of lithium in the form of Li_2O may be computed using the knowledge that spodumene theoretically contains 8.03% by weight of Li_2O . No additional lithium-carrying minerals were found by XRD, hence all of the Li_2O could be ascribed to spodumene. Even if more lithium-containing minerals are discovered, their contribution may be calculated using their chemical composition during the WPPF analysis. The quantitative analysis determined by XRD

did not differ significantly from the results of the standard assay technique analysis (Ulitzka, Chai, and Narbery, 2017).

XRD is used to determine the structure, strain, orientation, and crystal size of materials. This method produces quick analytical findings and may be used to identify unknown minerals and compounds. Rietveld analysis methodologies range from qualitative to semi-quantitative to fully quantitative. Each approach provides a variable level of accuracy and precision in proportion to the amount of labor necessary to increase accuracy through sample preparation, instrument operation, and analysis. However, XRD characterization has its own set of challenges in mineral analysis since there is always ambiguity regarding the mineral phase in the same diffraction peak. XRD has size constraints as well. Large crystal formations are far more precise to measure than tiny ones. Tiny structures that are only present in minuscule numbers are frequently missed by XRD measurements, resulting in incorrect findings. This might lead to ambiguity in mineral identification in bulk natural samples. To circumvent this, a more advanced XRD analysis approach is required.

3.1.1.2 AAS

The AAS is a characterization technique that is most commonly used for determining metallic elements in samples (Manfro et al., 2020). Its observations are based on the absorption of light at a certain wavelength by metal atoms in a free state. The Beer-Lambert law underpins the operation of AAS. However, Lambert Beer's law only applies to "free atoms" which are atoms that are not connected to other atoms. Meanwhile, the atoms in the sample are not free but are bound to other elements, which form molecules.

Meanwhile, the absorption process cannot be performed on molecules since molecules cannot absorb light. As a result, the molecule must be broken down to generate free atoms, a process known as atomization (D. Beaty and D.Kerber, 1993). The connection between the quantity of light absorbed and the concentration of the analyte present in a known standard material may be used to calculate the concentration of the analyte in the sample using a standard solution curve. An energy source (light), an atomizer, a monochromator, and a detector are the essential components of an AAS apparatus. A cathode lamp is utilized (hollow cathode lamp). In most cases, each cathode light detects only one element. The monochromator selects the spectrum of light supplied by the cathode lamp, and the detector receives the spectrum. The detector linked to the device is a photo-electron multiplier, which generates an electric charge proportionate to the intensity of the light emitted. The obtained spectrum is then calibrated with standard values before being processed by computer software (Winckelmann et al., 2022).

AAS instruments are classified as Flame AAS or Graphite Furnace AAS (GFAAS) depending on the atomization mechanism utilized (Butcher, 2021, Hazim et al., 2022, Donati and Jones, 2011). The heating process using a flame and an electric furnace is the most commonly used atomization method. The most common process is flame atomization. Standard gases that are frequently employed as a fuel in this process include air-hydrogen (Marr and Anwar, 1982), air-acetylene (Donati and Jones, 2011), argon-hydrogen (Donati and Jones, 2011), and nitrous oxide-acetylene (Koether, 2002, Paleologos et al., 2000, Dodson et al., 2011). However, this approach has the drawback of low atomization efficiency and sensitivity (D. Beaty and D.Kerber, 1993). Furthermore, the atomization procedure in GFAAS employs cylindrical graphite (Evans et al., 2019), which has a sensitivity of up to 200 times that of a flame (Resano et al., 2019). The atomization process is divided into three steps in this approach. The first stage is the drying stage, in which the graphite is heated to around 100 °C to totally evaporate the water in the sample. The second stage is the ashing stage, in which the graphite is heated to 1000 °C

to break down and evaporate any organic compounds. The final stage is the atomization stage, in which the metal remaining in the cylinder is heated to 3000 °C and atomized. The oxygen from the air and graphite is properly drained by an inert gas to prevent excessive burning of the graphite during heating (D. Beaty and D.Kerber, 1993).

GFAAS features numerous forms of interference, including spectral, matrix, background, and vapor phase interference, which can be induced by the analyte being atomized in a slightly cooler gas environment (Tyler, 2001). The most prevalent types of GFAAS disturbances are spectrophotometric disturbances and physical disturbances. Spectrophotometric interference occurs when the spectral lines employed for analysis are absorbed by elements other than the target element. When the examined sample does not fulfill the relevant quality standards, such as when the viscosity of the sample solution or the face tension is too high, physical disturbances occur. Because of the high viscosity, the sample is not evenly dispersed throughout the graphite cylinder (D. Beaty and D.Kerber, 1993).

The strategy for correcting spectrophotometric interference is mostly caused by a failure to separate the light spectrum or by the molecule's absorption of the light spectrum. The inability to separate the light spectrum occurs when the spectral line is employed for measurement and other neighboring spectral lines overlap. This form of interference is uncommon and may be avoided by picking spectral lines that do not show interference. Light absorption and scattering by unatomized molecules produce interference with the absorbance spectrum of light. Light scattering happens when solid particles travel through light. When the sample is heated, steam is produced. As the wavelength drops, the peak dispersion by vapor rises. This is frequently the case when measuring components with wavelengths of less than 250 nm. To address this, the heating parameters are altered such that more vapor is created during the ashing step, preventing steam formation during the atomization stage. Physical disturbances in the measurement are caused by the sample's physical state since the diffusion of the sample in the graphite cylinder is heterogeneous and generates bias (D. Beaty and D.Kerber, 1993).

The choice of graphite cylinders for GFAAS measurements affects the outcome of the analysis, and this choice depends on the kind of element and sample to be studied. Currently, three varieties of graphite cylinders are in use: pyrolytic coated graphite tube (PCGT), high-density graphite tube (HDGT), and platform type graphite tube (PTGT). HDGT is used to test elements with low atomization temperatures. This sort of graphite cylinder is also employed for poor measurement sensitivity in the event of large sample concentrations. Metal analysis using GFAAS is often conducted in conjunction with pre-treatment of test samples, such as extraction, precipitation, filtering utilizing membranes, ion-exchange chromatography, and so on, to produce appropriate measurement findings (D. Beaty and D.Kerber, 1993, Kawde, Baig, and Sajid, 2016).

3.1.1.3 ICP-OES

ICP-OES is a prominent analytical technique for testing components with higher detection limits than AAS. This sample ionization method employing high-temperature Argon plasma is capable of lowering the detection limit for evaluating the main elements and the majority of trace elements typically utilized in geological research, medicinal studies, and environmental pollution studies.

In general, ICP-OES devices are made up of numerous basic components, including a nebulizer, spray chamber, sample injector, ICP torch, RF generator, optical spectrometer, and detector. The sample is initially put into an inductively coupled argon plasma through a sample injection device, where it is atomized and ionized before being excited (Soltanpour *et al.*, 1996). When electrons return from an excited energy level to a lower energy level, the ions and atoms emit photons. This phenomenon is known as ionic emission or atomic emission. The emission is subsequently collected

in a detector with optical components that can differentiate distinct emission wavelengths based on the properties of each analyte element (Fassel and Knfseley, 1974, Ghosh *et al.*, 2013). The strength of the emission signal at each wavelength is then measured by the detector. This emission wavelength corresponds to the energy difference between the excited and ground states of the electron, and the intensity of the emission signal is related to the element's abundance in the plasma (Fassel and Knfseley, 1974, Khan *et al.*, 2021). Although quantitative dissolving of the sample is required beforehand, this approach is rapid and linear, suited for a wide concentration range, and permits simultaneous elemental analysis at reasonably high resolutions down to the part per billion (ppb) level. However, ICP-OES has certain interference, including spectrum interference, matrix effect, and ionization (Tyler, 2001). Spectral interference on ICP-OES can be observed when a species has a wavelength that is similar to that of the analyte. The wavelengths most typically employed for Li detection are 460.29 nm (Lürenbaum *et al.*, 2020), 610.35 nm (Laczai *et al.*, 2016, Resano *et al.*, 2019, Malik, Chan, and, Azimi 2021) and 670.78 nm (Z. Wang *et al.*, 2014). However, this ICP-OES technology has higher operating and maintenance expenses than AAS.

3.1.1.4 ICP-MS

ICP-MS is a highly sensitive analytical technique that can be used to measure multi-elements at trace levels, typically in liquid samples, but can also be performed directly on solid samples by using Laser Ablation ICP-MS (LA-ICP-MS), (Sylvester and Jackson, 2016, Schlöglöva, Wälle, and Heinrich, 2017, Yu *et al.*, 2021). This substantial advancement in ICP-MS instrumentation technology can enable reliable analysis with significantly lower detection limits than optical emission spectrometry (Houk *et al.*, 1980, Date and Gray, 1985, Meermann and Nischwitz, 2018).

