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MSc Research Project

Environmental economics of MinEx CRC's innovative laser based downhole geochemical sensor

By

Haopeng MA

1930866

First Supervisor: Prof. Caroline Tiddy
Second Supervisor: Dr. Ben van de Hoek

Department of Chemical Engineering
University College London (UCL)
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DECLARATION

I, Haopeng Ma, confirm that the work presented in this thesis is my own.

Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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ABSTRACT

Nowadays, where environmental issues are increasingly impacting all aspects of life, the principles of environmental economics are gaining widespread attention, and this is also true in the field of geochemistry. Geochemical data is extensively utilised across various domains of Earth sciences, including geology, leading to significant advancements. Currently, laboratory-based methods, such as the four-acid digestion technique, are considered high accuracy and are considered the only accepted data sources for critical reports and standards such as JORC code compliance. However, a new technology, Laser-Induced Breakdown Spectroscopy (LIBS), is gaining attention due to its rapid analysis, cost-effectiveness, and environmental friendliness.

This dissertation first establishes a specific scenario to analyse the environmental aspects of LIBS assays and laboratory-based four-acid digestion methods, focussing primarily on the acids used in laboratory analysis and the management of experimental waste, demonstrating their potential environmental threats. Then, examines the work, health, and safety (WHS) aspects of both methods, evaluating them based on the Hierarchy of Controls framework. Subsequently, the feasibility of integrating laboratory analysis with the LIBS method for geochemical data collection is discussed, along with the environmental economic advantages. The study concludes that using LIBS assays to screen samples before sending them for further laboratory analysis, rather than analysing all downhole samples, aligns with environmental sustainability, WHS advantages, and the principles of environmental economics.

CONTENTS

1 INTRODUCTION

Nowadays, extreme weather events, rising sea levels, and ecosystem disruptions due to climate change are having profound impacts on human society and the economy Anon (2017). Consequently, the study of environmental economics is becoming increasingly important, as its core mission is to explore how to achieve a win-win situation between environmental protection and economic development through economic activities (Iribarren & Iribarren, 2020). The emergence of concepts such as carbon footprint tracking and Environmental, Social, and Governance (ESG) frameworks further underscores the urgent need for environmental protection. However, according to Ma & Xu (2023), the mining exploration and extraction industry, known for its high energy consumption and significant pollution, accounts for a considerable portion of global carbon emissions. Traditional exploration methods not only consume vast amounts of energy but also cause multiple forms of pollution to soil, water bodies, and the atmosphere. With the growing emphasis on sustainable development worldwide, more advanced and environmentally friendly technologies have emerged within the industry. One of the areas of interest has been in developing methods for more efficient ways to collect geochemical data (Gazley et al., 2011).

In the resources industry, the highest quality geochemical data is traditionally collected via laboratory assay, specifically the four-acid digestion method, which involves dissolving a rock sample in a series of increasingly strong acids (Zivkovic et al., 2023). Despite its accuracy, this process is both costly and time-consuming. A promising alternative is the use of a drill hole Laser-Induced Breakdown Spectroscopy (LIBS) instrument, which enables near real-time collection of geochemical data directly within a drill hole. LIBS technology has garnered significant attention for its rapid elemental identification capabilities and minimal sample requirements (Bhatt et al., 2018). Compared to traditional methods, LIBS offers a rapid, non-contact analytical capability that enhances the accuracy and efficiency of mineral exploration, reduces unnecessary resource waste, and minimizes environmental pollution (Singh, 2023). This not only contributes to economic development but also better protects the environment. Researching the application of LIBS to reduce the reliance on chemicals in traditional laboratory assays could significantly lower environmental pollution, reduce exploration project costs, and improve economic benefits. This approach aligns with the principles of environmental economics and supports the achievement of sustainable development goals.

This dissertation considers, the environmental benefits of using LIBS over laboratory assay techniques that are commonly used in the resources industry (four-acid digestion). Environmental indicators, including the use of chemicals and the emission of waste, which are the primary factors affecting the environment. Simultaneously, work, health and safety (WHS) requirements and the accuracy of element identification are considered as negative externalities—adverse impacts on third parties resulting from economic activities—since these aspects are directly linked to the effects of environmental policies and economic activities on social welfare. According to The Joint Ore Reserves Committee (JORC) Code 2012 Edition (2012), laboratory geochemical data is the only compliant source for mineral resource reporting. Therefore, although LIBS technology cannot directly replace laboratory data, it serves as an efficient screening tool. Consequently, this dissertation explores the environmental economic benefits of introducing LIBS technology through a hypothetical mineral exploration scenario, supported by the analysis of environmental and WHS factors.

