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Perspective

Handheld Laser-Induced Breakdown Spectroscopy (hLIBS) Applied to On-Site Mine Waste Analysis/Evaluation in View of Its Recycling/Reuse

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Abstract: Nowadays, the recovery/recycling/reuse of mining and mineral processing wastes is considered the best approach to support the circular economy and sustainability of mining and metal extraction industries. Mine wastes can be used to restore surface and subsurface land damaged by mining operations, generate fuel for power plants, further extract their component minerals, and as building materials additives. The aim of this perspective paper is to briefly highlight and focus on the most recent analytical potential and performance achieved by handheld laser-induced breakdown spectroscopy (hLIBS) instrumentation in the perspective of its future application in the mine waste sector to quickly identify on-site the presence of useful chemical elements for their possible sustainable recovery.

Keywords: handheld laser-induced breakdown spectroscopy (hLIBS); mine wastes; recovery/recycling/reuse

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1. Introduction

Worldwide, mining and mineral processing wastes amount to about 7 billion tons per year [1], and their recycling/reuse is considered the best approach to support the circular economy and sustainability of mining and metal extraction industries. Mine wastes consist of heterogeneous, complex, and reactive mixtures of minerals; thus, any attempt at their recycling/reuse presents advantages and limitations [2,3]. The economic feasibility and appropriateness of recycling/reuse of these wastes mostly depend on the chemical and mineralogical composition of the source rock and their geotechnical characteristics. For example, mining wastes can be used to restore surface and subsurface land damaged by mining operations, generate fuel for power plants, further extract their component minerals, and as building material additives [4,5].

In recent years, the increasing anthropogenic pressure on the environment and the promotion of the growing use of strategic and critical raw materials (S-CRMs) are speeding up the shift from a linear "extraction–use–final disposal" model of production and consumption to a circular model. In this context, the EU Critical Raw Materials Act (EU Commission 2024) obliges each EU member to ensure a minimum of 10% internal supply of critical raw materials, together with a 15% rate of CRM recovery, originating either from mining tailings or in the context of mine reopening. Thus, the urgent need to maximize CRM recovery makes it strategically important to attempt the reuse of polluting residues from abandoned/dismissed mining sites, including tailings, stockpiles, and waste rocks from extractive and ore processing, which often still contain chemical elements and mineral resources worth of recovery. Furthermore, unveiling the source(s) of potential metal contaminants and the mechanisms governing their release into the environment is crucial for their possible reuse and/or evaluation of their environmental effects.

To infer the geo-availability and mobility of metals in mine-waste dumps and mechanisms governing their release, a combination of chemical extraction methods, bulk chemical analyses, X-ray diffraction (XRD), and X-ray microanalysis of the residence phase(s) of metals is required [6–8]. Field-portable analytical instrumentations have developed rapidly over the past two decades as the result of relevant technological advances, which have made on-site analysis possible and a credible alternative to laboratory analysis. By offering analytical results on the spot in almost real-time, on-site analysis satisfies the increasing need of exploration teams to achieve fast data that can provide immediate sample screening and decision-making support regarding site remediation, cleanup, disposal, and mitigation directly in the field before the transfer of selected samples to the laboratory for further, more detailed analysis [9]. This approach allows for time, flexibility, and analytical costs to be gained, with a significant impact on the efficiency and cost-effectiveness of field operations, especially in remote areas.

Laser-induced breakdown spectroscopy (LIBS) is an advanced optical emission spectroscopy technique that can perform rapid and trustable simultaneous multi-element analysis of several materials, including terrestrial and extraterrestrial minerals, rocks, and soils (Table 1). In particular, the availability of handheld (h) LIBS analyzers, which were developed commercially in the mid-2010s [10–12], has expanded the use of real-time in situ analysis of materials directly in the field and has promoted the use of LIBS across geosciences by providing some unique capabilities (Table 1).

Table 1. Reviews and book chapters published in the last ten years dealing with LIBS, and more specifically with hLIBS, applied to mineral and rock exploration.