In general, a single quadrupole ICP-MS has six fundamental compartments: sample identification system, ICP, interface, ion optics, mass analyzer, and detector. First, the liquid sample is nebulized in the sample recognition system, producing a fine aerosol that is subsequently transported to the argon plasma. High-temperature plasmas can atomize and ionize materials, producing ions that are subsequently extracted via the interface area and into a series of electrostatic lenses known as ion optics. This ion optic concentrates and directs the ion beam into the quadrupole mass analyzer. The ions are separated by the mass-charge ratio (m/z) in the mass analyzer. The ions then reach the detector and are examined in the form of a signal big enough to be accurately determined as the amount of analyte ion (Thomas, 2013). ICP-MS detection limits for solutions are typically in the 1–10 parts per trillion (ppt) range. It performs as well as or better than GF-AAS for the majority of the components in the water sample and includes more elements (Wysocka, 2021). ICP-MS generally has a detection limit of two to three times that of ICP-OES, with most elements falling within the 1–10 parts per billion (ppb) range. ICP-MS, on the other hand, has some interference, including spectrum interference, matrix effect, ionization, and doubly charged ions. Spectral interference in ICP-MS can occur when a species has a mass comparable to the analyte and the spectrometer resolution cannot handle it properly. For example, ^{58}Ni species can behave as interference for ^{58}Fe analytes (Tyler, 2001, Wilschefski and Baxter, 2019). Unfortunately, in addition to the high cost of standard reference materials, ICP-MS also has higher operating and maintenance expenses than AAS and ICP-OES. Then it cannot be done in situ or in real-time analysis in the field.

3.1.1.5 LIBS

LIBS is an analytical technique that employs a low-energy pulsed laser with tens to hundreds of millijoules (mJ) per pulse. It also has a focus lens to generate plasma, which vaporizes a small number of samples, which can be gas, liquid, aerosol, or solid, to make microplasma. An optical cable collects

a portion of the plasma light and directs it to the spectrometer. The light released by excited atoms, ions, and simple molecules in the plasma is then scattered by the spectrometer. The intensified coupled charge device (ICCD) detector system then records and analyzes the emission signal to digitize and show the findings (Fabre *et al.*, 2002, Pamu *et al.*, 2021).

However, the underlying physical and chemical processes are not that straightforward. The process of starting, producing, and dying laser plasma is exceedingly complicated. The reverse Bremsstrahlung process, which involves three-body collisions between photons, electrons, and atoms or molecules, is used to absorb incoming laser energy. Plasma creates shock waves in the surrounding medium and transmits energy via conduction, radiation, and shock waves in gases and liquids. It is also complicated to excite certain energy levels in distinct atoms. This is determined by variables such as thermodynamic equilibrium and interactions with other atoms and molecules, all of which are classified as matrix effects. The plasma decays in one to several microseconds after the laser pulse is ended, depending on the amount of laser energy stored. That temporary process is sped up in a vacuum. The majority of LIBS studies utilize repeated plasma at 10 Hz or higher. The optimization of the analysis findings is greatly reliant on the parameters of the plasma production and detection processes. Several factors influence plasma formation, including laser type, sample type, and buffer gas pressure (Fabre *et al.*, 2002, Cremers and Radziemski, 2013).

The LIBS system includes a sample holder that can move independently in three dimensions due to an electric motor. A computer operates and controls an optical multichannel analyzer (OMA) system. A set of filters is employed to alter the energy of the laser beam. The sample is located in the sample chamber. The samples were examined under one atmosphere of pressure. The LIBS technique has several advantages, including the fact that it does not destroy the sample, does not require sophisticated sample preparation processes, and can analyze all components in a sample at the same time (Cremers and Radziemski, 2006, Abdulmadjid *et al.*, 2015).

Pamu *et al.* (2021) indicated that external calibration processes that rely on matrices for quantitative analysis utilizing LIBS present difficulties. Quantitative LIBS analysis is achievable with calibration curves for each sample element, with the calibration curve constructed using the same matrix as the reference material. For improved accuracy, the matrix composition and measurement circumstances for the reference material must be similar to those for the target element. It is frequently difficult and time-consuming to create reference samples with similar matrices under such conditions. Calibration-Free-LIBS (CF-LIBS) is an alternative methodology that employs an internal calibration process and is particularly beneficial because it does not require an external calibration curve. The Maxwell-Boltzmann equation is used solely in this approach to connect the empirically observed atomic emission intensity to the elemental population density normalized by the internal mass standard within the plasma matrix itself. Pamu *et al.* (2021) published the findings of their study on the use of LIBS for the effective and efficient quantitative spectrochemical characterization of a layered Lithium metal oxide cathode comprising Mo and Cr dopants using an internal calibration approach. Precise quantitative determination of the composition of advanced electrode materials, including trace levels of dopants, will give critical information for creating high-capacity battery materials. The quantitative elemental ratio of main transition metals and trace dopants to bulk lithium concentration in several samples of sol-gel cathode materials was determined using an internal calibration process. The resultant emission lines reflect the spectral fingerprints of the target material elements, which reveal quantitative information and plasma properties after processing. Based on quantitative LIBS characterization results that indicate a satisfactory agreement between the elemental composition measured by LIBS and the computed stoichiometric value (Pamu *et al.*, 2021).

Furthermore, according to [Fabre et al. \(2002\)](#), lithium is a critical geochemical tracer for liquids and solids. In optical emission spectroscopy, the intensity of the lithium emission line at 670,706 nm was utilized to refine the analysis of lithium on a micrometric scale using LIBS. The LIBS calibration of the emission line at 670,706 nm was accomplished using synthetic glass materials and natural minerals to determine lithium amounts in various geological materials. Using LIBS, the Li₂O concentrations in spodumene and petalite from pegmatite granite dikes were 7.6 wt% and 6.3 wt%, respectively. The LIBS analysis results are consistent with the standard and microprobe data obtained for the same material. On the other hand, the analysis of eucryptite is inaccurate owing to a snug association with other minerals on a micrometric scale, and the grain size is smaller than the LIBS spatial resolution, resulting in the dilution of significant quantities of lithium concentration. The lithium concentrations in the melt inclusions from the Streltsovka deposit range from 2 to 6.2 wt% Li₂O for lithium-rich derived minerals. Estimates of lithium on silicate glass range between 90 and 400 ppm. This estimate is consistent with what can be deduced from the empirical EPMA formula for platy minerals. Thus, LIBS analysis is very interesting for magma geochemical characterization, exploration, and determination of lithium partitions between minerals and melts, particularly in the investigation of rare metal deposits. In addition, lithium has been identified as a trace element in quartz. Transverse profiles were taken in a barren hydrothermal quartz vein in the Sierra de Guadarrama, with lithium content ranging from 250 to 370 ppm. The fluid responsible for the enrichment of lithium in the quartz is most likely a high-salinity fluid from sedimentary basins. The LIBS approach, as compared to the electron microprobe technique, provides a direct determination of lithium with a lower detection limit of around 5 ppm at a somewhat lower spatial resolution of roughly 6 to 8 µm. LIBS's advancement in lithium analysis provides a new stride in accurately identifying lithium at trace element levels in minerals. Other trace elements can also be detected using the LIBS approach ([Fabre et al., 2002](#)).

3.1.2 Spectrophotocemical-based sensors

3.1.2.1 Remote sensing

Cardoso-Fernandes et al. (2019) have reported the results of their study to detect lithium with a remote sensing method approach that is used to describe exploration target areas for several types of deposits, especially those located in remote areas. This methodology has been used to detect several minerals indicated to contain lithium, especially pegmatite minerals. This study presents an innovative methodology that can detect indications of the spectral presence of lithium-containing pegmatites and a remote sensing algorithm used to identify light spectrum changes associated with pegmatite features. Therefore, in this study, we used Landsat5, Landsat8, Sentinel2, and ASTER images. Then, remote sensing techniques used include a combination of RGB, bandwidth ratio, and selective principal component analysis (PCA). This method can detect several hydrothermal alterations associated with lithium-containing pegmatites. The selective combination of RGB and PCA has been shown to be more effective than the band ratio in emphasizing areas of change. Band ratio is an excellent strategy for identifying and mapping compositional differences between different lithofacies. All combinations of RGB, band ratio, and selective PCA can distinguish the spectral signature of the pegmatite from the spectral signature of the lithium-containing source rock. ASTER's higher spectral resolution allows for better mineral identification. On the other hand, this method has a limitation in that Sentinel2 does not have a thermal band, which prevents it from being different from lithium-containing pegmatites when using only RGB combinations. In the future, other remote sensing techniques such as spectral unmixing and image classification algorithms can be tested to improve the proposed methodology. Validation

and verification with field geochemical data and collection of typical spectral data for each mineral are also required to increase geological confidence (Cardoso-Fernandes, Teodoro, and Lima, 2019).