2 BACKGROUND

Environmental changes and resource scarcity present significant challenges to human society, garnering widespread concern across various sectors. Consequently, the study of geology has become more critical than ever. In this context, the collection and analysis of geochemical data are paramount for geologists' research (Rice, King & Henson, 2016). Geochemistry is widely applied across various fields of Earth sciences, including petrology, economic geology, and tectonics (Inamuddin, 2021). By acquiring geochemical data, geologists can gain profound insights into the composition and evolution of the Earth, guide mineral resource exploration, assess environmental pollution, predict natural disasters, and even reconstruct ancient climates and environments (Rollinson, 1993). Particularly in mineral resource exploration, geochemical data are virtually indispensable. By analysing chemical elements in soil, rocks, and water, geologists can identify potential mineral resource areas, guiding exploration and extraction (Saleh & Hassan, 2022). Anomalous element concentrations may indicate ore deposits, providing essential clues (White, 2020). Additionally, geochemical data support environmental monitoring and impact assessments, helping to identify pollution sources, assess levels, and formulate remediation measures, which are crucial for preserving the environment and safeguarding human health (Sikakwe et al., 2020). This highlights the scientific and practical importance of geochemical data.

2.1 LIBS analysis

In the context of the continuous advancement of geochemical analysis technologies, Laser-Induced Breakdown Spectroscopy (LIBS) has garnered increasing attention in recent years within the realms of mineral exploration and environmental monitoring (Harmon & Senesi, 2021). The advantages of LIBS, including its speed, cost-effectiveness, environmental friendliness, and ability to simultaneously detect multiple elements, make it superior to traditional four-acid digestion laboratory assay methods. These benefits position LIBS as a more optimal choice for the collection and analysis of geochemical data, leading to its growing adoption by research institutions and companies. LIBS operates by focusing a high-energy pulsed laser on a sample's surface to create high-temperature plasma and analysing the emission spectra to determine the sample's composition both qualitatively and quantitatively (Singh, 2023).

The applications for LIBS in geosciences are extensive, encompassing mineral exploration, environmental monitoring, and geological structure analysis. In mineral exploration, LIBS technology is employed for the rapid identification and analysis of elemental compositions in rocks, minerals, and soils. By using laser pulses to instantaneously vaporize the surface material of a sample and generate plasma, LIBS can detect the elements present within the sample, thereby identifying potential locations of ore deposits (Kuhn et al., 2016). In environmental monitoring, LIBS is primarily used for the detection and assessment of heavy metal pollution. Its capability to perform in-situ analysis without complex sample preparation allows for real-time detection of pollutants in water, soil, and air, including elements such as lead, mercury, and cadmium. The high sensitivity and quick response of LIBS make it an ideal tool for environmental monitoring, providing timely information for pollution control and remediation (Zhang et al., 2021). LIBS also plays a significant role in the study of geological structures and rock formation processes. By analysing rock-thin sections and drill core samples, geologists can gain insights into the elemental migration and enrichment mechanisms during magmatic activity, metamorphism, and sedimentation (Fau et al., 2019). This information is crucial for advancing the understanding of geological structures and the processes involved in rock formation.

Today, LIBS technology has achieved numerous innovative applications in the fields of geosciences and geochemistry, particularly in drill hole analysis (Fontana et al., 2023). This emerging domain leverages the advantages of LIBS to perform real-time, non-contact, multi-element simultaneous analysis and mineral identification, significantly enhancing the efficiency of underground operations. The Mineral Exploration Cooperative Research Centre (MinEx CRC) is developing a downhole LIBS tool that will allow for direct and rapid analysis in a drill hole, eliminating the cumbersome process of transporting samples to laboratories, and thereby reducing data acquisition time and cost. Additionally, compared to traditional laboratory methods, LIBS requires no chemical reagents, making it environmentally friendly and cost-effective, while its rapid, real-time analysis capability improves efficiency (Fontana et al., 2023). Consequently, LIBS technology, with its green, fast, and efficient characteristics, has become an ideal analytical tool in geosciences. Hence, the application of LIBS in drill hole analysis provides a swift, efficient, and eco-friendly solution for real-time geochemical data collection, driving significant advancements in geoscientific research and mineral exploration. The use of a downhole LIBS tool also has the potential to reduce the use of chemicals in traditional laboratory assays, which not only significantly lowers environmental pollution but also reduces exploration project costs and improves economic benefits. This aligns perfectly with the core principles of environmental economics and provides strong support for achieving sustainable development goals.

2.2 Laboratory analysis

The collection of geochemical data typically involves various laboratory assay methods, among which the four-acid digestion method is widely utilised in mineral exploration and extraction (e.g., ALS 2024b). Four- acid digestion employs four potent acids—hydrofluoric acid, nitric acid, hydrochloric acid, and perchloric acid—to completely dissolve the minerals in a sample for more thorough geochemical analysis (Fu et al., 2008). The advantage of this method lies in its ability to dissolve nearly all types of minerals, thereby allowing for a comprehensive and accurate determination of the elements within the sample (e.g. Balaram & Subramanyam, 2022; ALS, 2024a). During the four-acid digestion process, the sample is first crushed and ground to an appropriate grain size, then mixed with the four acids at high temperatures. This acid combination effectively dissolves almost all refractory minerals in the sample. The resulting solution is then centrifuged or filtered to remove any undissolved residues, followed by the determination of element concentrations using analytical instruments such as Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Actlabs, 2021).

However, the four-acid digestion method presents certain limitations. Firstly, the method is time-consuming, often requiring several hours to several days to complete the entire assay process, which can significantly extend project timelines when dealing with large-scale sample analyses and impact the timeliness of subsequent decision-making (Zivkovic, 2023). Secondly, the cost of the assay is high due to the expensive nature of the strong acids and analytical instruments such as ICP-MS (LabX, 2024), as well as the need for extensive training of personnel to handle these materials safely and effectively. Additionally, this method poses potential environmental pollution risks. The use and handling of strong acids generate hazardous waste gases and liquids which, if not properly managed, can lead to environmental contamination. The waste materials typically contain high concentrations of acids and dissolved heavy metals, necessitating specialised waste treatment and neutralisation procedures to ensure safe disposal, thus further increasing the cost and requiring additional time and resources. Furthermore, stringent safety measures are essential when handling these chemicals due to their highly corrosive and toxic nature, posing potential hazards to laboratory personnel and the environment (Jones & Cetin, 2017).

These limitations mean that, despite the high efficiency and precision of the four-acid digestion method, its time and cost requirements are substantial, necessitating a controlled laboratory environment to mitigate environmental impact. Researchers must, therefore, carefully weigh the practical needs and conditions of their studies when selecting geochemical assay methods, often seeking more economical, safe, efficient, and environmentally friendly alternatives.

3 METHODOLOGY

3.1 Mine scenario

A hypothetical mine scenario is used in this study to assess the environmental impact of collecting geochemical data using laboratory analysis four-acid digestion methods versus downhole LIBS technology. The mine sites modelled is based on the real-world example of the Olympic Dam Deeps drilling campaign that involve drilling 15 holes for a total 62 kilometres of drill core (BHP, 2024). The drill holes, averaged 1.5 kilometres in depth each, with core samples taken at 1 metre intervals. Based on this, the campaign produced 62,000 samples.

The Olympic Dam mine contains Cu, U, Ag, and Au (BHP, 2023). Olympic Dam is situated in a desert region with relatively flat terrain, located in northern South Australia, approximately 10 kilometres north of the town of Roxby Downs and about 560 kilometres from the state capital, Adelaide, at approximately 30.5 degrees south latitude and 136.9 degrees east longitude.

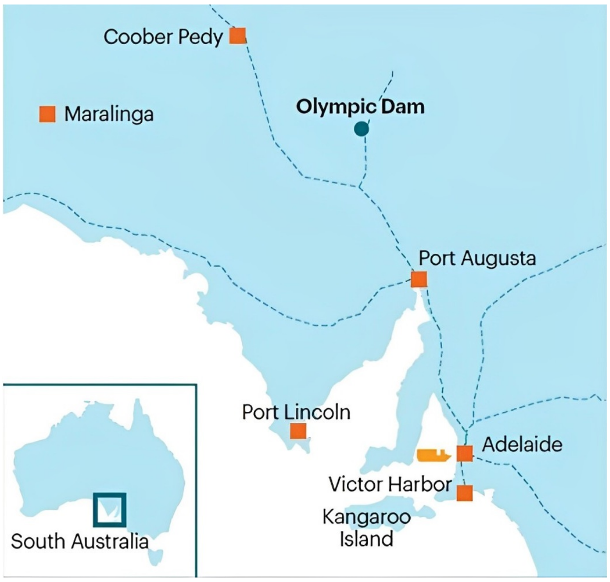

Figure 3.1: Olympic Dam Mine Directions Map (Baylis et al., 2020)

3.2 Data sources

The data for the four-acid digestion method was obtained from online resources and laboratory records (Hu & Qi, 2014). This includes information on the quantities and prices of the acids required for the digestion reactions, and the costs of the necessary instruments.

Information on the LIBS method including set up and experimental workflow are taken from learnings of the MinEx CRC Project 3, including from field trials conducted at the Australian Automation and Robotics Precinct (AARP: www.theaarp.com.au) in early July 2024.

3.3 Environmental analysis

The environmental impact analysis undertaken here will concentrate on the chemicals used for geochemical analysis via LIBS and in a laboratory environment. For downhole LIBS analysis, chemical usage is considered minimal as the method involves collection of geochemical data directly from a drill hole wall.

For laboratory analysis, it is assumed that the four-acid digestion method is used for all samples. The four-acid digestion method is commonly used in the preparation of rock samples for geological analysis, as it ensures (almost) complete digestion of the sample matrix, thus producing results that are representative of the whole rock sample (e.g. Balaram & Subramanyam, 2022; ALS, 2024a). It is also assumed that closed vessel digestion is used, as this will further ensure the digestion of many refractory minerals and compounds that are otherwise difficult to be decomposed (Hu & Qi, 2014). The sample treatment procedure for the closed acid digestion is taken from Hu & Qi (2014), is a typical method appropriate for digestion of rocks including felsic to mafic igneous rocks, which are commonly found in the Olympic Dam mine area (BHP, 2024).