3.1.2.2 Optical-Based Lithium Sensor

Elise Villemin and Olivier Raccurtstudi., 2021 explain the results of their study on the development of technology to detect lithium using a calorimetric or luminescence method approach. The method was used to identify signal changes that correlated with the lithium concentration contained in the sample. The advantages of using the optical method are the fast detection process, easy maintenance, and the lack of any electrode needed for sample analysis. There are several techniques for controlling the optical properties of spectrophotocatalytic-based sensors, namely the formation of complex compounds and the use of nanoparticles. The nanoparticles act like chromophores, which are sensitive to the refractive index of the surrounding environment. Then, the Localized surface plasmon resonance (LSPR) frequency is also highly dependent on the local environment of the precious metal nanoparticles, such as the refractive index of the solvent. Furthermore, the development of optically based lithium sensors for in vivo and in-situ applications remains an exciting challenge due to various requirements such as sensor reversibility, response time, and good sensor stability over a large temperature range. The intrinsic physical properties of lithium cations, such as their small size and high charge density, are largely responsible for their difficult coordination ability and low selectivity to alkaline cation interference. Then, another problem is that the synthesis of ligands or complex compounds is difficult and time-consuming (Villemin and Raccurt, 2021).

3.2 Lithium Analysis by Electrochemical Approaches

Electrochemistry is one of the analytical methods based on the reduction and oxidation reactions that take place at the electrodes in an electrochemical cell system. Many applications of electrochemical cells are used to create new analytical techniques. Electrolysis cells and voltaic cells are the results of the application of electrochemical cells using electrode media and electrolyte solution. Currently, electrochemical cells still play an important role in the latest technological advances in the automotive, environmental, mining, and medical industries. One of the common techniques that is widely used as the basis for making sensors are potentiometry and voltammetry.

Potentiometry is a quantitative method for identifying analytes in a solution based on electrochemical principles. The potentiometric approach offers various advantages, including low cost, quick analysis, and excellent accuracy and selectivity (Abd-Rabboh *et al.*, 2021). The potentiometric technique is made up of multiple parts, including a working electrode, a reference electrode, a salt bridge circuit, and a voltage meter. The usage of potentiometric sensors has risen fast, with paper-based sensors currently being used in various applications such as pharmaceutical, medical, environmental, and geological investigations (Manjakkal, Dervin, and Dahiya, 2020, Kamel *et al.*, 2021). Voltammetry, on the other hand, is an analytical technique widely used in various fields, including medicine, environmental science, and mining. The current from the working electrode is monitored as a function of potential in this approach. The benefit of this approach is its excellent sensitivity across a wide concentration range, which is useful for both organic and inorganic species analysis (J. Wang, 2001; Szłósarczyk *et al.*, 2021).

Voltammetric methods are often employed in quantitative analysis, oxidation and reduction reaction studies in a variety of media, reaction mechanism investigations, electron transfer kinetics studies, and other studies. The voltammetry cell is made up of three electrodes: the working electrode, the reference electrode, and the auxiliary electrode. The oxidation or reduction processes that occur at

the working electrode are affected by the applied voltage. Saturated calomel and Ag/AgCl electrodes are commonly employed as reference electrodes. Because it is inert, the platinum electrode is the most commonly used auxiliary electrode. However, this approach is still relatively restricted in its application for measuring the lithium content in a sample. This is both a problem and an opportunity for researchers to develop lithium analytical methods based on electrochemical principles, particularly voltammetry and potentiometric approaches. The benefits of this technology include the ability to perform in-situ analysis, which is easier, quicker, and more user-friendly. Thus, this approach can avoid the expense of delivering samples from the field and can be utilized for routine monitoring of bipolar disorder patients.

Lithium metal has a low density, a really high theoretical specific capacity, and a redox potential of roughly -3.04 V (versus Standard hydrogen electrode “SHE”) (F. Ding *et al.* 2013, Song *et al.*, 2014, Q. Wang *et al.*, 2021) and 0.86 V (versus Saturated calomel electrode “SCE”) (Kushwaha *et al.*, 2017, A L Suherman *et al.*, 2019). These properties may be utilized to construct analytical procedures based on voltammetry and potentiometry, which measure numerous electrical parameters (potential, current, charge, and conductivity) in correlation to chemical parameters (reaction or concentration). The following is a review of some of the literature that develops analytical techniques based on electrochemical principles for diverse domains of application.

3.2.1 LMO-Modified Electrodes for Lithium Detection

Suherman *et al.*, (2019) published the findings of their study on electrochemical sensors using voltammetric techniques used to detect lithium ions in human saliva using glass carbon electrodes modified by lithium manganese oxides (LMO-GCE) and screen-printing electrodes modified by lithium manganese oxides (LMO-SPE). The LMO-GCE was made by drop casting 5.0 μl of LMO slurry and annealing it for 10 minutes at 65 °C to evaporate the solvent (Alex L. Suherman *et al.*, 2019).

The sensing technique is based on the first galvanostatic delithiation of the LMO, followed by linear stripping voltammetry (LSV) to detect the reinsertion of lithium in the analyte. This technique was examined using X-ray diffraction and voltammetry. The LSV measurements revealed a lower measurable limit of LMO-SPE and excellent sensing performance in detecting lithium ions contained in human saliva. In both LiClO_4 solution and synthetic saliva, LMO-SPE showed good selectivity against the possibility of interference from other cations, with a sensitivity value of 50.0 μM . Subsequently, four different samples of human saliva were analyzed by LMO-SPE. Based on the results of LMO-SPE analysis, good linearity was shown in the lithium concentration range up to 5.0 μM and high reproducibility. In addition, LMO-SPE showed that the total time required to analyze the sample was less than 3 minutes (Alex L. Suherman *et al.*, 2019). Unfortunately, this technology has only been studied and developed to determine lithium in saliva. More study is needed into monitoring lithium levels in the environment and geological surveys so that it can be utilized in line with the operational range of lithium levels in nature.

3.2.2 Ion-selective electrode based on nanoparticles

Criscuolo *et al.* (2018) used precious metal nanostructures as ion-to-electron transducers to create Ion-Selective Electrodes (ISEs) for detecting lithium (Criscuolo *et al.*, 2018). Precious metals provide significant benefits over conductive polymers and carbon for ion-to-electron transduction. For the first time, gold nanocorals formed in a quick one-step electrochemical deposition procedure were employed as Solid-Contact, and they were compared to platinum nanoflowers created in the same way. The nanostructured Solid-Contact suggested in this study has various benefits, including a quick deposition

procedure, excellent stability, and non-toxicity, allowing it to manufacture high-quality and stable ISEs for other target ions in a range of applications. The morphology and cross-sectional area of the electrode surface were characterized using Scanning Electron Microscopy (SEM) before and after the electrodeposition procedure. Meanwhile, Current Reversal Chronopotentiometry (CRC) and Cyclic Voltammetry (CV) were utilized to assess the sensor's electrochemical performance. According to the study findings, the sensor exhibits Nernstian behavior (58.70.8 mV/decade) in the operating range of 10^{-5} M to 0.1 M and has a reaction time of 15 seconds. The sensor has great selectivity for all clinically significant ions, with readings that are quite comparable to traditional ISE measurements (Criscuolo et al., 2018).

3.2.3 Ion-selective electrode based on Metal-Organic Framework (MOF)

Abdollahzadeh et al. (2022) have developed an ion-selective electrode for the detection of lithium ions using Nickel Hexaaminobenzene-MOF (NiHAB-MOF) as an ion-to-electron transducer (Abdollahzadeh et al., 2022). The structure of NiHAB-MOF was confirmed using XRD, SEM, Fourier Transform Infrared Spectroscopy (FTIR), and Energy Dispersive Spectroscopy (EDS). MOF-GCE was made by the drop-casting method. For degassing purposes, 40 μ L of MOF suspension was dropped on the surface of the GCE and dried in a vacuum. Furthermore, the modification using an ion-selective membrane (ISM) was prepared by dropping a membrane cocktail on the sensor and drying it under a vacuum similar to MOF-GCE under the same conditions to obtain GCE-MOF-ISM. The sensor performance and the effect of MOF thickness were characterized using the Electrochemical Impedance Spectroscopy (EIS) technique.

Based on research data, the addition of NiHAB-MOF has shown an increase in capacitance. Then, adding the thickness of the MOF provides the best performance in terms of stability and sensitivity of the sensor. The sensor has shown excellent output stability and detection limit. In addition, this sensor also shows a good sensitivity of 57.56 mV/dec and provides high reproducibility. The sensor is tested to determine the concentration of lithium ions in the synthetic salt solution. To measure the concentration of Li^+ ions in synthetic brine, the sensor is calibrated with a high ionic strength similar to that of real brine. After that, the Li^+ concentration was measured by matching the measured potential with the sensor calibration curve. In this brine, the concentration of Na^+ ions is much higher than that of Li^+ and can affect the sensor output. Apart from Na^+ and Li^+ , other ions such as K^+ , Mg^{2+} , Ca^{2+} , and Cl^- are also present in the synthetic brine, which may affect sensor performance. However, research data shows that the lithium-ion concentration measured by the sensor in saltwater is 2.2×10^{-1} M. The measured value is close to the current value of 2.1×10^{-1} M (2 Abdollahzadeh et al., 2022).

3.2.4 Lithium sensors based on ionophores

Kothur et al. (2016) published the research findings on a newly synthesized copillar [4+1] arene derivative. The ionophore chemical is then employed to modify the gold electrode's surface. Dip-coating is a technique for attaching ionophore chemicals to the surface of gold electrodes. The electrode was modified in a glass tube with just the gold surface in contact with the organic reagent. It can also be used to protect gold nanoparticles. The two thiol groups attached to the gold surface allow the ionophore to lie parallel to the surface, allowing guest species to flow through. The capacitive signal was characterized using cyclic voltammetry at 1×10^{-2} mol / L alkali metal salt solution. The ionophore's electrochemical reaction to alkali metal salt revealed a significant selectivity for lithium over other cations. All cyclic voltammetry measurements were performed with an Ag|AgCl reference electrode and a platinum wire counter electrode (Kothur et al., 2016, Kamenica et al., 2017).

3.2.5 Ion-selective electrode based on Conductive Polymer Sensors

Lindino (2011) published his findings on the development of lithium sensors using poly(o)-methoxyaniline-modified electrodes, demonstrating that the electrode modified with a conducting polymer could detect lithium ions in solutions ranging from 1.0×10^{-5} to 1.0×10^{-4} mol/dm³ (Lindino *et al.*, 2012). Then the results were confirmed by standard methods using atomic emission spectrophotometry. The results show that the presence of lithium in the solution has a significant impact on the electrochemical properties of poly (o-methoxyaniline) as well as sensor performance. The ease of polymerization of o-methoxyaniline and its response to lithium ions allows the fabrication of microsensors that can be used in situ. Then, the use of optimal flow injection analysis is suggested to reduce the contact time between the conductive polymer and lithium ions (Lindino *et al.*, 2012).

4. Lithium detection applications

4.1 Lithium estimation in geological exploration applications

One of the cornerstones of geochemistry's growth is understanding the composition of major, minor, and trace elements in Earth's substance. Trace elements, including lithium, play an important role in the characterization and overcoming of numerous issues of chemical and petrogenic variability of earth materials in all types of magma systems. Thus, fluctuations in trace element concentrations and elemental ratios are one of the keys to understanding the phenomena of the creation and progress of a rock formation or ore deposit so that geological maps and mitigation studies of volcanic eruptions and other geological catastrophes may be created (Alvarez *et al.*, 1980, Rohiman *et al.*, 2017, Rohiman *et al.*, 2019). Trace elements are also significant in geochemical modeling, which may be used to explain and estimate prospective reserves of natural resources, allowing for cost-effective exploration and utilization. Lithium is one of the most in-demand natural resources. Demand for lithium and related compounds has grown by around 10% in the last decade (Yelatontsev and Mukhachev, 2021). An effective and efficient exploration analysis technology is required to fulfill market demand. Generally, in the early phases of exploration, a qualitative lithium analysis is performed to serve as the foundation for outlining geological maps that lead to lithium-containing rock sources. Then, for quantitative lithium analysis, a representative sample is performed more precisely and in detail. Additionally, the quantitative analytical data is utilized to calculate the potential for lithium deposits.

Lithium is predominantly reported in earth's crustal rocks and brines (Hal Aral and Vecchio-Sadus, 2008, Flexer, Baspineiro, and Galli, 2018, Razmjou *et al.*, 2020). Geothermal brine is an important source of lithium that may be recovered (Razmjou, Asadnia, *et al.*, 2019, G. Liu, Zhao, and Ghahreman, 2019, Ahmadi *et al.*, 2021). Before geothermal brines can be commercially extracted, they are generally investigated and studied to determine their lithium content. The concentration of lithium in geothermal brine ranges from 1 to 100 ppm, but the concentration of lithium in saltwater is around 0.17 ppm or approximately 170 ppb (Flexer, Baspineiro, and Galli, 2018). Based on the most recent predictions, saltwater will quickly become one of the most important sources of lithium (Vikström, Davidsson, and Höök, 2013, Battistel *et al.*, 2020). The quantity of lithium in brine is about 200 to 700 ppm (Razmjou, Asadnia, *et al.*, 2019).

Due to the growing usage of lithium in numerous industries, lithium extraction has earned massive attention and is fast increasing (G. Liu, Zhao, and Ghahreman, 2019). Lithium extraction may be uneconomically dependent on the concentration of lithium; hence, determining lithium from natural sources is critical for decision-makers. The rapid and precise detection of lithium has become an

essential sector for exploration efforts for new lithium sources in order to accommodate the lithium industry's demands.

AAS methods are commonly used to measure lithium levels in a sample (Yogendra Kumar *et al.*, 2007, Mubarak *et al.*, 2021, Abbas *et al.*, 2021); Atomic emission spectroscopy (AES) (Yildirim *et al.*, 2020); colorimetric (Komatsu *et al.*, 2020); ICP-OES (Parchami *et al.*, 2020, Kröger *et al.*, 2021); ICP-MS (Voica, Roba, and Iordache, 2021); ICP-AES (Pathak *et al.*, 2019) ; XRF (Balaram, 2021); and XRD (Pöllmann and König, 2021). The common procedure for analyzing lithium in samples has been to undertake a sampling process in the field and then test them in the laboratory to determine lithium levels. This procedure takes a long time, a lot of chemicals are costly, and it involves specialized sample management. As a result, alternative technologies that are inexpensive, real-time, and accurate are required. It is a fascinating task to build a new approach that is trustworthy and can be measured in situ.

According to Cardoso-Fernandes (2019), remote sensing technologies may be the solution to this challenge because they have been shown to be a valuable resource for identifying exploration target regions for various types of deposits (Cardoso-Fernandes *et al.*, 2019). Since the 1970s, remote sensing has been employed in mineral discovery worldwide. The majority of research focuses on the use of remote sensing in gold prospecting (Moradi *et al.*, 2015). This technology offers relatively quick and affordable information, and it may be employed in exploratory efforts, particularly in difficult or isolated locations.

However, H.M. Rajesh (2004) argues that in its application, it is difficult to evaluate mineralization directly using just remote sensing data and underlines the significance of integration with other forms of geological data (H.M. Rajesh, 2004). Then, Cardoso-Fernandes, (2019), indicated that both the alteration mapping and the findings of the lithium pegmatite mapping revealed various things depending on the area or image processing method used (Cardoso-Fernandes *et al.*, 2019). This shows a lack of automated techniques to target lithium mineralization. Other challenges mentioned include spectrum confusion with metropolitan areas and agricultural fields, as well as spectral noise caused by pixel-level mixing. The difficulty is naturally induced by the limited spectral and spatial resolution.

Thus, it is very important to choose the right analytical method to determine the cost of exploration activities more efficiently. Initial exploration activities can use handheld instruments or sensors for lithium analysis so as to reduce shipping costs and sample analysis. Meanwhile, exploration activities in remote areas or those that are difficult to access can use satellite imagery in the initial survey. After knowing the direction of the outcrop containing lithium, a more detailed sampling was carried out and analyzed using more accurate instrumentation and precession in the laboratory.

4.2 Determination of lithium in medicine and environmental monitoring

Elemental lithium's biological, medicinal, and environmental consequences have gotten a lot of attention over the years. ICP-AES has been used effectively over the past decade to determine reference values for lithium concentrations in urine. Given the short biological half-life of elemental lithium and the fact that the primary route of excretion is through the kidneys and urine, the kidneys and urine are considered ideal materials for measuring lithium exposure. The geometric mean reference value for lithium is 23.5 µg/l (11.0–50.5 g/l) with a 95 percent confidence interval of 23.5 µg/l (Usuda *et al.*, 2007).

Recently, sustained technological advances in the chemical industry have created several prospects for using lithium in a variety of applications, including battery materials, electronic gadgets, and electric vehicle technology. As a result, the majority of the linked studies evaluated have given close

attention to mining exploration and the health impacts of this element (Schrauzer 2002, Grandjean and Aubry, 2009, Avila-Arias *et al.*, 2019, Sogawa *et al.*, 2021). For that purpose, in this review paper, we discuss the reference value and lithium analysis methods that have been developed to screen patients at risk and provide an early diagnosis of lithium waste exposure.

Clinicians and researchers receive assistance from reference values (background exposure levels), since levels over the reference range generally indicate exposure to a specific source. There have been few studies to date on acceptable analytical procedures and reference values for lithium in human biological samples, which are essential for appropriately measuring nutritional intake and diagnosing occupational exposure. ICP-AES is a powerful and sophisticated technology for determining concentrations in a wide range of biological fluid specimens. This approach features a low detection limit, the capacity to do simultaneous multielement analysis, and a large linear calibration dynamic range (Zhang *et al.*, 2019, Pathak *et al.*, 2019, Balaram, 2021).