The environmental analysis will also consider the CO_2 emissions produced by each method, as determined by Guo (2024).

3.4 WHS comparison

The WHS analysis for LIBS is focused on two key areas: deployment and operation. Regarding the deployment process, the analysis will focus on the deployment of wireline tools, which is the core of LIBS technology. This will involve a comprehensive assessment the size, weight of the tool, and the risks associated with transportation. For the operational aspect, the analysis will first address the environmental risks posed by the deployment site, specifically the Olympic Dam Deeps. Subsequently, will explore the potential health and operational risks associated with LIBS, since it is a laser-based tool.

Laboratory geochemical analysis requires handling of strong acids for the four-acid digestion process: hydrofluoric acid, nitric acid, hydrochloric acid, and perchloric acid. These four strong acids are classified as hazardous chemicals, substances that pose potential risks to human health or physical integrity, such as being toxic, causing skin corrosion, or possessing carcinogenic properties. Accidental inhalation, ingestion, or skin contact with these chemicals can result in severe harm to the human body. The Hazardous Chemical Information System (HCIS), established by Safe Work Australia (2024) in accordance with the Globally Harmonized System of Classification and Labelling of Chemicals and related classification standards, serves as a database for chemical classifications and exposure standards. WHS considerations will include a comparative risk analysis of the target chemicals based on the Safety Data Sheets (2021). Finally, WHS considerations will be evaluated according to the Hierarchy of Controls framework (2024).

4 RESULTS

4.1 Downhole LIBS analysis

4.1.1 Environmental considerations

The consumption of chemicals during deployment of the downhole LIBS instrument is considered negligible as the geochemical data is collected directly from the drill hole wall without any sample preparation.

The CO_2 emissions of downhole LIBS deployment have been calculated as 100.59 kilogram (Guo, 2024).

4.1.2 WHS considerations

In analysing the WHS considerations for LIBS, the first is the risk concern associated with deployment. The LIBS instrument, which weighs 12 kg and has dimensions of 76 mm in length and 2400 mm in width, presents significant bulk and weight, posing a risk of injury during handling, particularly in terms of potential crushing hazards. Additionally, as the downhole LIBS instrument is deployed as a wireline logging tool, the analysis must focus on the specific processes involved in wireline logging. The dangers of wireline logging operation are mainly associated with tension on the steel cable of the wireline. Firstly, the electrical equipment utilised in wireline logging operations, such as cables and related tools, carries the risk of electrical malfunctions. This risk is particularly heightened in humid environments, for instance, on days with significant rainfall, which may increase the likelihood of electrical failures and consequently result in personnel injuries. Secondly, there is an inherent risk of mechanical failure during operations, particularly with winches and cable systems. In the event of mechanical malfunction or unstable power supply, the equipment may become uncontrollable, posing a significant threat to the safety of the personnel involved.

Furthermore, according to the standards outlined by Laser Safety Facts (2014), the MinEx downhole LIBS tool utilises a Class 4 laser. For visible light lasers, Class 4 lasers, with an output power exceeding 500 milliwatts, represent the most hazardous laser classification. Firstly, Class 4 lasers pose a significant risk to the eyes, with even brief direct or reflected exposure capable of causing severe ocular damage, potentially leading to permanent blindness. Secondly, direct exposure to such lasers can result in serious skin burns; the high power of these lasers means that even short-term contact can cause considerable skin injury. Therefore, it is imperative that the operator receives appropriate training in laser safety. In Australia, operators of LIBS equipment are required to undergo relevant training to ensure a comprehensive understanding of laser safety practices, thereby meeting the standards set for a Laser Safety Supervisor (LSS) or Defence Level 2 Laser Safety Officer (LSO2) in accordance with Australian and International standards.

Finally, as operational mine and/or exploration sites are typically in remote locations, considerations of the working environment must be made. Firstly, General slips, trips and fall injuries need to be considered as the instrument would be deployed in the field, likely on an operational mine or exploration site. Secondly, the temperature at the mine site is notably high. Given the geographical location of the Olympic Dam mine, where the maximum temperature over 37℃ throughout the year and the average temperature exceeds 23℃ (Timeanddate, 2024), combined with a high level of ultraviolet radiation (The Weather Channel, 2024), the health risks associated with heat exhaustion and sunburn cannot be overlooked. Thirdly, the presence of wildlife may pose safety hazards. According to the Department for Environment and Water (2024), South Australia is home to numerous species of venomous snakes, including some of the most toxic, such as Notechis scutatus and Pseudonaja textilis. These snakes exhibit formidable aggression when startled, particularly in hotter regions where their propensity to attack is heightened. At the Olympic Dam mine, snakes are frequently encountered, and due to their visual similarity to the LIBS equipment, there is a heightened risk of misidentification. Fourthly, transportation to and from the location also presents potential hazards. The transportation of LIBS equipment from companies based in cities such as Melbourne to the deployment site is time-consuming, and the prolonged driving required could lead to fatigue, increasing the risk of accidents.