Lithium is a common element in plants, animals, and people at tiny levels. According to the US EPA, the typical daily lithium consumption ranges from 650 to 3100 µg/day (U.S.EPA, 2008) (U.S.EPA, 2008). Lithium was discovered in human organs and fetal tissues in the late 1800s, prompting early speculation that it could be necessary for humans. However, the use of lithium carbonate in the treatment of high blood pressure precedes the study of lithium as an essential micronutrient. As a result, Schrauzer predicts that evidence of lithium's importance will not be available for another century (Usuda *et al.*, 2007).

The portable electronics sector is still expanding, and the demand for rechargeable batteries has boosted the demand for lithium (Kang *et al.*, 2006; Y. Ding *et al.*, 2019). Lithium compounds, which are very corrosive and represent a major risk to people, are found in lithium-based batteries (Iwai *et al.*, 2021). Lithium salt, in addition to its employment in high-tech industries, is also utilized as a treatment for bipolar disorder sufferers (Scott, Etain, and Bellivier, 2018, Patrick *et al.*, 2020, Komatsu *et al.*, 2020, Santos *et al.*, 2021, Iwai *et al.*, 2021, McGhee *et al.*, 2021, Hsu *et al.*, 2021). Chile is the world's largest producer of lithium metal, followed by China (Gil-Alana and Monge, 2019). Several current studies have raised severe concerns regarding the dangers of lithium exposure from a contaminated environment (Figuerola *et al.*, 2012, Shahzad *et al.*, 2016, Shahzad *et al.*, 2017, Shao *et al.*, 2017, Viana *et al.*, 2020, Gao *et al.*, 2021, Jing, Zhang, and Gao, 2021, Török *et al.*, 2021, Sogawa *et al.*, 2021, Bhattacharyya *et al.*, 2021, Verdoux *et al.*, 2021).

To preserve and protect human health, the American Conference of Governmental Hygienists (ACGIH) establishes permissible exposure limits (PEL) of 0.025 mg/m³ and an immediately dangerous to life or health concentration value (IDLH) of 50 mg/m³ for lithium hydride. Occupational Safety and Health Administration (OSHA) has established the time-weighted average (TWA) for work environment air quality recommendations at 0.025 mg/m³, while the EPA advises that lithium concentrations in drinking water sources not exceed 0.70 mg/l (U.S.EPA, 2008). More than 90% of the lithium in the human body is removed by the kidneys (Grandjean and Aubry, 2009). It has been observed that the half-life of lithium in human serum is less than 24 hours (Grandjean and Aubry, 2009). Because of these characteristics, urine is a good material for screening for lithium exposure.

In addition, bipolar-disorders affect approximately 2% of the world's population (Santos *et al.*, 2021; Tomasik *et al.*, 2021). Meanwhile, the estimated number of Indonesians with bipolar disorder is over 6 % of the Indonesian population (Maramis *et al.*, 2017, Gunawan, Satiadarma, and Idulfilastri, 2020, Wirasugianto *et al.*, 2021). Lithium is a medicine still used in psychiatric therapy to help people with bipolar disorder reduce risk factors (Komatsu *et al.*, 2020). Furthermore, in clinical practice, lithium's anti-aggressive and suicide prevention abilities are well proven. However, little is known

about the trace distribution of lithium and its metabolic consequences in the human body. Schoepfer et al. (2021) developed a novel approach (the “NIK” neutron-induced coincidence method) based on the ${}^6\text{Li} (n,) {}^3\text{H}$ reaction to identify lithium traces in untreated human brain tissue in a position-sensitive, 3D spatially produced way (Schoepfer et al., 2021). The NIK technique maps the distribution pattern of endogenous lithium concentration in distinct areas of the human brain using Prompt Gamma Activation Analysis (PGAA). The findings demonstrate that lithium has an anisotropic distribution, exhibiting homeostatic control under physiological settings and a remarkable correlation with essentiality. According to empirical evidence by Schoepfer et al., (2021), endogenous lithium concentrations are significantly relatively high in brain areas regulating suicidal feelings and lower in brain regions modulating emotions in suicide (Schoepfer et al., 2021, Lichtinger et al., 2013).

Thus, the ability to detect lithium ions selectively and reliably in both medical and environmental samples is a critical and fascinating problem for researchers. This is mostly connected to lithium’s position as a therapeutic medication for neurological illnesses. However, providing bipolar disorder patients with the correct dosage is critical. This is due to lithium’s relatively limited therapeutic index range of roughly $0.6 \times 10^{-3} \text{ mol.dm}^{-3}$ to $1.2 \times 10^{-3} \text{ mol.dm}^{-3}$. If the dose is too low, the drug’s impact is less effective. Meanwhile, administering a large dosage with a concentration greater than $1.2 \times 10^{-3} \text{ mol.dm}^{-3}$ is possibly hazardous and can harm the patient (Stubing et al., 2016). Since pharmacokinetic profile is unique, serum lithium levels should be monitored regularly to avoid unwanted side effects. Therefore, rapid action to respond to fluctuations in lithium concentration is required. Thus, a lithium sensor with excellent selectivity and accuracy in a working range matching the therapeutic range of lithium is required. One of the major obstacles in the development of lithium sensors is the ability to measure the therapeutic amount of lithium from the sensor without interference by sodium ions, which include roughly 0.15 mol.dm^{-3} sodium at healthy levels in the blood serum (Kamenica et al., 2017). Portable systems based on the chemical and physical properties of lithium, interfering ions, and sensor technology based on ion-selective electrodes may be constructed to enable more precise in situ detection of lithium and can be utilized anywhere, even in isolated places.

4.3 Future directions in lithium research and the advancement of analytical methods

Scientific publication is one phase in the development of research and technology that relies on peer review to assure validity and objectivity (Panori et al., 2019, J. Liu et al., 2021). Thus, bibliometric analysis methods may be employed to acquire the intellectual structure of past works on the determination and analysis of lithium in a sample. This approach requires the identification, collection, sorting, and processing of relevant articles to extract key information that may be utilized as a foundation for further development and study with a high level of originality (Casillas and Acedo, 2007; Mora et al., 2017; Hirawan et al., 2022).

The scientific literature on lithium determination and analysis is drawn from the Scopus database, which is one of the most recognized index databases globally and collects high-quality bibliographic information on publications in various disciplines (Yang et al., 2013; Li et al., 2019). The dataset was retrieved on February 11, 2023, and the document type is limited to “articles” and “conference proceedings”. As a result, a total of 4,873 publications were obtained. Then, to see the trend of research interest regarding the determination and analysis of lithium, which is currently being carried out and has been carried out, data from the publications in the last five years are taken. It should be noted that if the same capture mode is used on another day, the results obtained will be slightly different. This is mainly associated with continuous updates to the Scopus database, resulting in changes all the time as new publications are added (X. Liu et al., 2012).

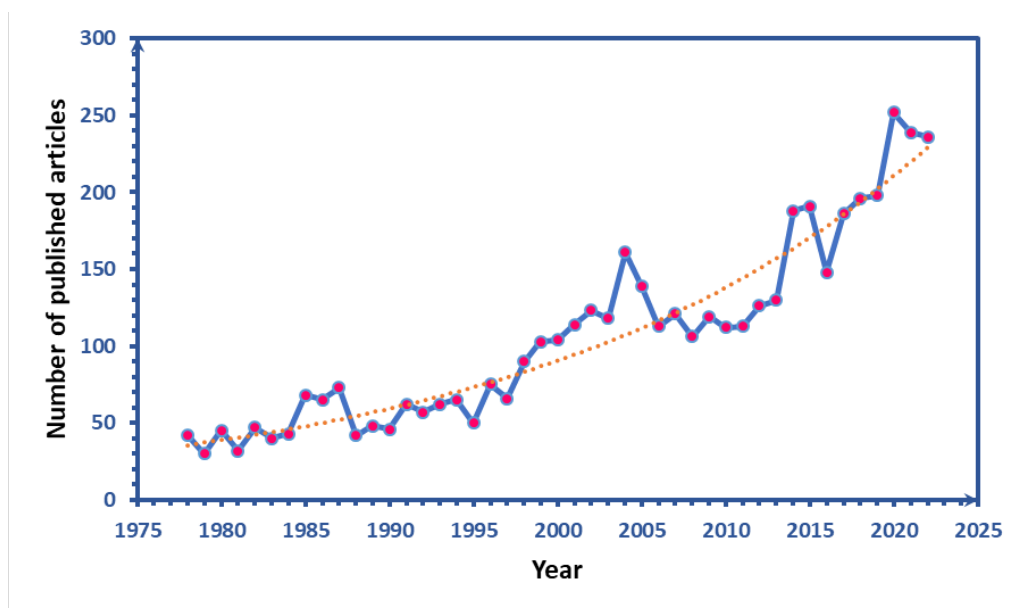


Figure 1. The chronology of trends in lithium analysis articles from 1978 to 2023.

According to the results of data processing literature, lithium research has expanded dramatically. This is supported by the growing number of lithium-related scholarly papers, as seen in **Figure 1**. It demonstrates that the greatest increase and growth happened in 2020, with 252 publications, representing a 12.83% increase over the previous 10 years. The years 2021 (239 publications, or 12.17%) and 2022 (236 publications, or 12.02%) followed. Because the world's fossil energy supplies continue to dwindle, this trend implies that lithium is still in high demand, particularly for battery raw materials and the conversion process from fossil fuel cars to electric vehicles. **Figure 2a**, shows that the United States ranks first as a country that intensively conducts research on lithium. Meanwhile, Germany followed in second place as the country most interested in conducting research and development on lithium. Furthermore, the Center national de la recherche scientifique (France) is the first research institution to conduct research on lithium, with a total of 140 scientific publications as shown in (**Figure 2b**). The Chinese Academy of Sciences comes in second, with 92 articles published.

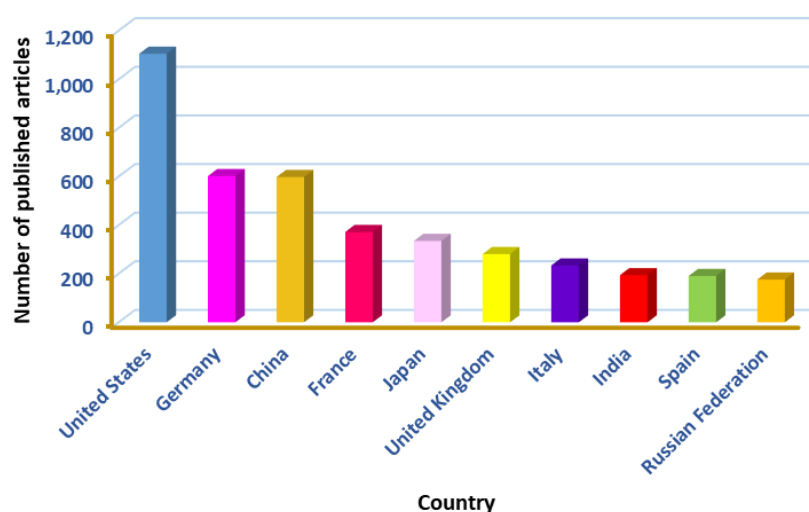


Figure 2a. The world's top 10 countries with a strong interest in lithium analysis research

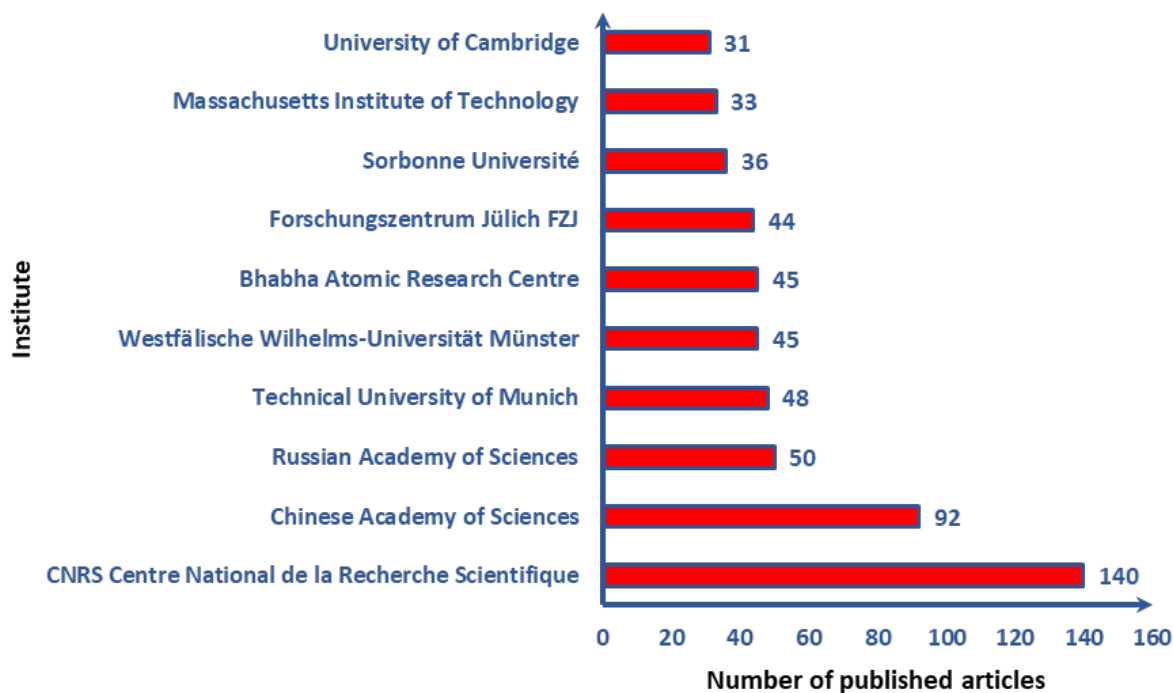


Figure 2b. The top ten institutes in the world with a strong interest in lithium analysis research

Furthermore, **Figure 3** shows a map of the development of research publications on lithium analysis based on research collaborations between countries indexed by Scopus from 1978 to 2023. The figure clearly shows seven clusters. Cluster 1 is colored red and consists of the Russian Federation, Croatia, the Czech Republic, Iran, Ireland, Israel, Kazakhstan, Romania, Serbia, Slovakia, and Slovenia. Cluster 2 is green, consisting of Malaysia, Algeria, Egypt, Iraq, Pakistan, Saudi Arabia, South Korea, Tunisia, Turkey, and the United Arab Emirates. Cluster 3 is blue, consisting of France, the United Kingdom, Italy, Spain, Chile, Denmark, Lithuania, Poland, Portugal, and Sweden. Cluster 4 is yellow, consisting of the United States, China, Japan, Belgium, Canada, Finland, Indonesia, and Singapore. Cluster 5 is purple, consisting of Germany, India, Australia, Bulgaria, Nigeria, South Africa, Taiwan, and Vietnam. Cluster 6 is colored cyan, consisting of Austria, Greece, Hungary, the Netherlands, Norway, and Thailand. Furthermore, Cluster 7 is colored orange and consists of Argentina, Brazil, Mexico, Switzerland, and Ukraine.

Meanwhile, the number of research publications on lithium-based Scopus-indexed subject areas from 1978 to 2023 shows that chemistry is the most popular subject. Then, it is followed by the subjects of material science, physics and astronomy, biochemistry, engineering, medicine, and energy. **Figure 4a** shows that the subject of most publications is chemistry, with as many as 2,381 articles (24.72%). The subject of material science was next, with 1,094 articles (11.36%). Meanwhile, the National Natural Science Foundation of China is the largest funder of research on lithium, with a total of 170 articles (25.30%) published as shown in **Figure 4b**. This was followed by the National Science Foundation and the U.S. The Department of Energy has 95 articles (14.14%) and 79 articles (11.76%), respectively. Furthermore, **Figure 5** shows that articles and conferences are the most popular publication platforms, accounting for 4,518 (87.92%) and 355 (6.91%) of the total, respectively. **Figure 6** depicts future uses of technology that are highly desirable and required.