4.2 Laboratory analysis

The environmental and WHS aspects of the laboratory geochemical analysis considered in this study revolve around the digestion of the sample into solution using the four-acid digestion method. This method is commonly used as it ensures that all the sample (including hard to dissolve resistate minerals) are dissolved, thereby allowing for generation of high-quality data representative of the bulk rock sample (Zivkovic et al., 2023).

4.2.1 Environmental considerations

The four-acid digestion technique requires substantial amounts of various acids and chemicals per sample, including nitric acid (HNO_3), hydrochloric acid (HCl), hydrofluoric acid (HF), and perchloric acid ($HClO_4$). According to the research conducted by Hu & Qi (2014), in closed vessel acid digestion, the quantity of acid used in the four-acid digestion method is calculated based on using 100 mg aliquot of each sample. Describe the process. Provide a figure that shows the workflow of the four-acid digestion method including detail such as how much acid, the acid strength, temperatures used etc.

The 62, 000 samples generated for the case study scenario being used in this study would each require digestion. Assuming a 100mg aliquot of each sample is used in the four-acid digestion process as described by Hu & Qi (2014), the estimated total acid consumption is calculated and shown in Table 4.1.

Table 4.1: The total acid volume used in the 62,000 samples generated for the Olympic Dam Deeps scenario

Acid type	Acid usage/100mg (Hu & Qi, 2014)	Total acid used in digestion of Olympic Dam Deeps samples
HNO_3	1.714 ml	106,268 ml (106.268 L)
HCl	6 ml	372,000 ml (372 L)
HF	5 ml	310,000 ml (310 L)
$HClO_4$	0.714 ml	44,268 ml (44.268 L)

Assuming complete digestion, no solid waste would be generated during the digestion process. However, liquid and gas waste should be considered. Exhaust gases such as nitrogen oxides (NO_x) and chlorine (Cl_2), are produced during the digestion process (Zivkovic et al., 2023). As well as the wastewater from the reaction, which needs to be carefully managed and treated to mitigate the environmental hazards posed by the residual acid and the reaction products. For example, HNO_3 reacts with metal oxides and may produce oxides of nitrogen:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO(gas) + 4H_2O \quad (4.1)$$

$$(2NO + O_2 \rightarrow 2NO_2) \quad (4.2)$$

HCl may produce chlorine Cl_2 gas when it reacts with metal oxides:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2(gas) + 2H_2O \quad (4.3)$$

As $HClO_4$ is a strong oxidising agent, it may also decompose under certain conditions to produce Cl_2 gas:

$$2HClO_4 \rightarrow Cl_2(gas) + 3O_2 + 2H_2O \quad (4.4)$$

Guo (2024) calculated the CO_2 emissions of laboratory analysis for the samples used in the Olympic Dam Deeps mine scenario as 2,523.19 kilogram.

4.2.2 WHS considerations

According to the Safety Data Sheets (2021), the use of the four acids poses varying degrees of potential health risks and all exhibit strong skin corrosivity. Uncorrective handling could have severe consequences. Table 4.2 summarises the Hazard Categories of the four acids together with their corresponding explanations.

Table 4.2: Four acid solutions with Cas numbers, hazard categories and Interpretations

	Cas No.	**Hazard Category**	**Interpretations**
HNO_3	7697-37-2	Skin corrosion – category 1 Oxidising liquid – category 2	Improper handling may result in severe skin burns and eye injuries. Additionally, misuse could exacerbate fires as it acts as an oxidiser.

HCl	7647-01-0	Skin corrosion – category 1B Specific target organ toxicity (single exposure) – category 3	Improper use may lead to severe skin burns and eye injuries, and during use, it may irritate the respiratory tract, potentially triggering related illnesses.
HF	7664-39-3	Acute toxicity (inhalation) – category 2 Acute toxicity (dermal) – category 1 Acute toxicity (ingestion) – category 2 Skin corrosion – category 1A	Inhalation, skin contact, or ingestion due to improper handling may be fatal, with contact leading to severe skin burns and eye injuries.
$HClO_4$	7601-90-3	Oxidising liquid – category 1 Acute toxicity – category 4 Skin corrosion – category 1A	Misuse may cause fire or explosion as it is a strong oxidiser. Ingestion is harmful to human health, and skin contact will result in severe burns and eye injuries.

5 DISCUSSION

5.1 Environmental comparison

There is a significant difference in environmental impact between the LIBS method and the laboratory's four-acid digestion method, primarily in terms of chemical usage, waste generation and greenhouse gas emissions, particularly CO_2. While the four-acid digestion method offers a more comprehensive analysis, it requires substantial quantities of chemicals and involves subsequent waste management, with CO_2 emissions far exceeding those of the LIBS method, thereby posing a greater environmental risk. In contrast, the LIBS method uses fewer chemicals, generates less waste, and produces significantly lower CO_2 emissions, making it a more environmentally sustainable option.

5.1.1 Chemical usage

The deployment of the LIBS instrument offers clear environmental advantages, as it requires virtually no use of chemicals. Geochemical data is collected directly from the drill hole wall through spectroscopic analysis, eliminating the need for sample extraction or chemical digestion. As a result, waste generation and the use of potentially harmful substances are minimised during the process, leading to negligible environmental pollution.

In contrast, the laboratory-based four-acid digestion method requires the extensive use of chemicals, including HNO_3, HCl, HF, and $HClO_4$. For a drill hole with a total depth of 62 kilometres, such as in the example of Olympic Dam mine, the total consumption of these acids can reach approximately 106 L, 370 L, 310 L, and 44 L, respectively—these are substantial quantities.

Based on the information provided by the Australian Government Department for Industry Science and Resources (2017) and Sigma-Aldrich Co. LLC. (2020) in their safety data sheets that comply with WHS and Australian Dangerous Goods (ADG) requirements, the following Table 5.1 summarizes key details about the toxicity, ecological information, and disposal considerations for four specific acids.

Table 5.1: Four acid solutions summary of toxicity, ecological information and disposal considerations

	Toxicity	**Ecological information**	**Disposal considerations**
HNO_3	Lethal concentration 50% (LC50) for inhalation: 2500 ppm. (Rat) 1h	Can not discharge into sewers, surface water, or wastewater systems. Prevent leakage from contaminating ground-water systems. In large quantities, it can affect pH levels and pose a threat to aquatic life such as freshwater fish and daphnia. High potential for bioaccumulation.	Neutralize before disposal, avoid release to environment, strictly control disposal.
HCl	Oral 50% lethal dose (LD50): 238 - 277 mg/kg (Rat); Dermal 50% lethal dose (LD50): > 5010 mg/kg (Rabbit); Lethal concentration 50% (LC50) for inhalation: 1.68 mg/L (Rat) 1h		Neutralize carefully, avoid direct disposal into water systems, follow local regulations.
HF	Dermal 50% lethal dose (LD50): 5.1 mg/kg (Rat); Lethal concentration 50% (LC50) for inhalation: 1.34 mg/L (Rat) 1h		Dilute and neutralize before disposal,avoid release into sewers, ensure compliance with regulations.
$HClO_4$	Oral 50% lethal dose (LD50): 3310 mg/kg (Rat); Lethal concentration 50% (LC50) for inhalation: 2819 mg/L (Rat) 4h		Neutralize cautiously, store separately from combustible materials, follow strict disposal guidelines.

Moreover, although this method does not generate solid waste, it still produces liquid waste containing residual acids and their reaction products, as well as gaseous emissions such as nitrogen oxides, chlorine and hydrofluoric acid. These by-products require proper management, including the treatment of wastewater containing residual acids and their reaction products, to mitigate environmental harm. NO_x gases and Cl_2 gas are typically treated using alkaline scrubbers, where they are neutralized with sodium hydroxide solution, resulting in the formation of harmless sodium chloride (Thomas & Vanderschuren, 2000) and nitrates or nitrites (Malkov et al., 2002). Alternatively, specific reducing agents may be employed to neutralize their toxicity, ensuring that emission standards are met. For laboratory wastewater, pH is typically adjusted to neutral using sodium hydroxide or sulfuric acid. Following further testing to ensure compliance with discharge standards, the treated wastewater can then be safely discharged into the sewage treatment system (Klein, 2006).

5.1.2 Greenhouse gas emissions

Based on the Olympic Dam Deeps scenario and according to Guo (2024), the CO_2 emissions associated with the LIBS instrument and laboratory methods primarily stem from three areas: energy consumption, material production, and waste management. The resulting emissions, with CO_2 as the primary greenhouse gas, are summarised in table 5.2 below.

Table 5.2: CO_2 emissions (kg) compared between downhole LIBS measurements and laboratory methods

	LIBS (kg CO_2)	**Laboratory (kg CO_2)**
CO_2 emissions	100.59	2,523.19

In terms of carbon emissions, the LIBS method used in the underground setting reduces emissions by nearly 2423 kg compared to traditional laboratory methods, amounting to only one-twenty-fifth of the emissions from the laboratory approach, thus demonstrating a significant environmental advantage.

5.2 WHS risks

The WHS risks associated with laboratory environments and the on-site deployment of LIBS tools, though distinct in nature, can both be effectively managed using the Hierarchy of Controls framework. In laboratory settings, the primary risks stem from the corrosive and toxic properties of chemicals, while the deployment of LIBS tools involves safety concerns related to field operations, such as steel cable tension, the use of high-power lasers, and potential environmental hazards (e.g., high temperatures, wildlife). Regardless of the context, systematically implementing elimination, substitution, engineering controls, administrative controls, and personal protective equipment (PPE) can significantly enhance operator safety.