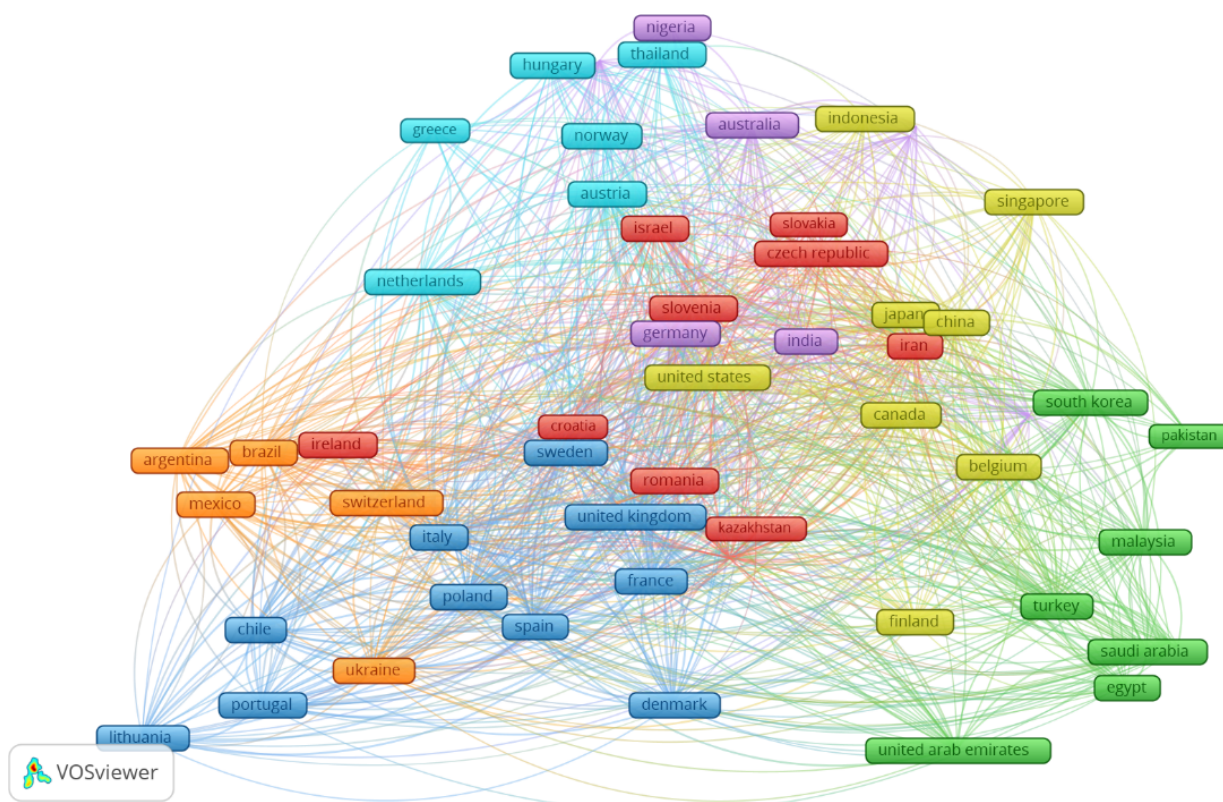


Figure 3. Map of the International Partnership Network for Lithium Analytical Research

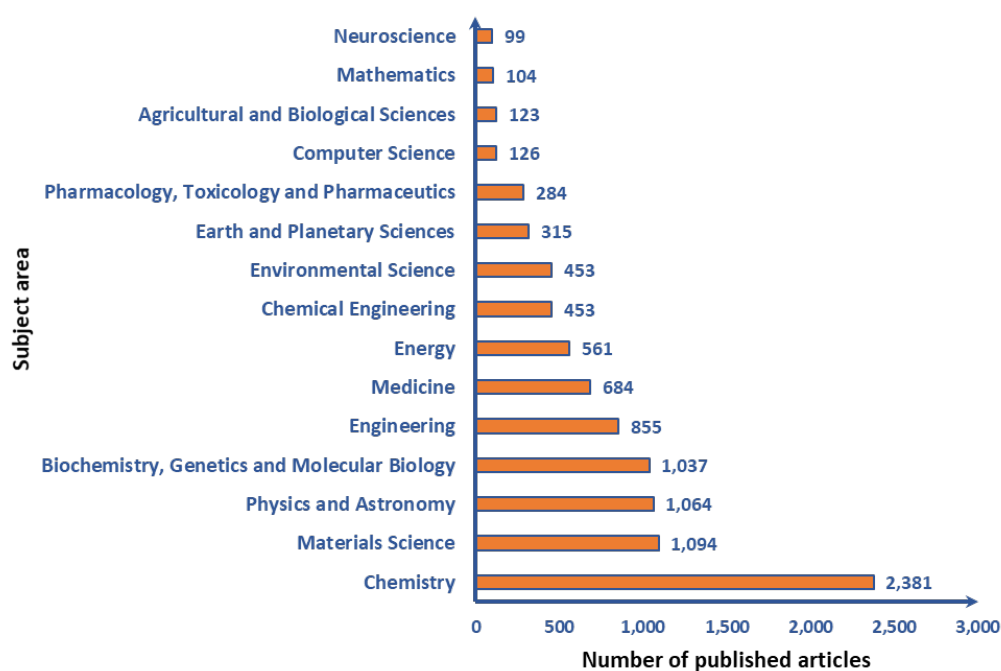


Figure 4a. Research characteristics profile for lithium analysis by subject area

Based on the existing literature, generally, the research topic that has been done is the development of lithium batteries. Then, research on the development of lithium testing methods in medical samples such as serum, saliva, urine, brain, and blood (Gaitsch *et al.*, 2023; Sheikh *et al.*, 2022; Ingle *et al.*, 2022). Meanwhile, lithium testing methods for the purpose of exploration and environmental

monitoring are still limited and still use stationary instrumentation in the laboratory. As shown in [Table 1](#), potentiometric and colorimetric/optical techniques are the most widely used techniques for using lithium in medical samples. Furthermore, the use of conductive polymers and ionophores as modifiers is still attractive. However, there are its own challenges in the synthesis and purification processes in accordance with the expected compounds.

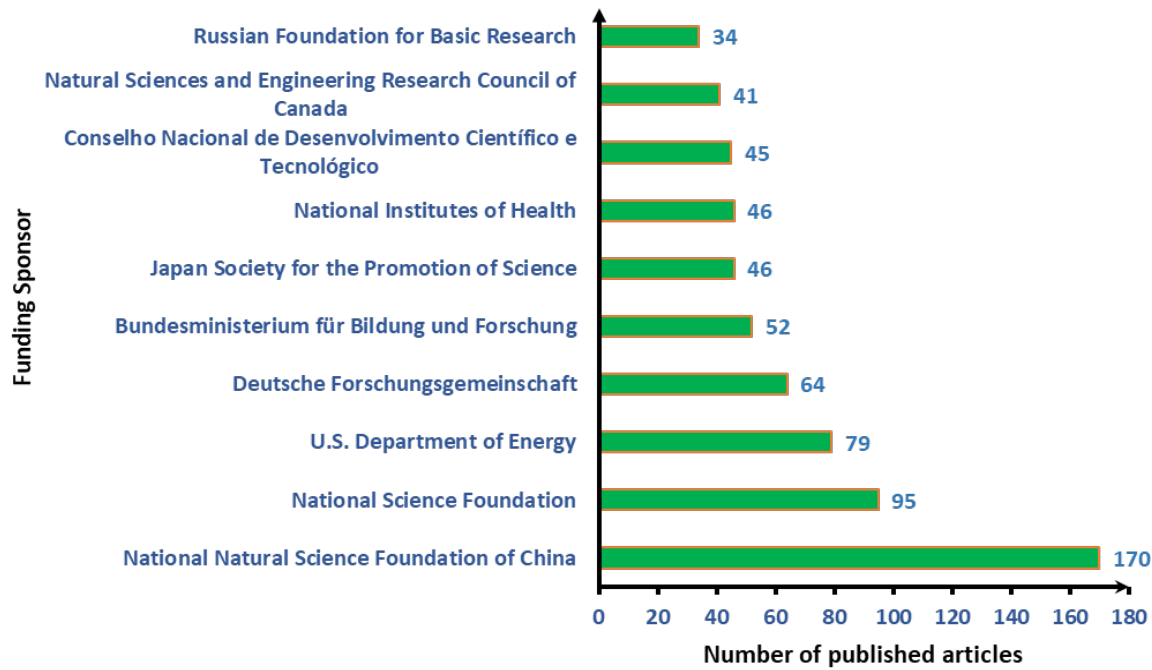


Figure 4b. Research characteristics profile for lithium analysis by funding sponsor

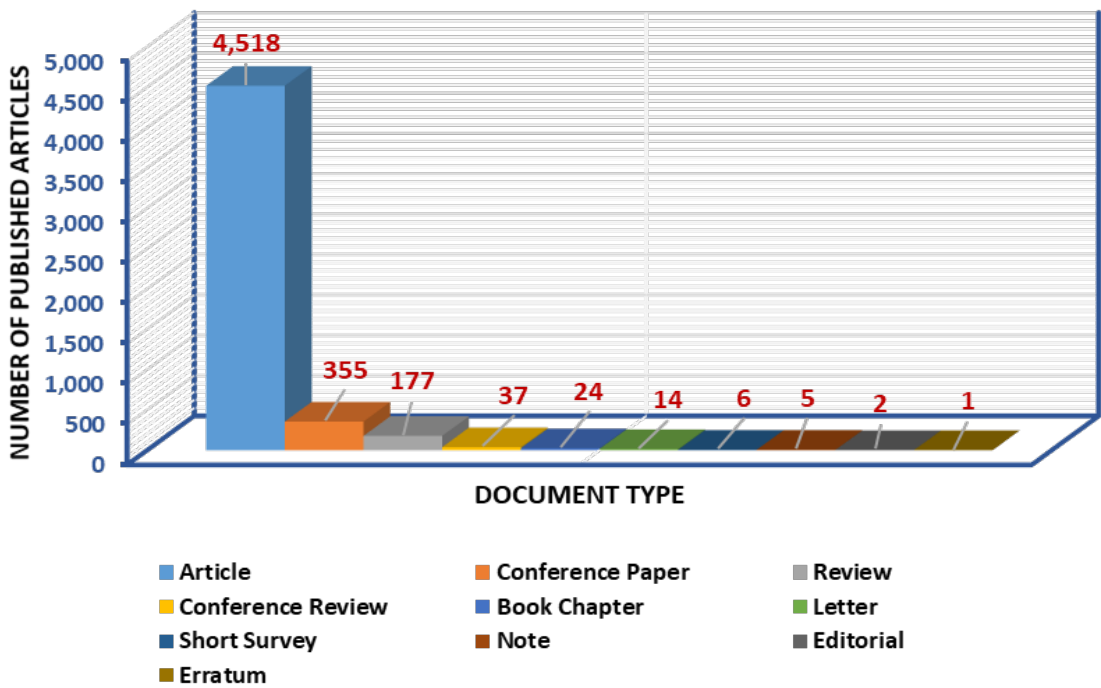


Figure 5. Profile of the publication platform used for research analysis and determination of lithium