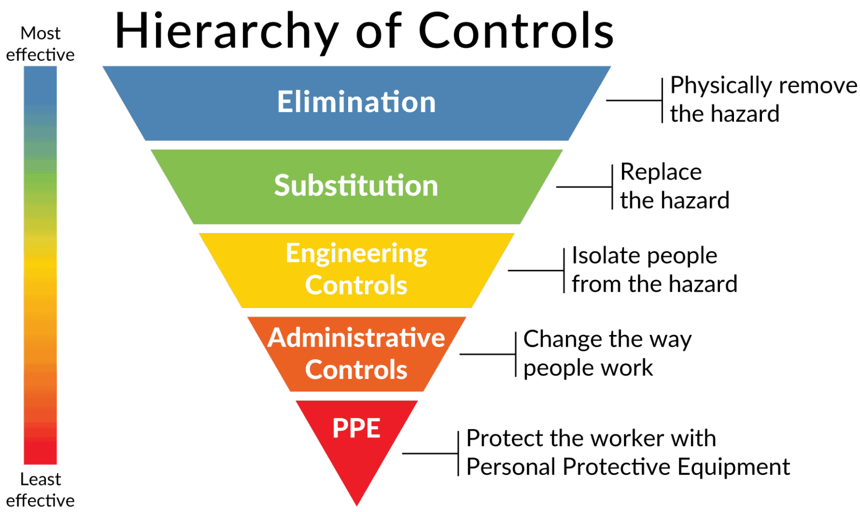

Figure 5.1: Hierarchy of controls framework (MAKESafe Tools, 2020)

5.2.1 PPE

For laboratory analysis, personnel should be equipped with appropriate PPE, including acid-resistant gloves, safety goggles, and laboratory-specific protective clothing, to prevent direct contact with skin and eyes.

For LIBS assay, field operators should be equipped with protective helmets, safety boots, gloves, and laser safety goggles to mitigate risks posed by the equipment and the environment.

5.2.2 Administrative Controls

For laboratory analysis, establishing strict protocols for chemical handling and safety guidelines for acid use, along with ensuring comprehensive training for laboratory personnel on safe handling practices, can significantly reduce the potential hazards associated with incorrect handling.

For LIBS assay, developing detailed operational procedures and emergency response mechanisms, such as emergency shutdown protocols and ensuring operators are trained in laser safety, will further enhance safety measures.

5.2.3 Engineering Controls

For laboratories analysis, the use of well-functioning ventilation systems and certified fume hoods can effectively isolate personnel from corrosive gases, reducing the risk of harmful exposure.

For the LIBS assay, the safety concerns during deployment arise from the tool's nature as a wireline instrument. However, the blue sky goal for the downhole LIBS instrument is to position it directly behind the drill bit, enabling the collection of geochemical data in real-time during drilling, rather than deploying it as a wireline tool after the drill hole is completed. This long term goal would eliminate the need for wireline deployment. Regarding laser risks, implementing laser safety barriers within the operational area can mitigate the risk of laser exposure during operations.

5.2.4 Substitution

For laboratory analysis, the four-acid digestion method discussed in this study is already a well-established technique. However, as chemical assay technologies advance, the development of more efficient methods for component detection, such as by adjusting the concentration of acid solutions to reduce the overall use of acidic substances, could achieve the Substitution level of risk control.

For LIBS assays, the blue sky goal which is upgrading tools to eliminate the safety risks associated with wireline deployment, can also achieve the Substitution level of risk control by shifting the risk. This approach would significantly transfer the risk associated with using instruments for data collection to the risks inherent in the drilling process.

5.2.5 Elimination

Completely eliminating risk from a physical standpoint is nearly impossible for both methods; however, combining the two approaches can yield optimal results. For the laboratory method, one way to minimise the elimination of sorts is by reducing the number of samples to be sent for laboratory geochemical analysis. This could be achieved by doing the downhole LIBS assay of all drill holes, and then strategically selecting samples for further laboratory analysis.

For example, based on the LIBS assay results, one might choose 50% or even as little as 25% of the 62,000 samples for laboratory analysis, especially for samples with unique spectral characteristics. The samples screening process can be enhanced using big data and machine learning technologies to develop more intelligent sample selection models, thereby optimising the efficiency and accuracy of sample selection. This approach would significantly reduce the use of acids and consequently mitigate associated risks. The specific outcomes of this reduction can be observed in Table 5.3.

Table 5.3: Amount of acid needed for laboratory analysis of one half and one quarter of the samples

	50% of samples	**25% of samples**
HNO_3	53,134 ml (53.134 L)	26,567 ml (26.567 L)
HCl	186,000 ml (186 L)	93,000 ml (93 L)
HF	155,000 ml (155 L)	77,500 ml (77.5 L)
$HClO_4$	22,134 ml (22.134 L)	11,067 ml (11.067 L)

For LIBS assays, upgrading and enhancing the tools to achieve the blue sky goal is a prudent strategy for maximising risk elimination. Currently, the operation of downhole LIBS instruments requires drilling a hole first, followed by the use of the LIBS device for analysis. However, if new equipment could support data collection concurrently with drilling, it would save operational time, thereby reducing the duration that personnel are exposed to sunlight and their time spent on-site. This would significantly minimise the environmental risks and potential threats, thereby reducing overall risk to the lowest possible level.