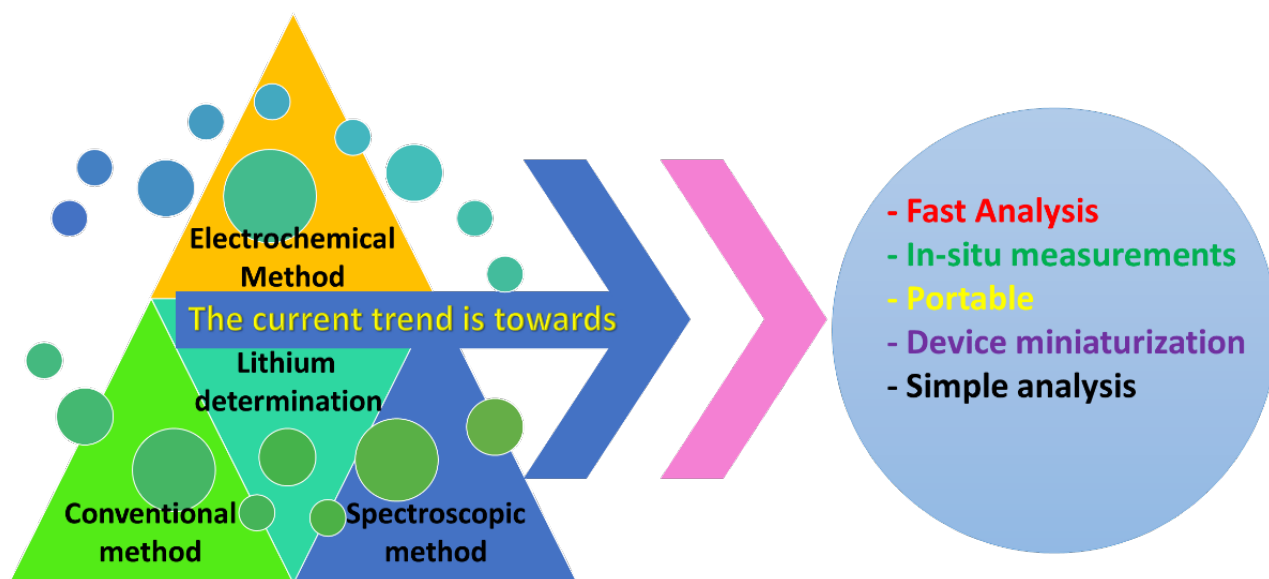


Figure 6. Illustration of the development of a method for determining lithium in the future

Table 1. Simplified comparison of stationary and portable instruments' performance

Analysis Technique	Sample Matrix	Range	LOD; Precision	Ref.
Potentiometry Modifier: Platinum, gold dan Li Ionophore VI	LiCl solution	0.69 10^{-4} to 0.69 g/L	$9.02 \times 10^{-5} \pm 2.78 \times 10^{-5}$ g/L	(Criscuolo et al., 2018)
Potentiometry Modifier: Ni-HAB MOF, Ionophore VI	LiCl solution and brine	6.94×10^{-6} to 6.94 g/L	6.90×10^{-6} g/L	(Abdollahzadeh et al., 2022)
Voltammetry Modifier: LiMn_2O_4	LiClO_4 solution and saliva	Up to 3.47×10^{-2} g/L	$>3.47 \times 10^{-2}$ g/L; RSD< 7%	(Alex L. Suherman et al., 2019)
Potentiometry MODIFIER: Lithium Ionophore VI, trioctylphosphine oxide and PVC membrane	Serum	3.47×10^{-4} to 0.69 g/L	3.47×10^{-4} g/L	(Coldur and Andac, 2013)
Potentiometry MODIFIER: Lithium Ionophore VI, polymeric membrane	Blood	2.50×10^{-4} to 0.69 g/L	6.18×10^{-4} g/L	(Novell et al., 2014)
Potentiometry MODIFIER: N,N-dicyclohexyl-N',N'-diisobutyl cyclohexane-1,2 dicarboxamide	Serum	4.86 to 1.04×10^{-2} g/L	9.02×10^{-3} g/L	(Metzger et al., 1986)
Potentiometry MODIFIER: PVC, Ionophore VI, Potassium tetrakis (4-chlorophenyl)	Water	6.94×10^{-5} to 6.94×10^{-2} g/L	$7.63 \pm 2.43 \times 10^{-5}$ g/L	(Hanitra et al., 2020)

Table 1. Cont.1

borate, and 2-Nitrophenyl
octyl ether

Analysis Technique	Sample Matrix	Range	LOD; Precision	Ref.
Potentiometry MODIFIER: poly(o-methoxyaniline)	Serum	6.94×10^{-5} to 6.94×10^{-4} g/L	2.86×10^{-5} g/L	(Lindino et al., 2012)
Voltammetry MODIFIER: 6,6'-dibenzyl-14-crown-4 ether	Serum	0.69×10^{-3} to 1.73×10^{-2} g/L	0.69×10^{-3} g/L	(Singh and Kumbhat, 2021)
Potentiometry MODIFIER: SWCNT, LiTPFPB, and PVC	LiCl solution	0.69×10^{-3} to 0.44 g/L	N/A	(Sweilam et al., 2020)
Spectrophotometric and electrical impedance	Blood	0.69×10^{-3} g/L \leq	$< 0.69 \times 10^{-3}$ g/L	(Qassem et al., 2019)
Colorimetry Lithium Assay kit LS	Blood and urine	0.5 to 2.0×10^{-2} g/L	0.5×10^{-3} g/L	(Iwai et al., 2021)
Colorimetry Modifier: quinizarin	Saliva	1.73×10^{-3} to 4.16×10^{-2} g/L	N/A	(Kim,et.al., 2011)
Colorimetry Colorimetric Assay	Serum	1.04×10^{-3} to 3.40×10^{-2} g/L	$< 0.55 \times 10^{-3}$ g/L	(Gruson et al., 2004)
Colorimetry spectrophotometric lithium assay	Serum	3.47×10^{-3} to 2.08×10^{-2} g/L	$< 0.69 \times 10^{-3}$ g/L	(Rumbelow and Peake, 2001)
Optical lithium sensor Modifier: Ionophore and AuNPs	LiClO ₄ solution	$\sim 6.94 \times 10^{-2}$ to 0.69 g/L	N/A	(Obare et.al., 2002)
Spectrophotometry ICP-MS (Horiba)	-	N/A	$< 0.020 \times 10^{-6}$ g/L; Short term (in-run): 1-3%RSD; Long term (4hrs) : RSD <5%	(Tyler, 2001)
Spectrophotometry ICP-OES (Horiba)	-	N/A	$< 1 \times 10^{-6}$ g/L; Short term (in-run): 0.3-1% RSD; Long term (4hrs) : RSD <3%	(Tyler, 2001)
Spectrophotometry GF-AAS (Horiba)	-	N/A	$< 0.5 \times 10^{-6}$ g/L; 1-5%	(Tyler, 2001)
Spectrophotometry Flame AAS (Horiba)	-	N/A	$< 5 \times 10^{-6}$ g/L; 0.1-1% RSD	(Tyler, 2001)

Conclusion

The utilization of lithium in laptops and portable devices, grid-scale energy storage systems, and medicinal applications is increasing rapidly. To explore lithium in nature, we need a technology that can detect the presence of lithium elements quickly and accurately. So that it can provide geochemical data to calculate its economic reserves more effectively and efficiently. Fast and accurate lithium

detection technology is also needed when determining the dose of lithium salt for bipolar disorder medication. Because the concentration of lithium in the patient's blood is excessive, it can be toxic to the patient's body. Furthermore, it is also necessary to monitor the level of water pollution caused by lithium battery waste. Based on literature studies, in general, they still use laboratory equipment that requires a relatively long preparation time, complicated sample handling, and requires a lot of chemicals at a high cost. Meanwhile, research that develops sensor technology that allows for the determination of lithium in situ, in real-time, and has high accuracy is still limited.

Acknowledgement: The authors thank Keni Vidilaseris, Ph.D. (Faculty of Biological and Environmental Sciences, University of Helsinki) for the insightful discussion, comments, and suggestions. The authors also acknowledge the facilities and scientific and technical support of the Analytical Chemistry Research Group, Faculty of Mathematics and Natural Sciences, Bandung Institute of Technology, Indonesia.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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(2023) ; <https://revues.imist.ma/index.php/morjchem/index>