Based on this, laboratory analysis can effectively achieve PPE, Administrative Controls, and Engineering Controls levels of risk management. For Substitution and Elimination levels, laboratory analysis can be enhanced by introducing LIBS tools as a supplementary measure. This would involve using LIBS to conduct preliminary geochemical analyses of entire drill holes, followed by laboratory analysis of complex or unique samples. The objective is to reduce the risk by 50% or even 25%, thereby minimising overall risk.

The LIBS assay can also effectively achieve the PPE and Administrative Controls levels of risk management. For the Engineering Controls, Substitution, and Elimination levels, the blue sky goal of the downhole LIBS assay is to gather data during drilling, which would eliminate the potential hazards associated with wireline deployment. Achieving this long-term goal would significantly enhance the control over the safety risks involved in the deployment and operation of LIBS.

5.3 Economic benefit assessment

The core of environmental economics is the study of the relationship between economic activities and the environment, with a focus on achieving economic growth while minimising negative environmental impacts to attain sustainable development (Florax et al., 2002). The introduction of LIBS tools for geochemical data collection can effectively reduce laboratory and environmental restoration costs while enhancing experimental efficiency, thereby aligning with the objectives of environmental economics.

Firstly, the introduction of LIBS technology can significantly reduce the costs associated with chemical usage and waste management. Reducing the use of chemicals (HNO_3, HCl, HF and $HClO_4$) translates into lower laboratory costs. For instance, when LIBS screening reduces the number of samples sent for laboratory analysis by half (31,000 samples) the laboratory expenses are also halved. Similarly, the cost of handling laboratory waste will also be reduced by half. Thus, LIBS technology is more economically friendly, and its ability to minimise chemical pollution is crucial to the sustainable development goals of environmental economics.

Secondly, the costs associated with environmental impact mitigation will also decrease with the use of LIBS technology. For example, lower ecological impacts translate into reduced environmental restoration costs, which would be reflected as advantages in comprehensive financial analyses.

Thirdly, the increased efficiency brought about by the LIBS method enhances its economic viability. Due to its laser detection combined with computational analysis, LIBS can produce results in a very short time. When used in conjunction with laboratory methods, it can potentially save up to half the time required for analysis. This increase in speed not only boosts laboratory throughput but also reduces labour and energy costs, thereby supporting environmental economics and promoting a greener model of economic development.

6 CONCLUSION

This dissertation uses Olympic Dam Deeps as a reference to analyse the environmental and WHS differences between LIBS assays tool and the laboratory-based four-acid digestion method in acquiring geochemical data. Finally, discusses the advantages and environmental economic benefits of using LIBS assays as a preliminary sample screening tool for laboratory analysis from environmental, WHS, and environmental economics perspectives.

Firstly, the study analysed the environmental differences between LIBS assays and laboratory-based four-acid digestion under the Olympic Dam Deeps scenario. LIBS tools have minimal environmental impact during deployment and operation, emitting relatively low greenhouse gases, approximately 101 kg of CO_2. In stark contrast, laboratory analysis has a much greater environmental impact due to the inevitable use of large quantities of acids—approximately 106 L of HNO_3, 372 L of HCl, 310 L of HF, and 44 L of $HClO_4$. If these acids are not properly managed, they could severely threaten the environment. Additionally, the laboratory process emits approximately 2,523 kg of CO_2, nearly 25 times that of the LIBS method.

Furthermore, the WHS was analysed for both methods. the health and personnel risks associated with LIBS assays primarily stem from three factors: potential accidents during the deployment of the instrument, challenges posed by the environment of the Olympic Dam mine, and the hazards related to the use of a Class 4 laser. Through the Hierarchy of Controls framework, LIBS can achieve the Engineering Controls level and is working towards fulfilling the blue sky goal for the downhole LIBS instrument, potentially meeting Substitution and Elimination levels to some extent. The laboratory method's risks stem from improper handling of the four acids and waste management, which pose serious health risks if inhaled or in direct contact with the human body. By employing the Hierarchy of Controls framework, laboratory analysis can also achieve the Engineering Controls level. Introducing LIBS as a preliminary sample screening tool could reduce the number of samples sent for laboratory analysis by 50% or even 75%, thereby partially achieving the Elimination level.

Finally, from an environmental economics perspective, introducing LIBS for preliminary screening allows companies to significantly reduce the number of samples sent for laboratory analysis, thereby lowering acid usage and waste generation. This not only reduces the costs associated with laboratory testing and environmental remediation but also decreases the carbon emissions from the transportation and disposal of chemicals, aligning with the sustainability goals of environmental economics. Moreover, increased efficiency leads to further reductions in labour and energy costs, consistent with the principles of environmental economics.

In summary, while the accuracy of the laboratory four-acid digestion method makes it the only option for JORC Code compliance, supplementing it with the downhole LIBS assay by recording geochemical data for all drill holes and strategically selecting 50% (for example) of drill cores for laboratory analysis would have significant positive impacts on both the environment and WHS. This approach aligns more closely with the principles of environmental economics.

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