Authors	Year	Title	Journal/Book
Hark and Harmon	2014	Geochemical Fingerprinting Using LIBS	In *Laser-Induced Breakdown Spectroscopy-Theory & Applications*. Springer: Berlin/Heidelberg, Germany, pp. 309–348
Senesi	2014	Laser-Induced Breakdown Spectroscopy (LIBS) applied to terrestrial and extraterrestrial analogue geomaterials with emphasis to minerals and rocks	*Earth Sci. Rev.*, 139, 231–267
Qiao et al.	2015	A review of laser-induced breakdown spectroscopy for analysis of geological materials	*App. Spect. Rev.*, 50, 1–26
Balaram	2016	Current Advances in Miniaturization of Analytical Instruments-Applications in Cosmochemistry, Geochemistry, Exploration and Environmental Sciences	*Spectroscopy*, 31, 40–44
Balaram	2017	Field-portable instruments in mineral exploration: Past, present, and future	*J. Appl. Geochem.*, 19, 382–399
Crocombe	2018	Portable Spectroscopy	*Appl. Spectrosc.*, 72, 1701–1751

Table 1. *Cont.*

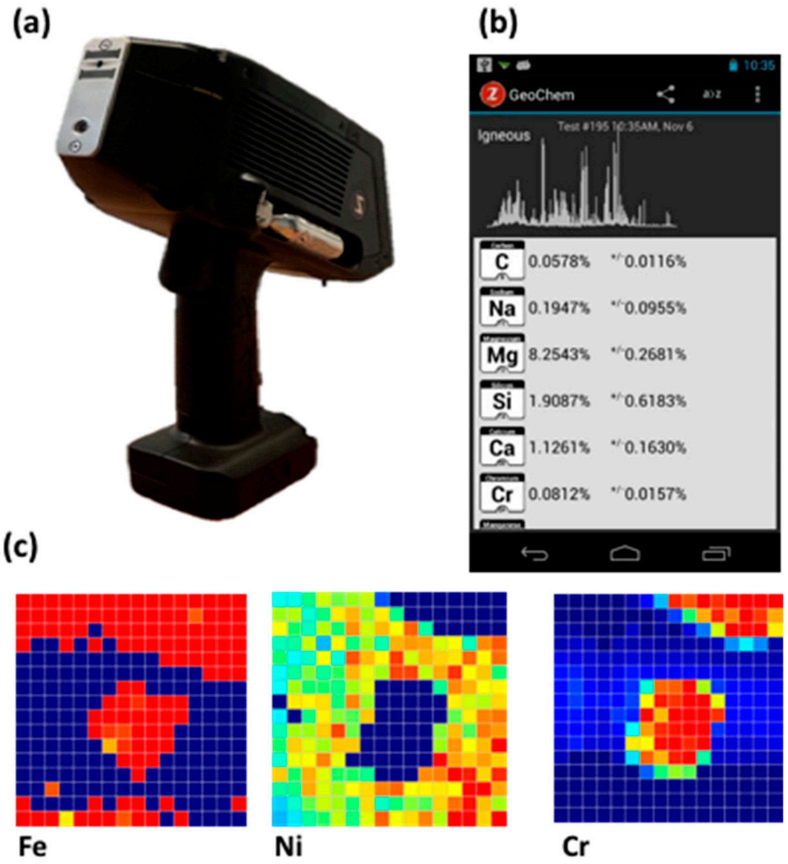
Authors	Year	Title	Journal/Book
Lemière and Uvarova	2019	New developments in field portable geochemical techniques and on-site technologies and their place in mineral exploration	*Geochem. Explor. Environ. Anal.*, 20, 205–216
Harmon et al.	2019	Laser-Induced Breakdown Spectroscopy-An Emerging Analytical Tool for Mineral Exploration	*Minerals*, 9, 718
Fabre	2020	Advances in Laser-Induced Breakdown Spectroscopy analysis for geology: A critical review	*Spectrochim. Acta Part B At. Spectrosc.*, 166, 105799
Senesi et al.	2020	Field-portable and handheld LIBS: Historical review, current status, and future prospects	*Spectrochim. Acta Part B At. Spectrosc.*, 175, 106013
Senesi et al.	2020	Field-portable and Handheld LIBS.	In *Laser-Induced Breakdown Spectroscopy*, 2nd ed. Elsevier, pp. 537–560
Buckley	2021	Geochemical analysis using laser-induced breakdown spectroscopy	*Spectroscopy*, 36, 9–14
Day	2021	Handheld Laser-Induced Breakdown Spectroscopy (HHLIBS).	In *Portable Spectroscopy and Spectrometry 1: Technologies and Instrumentation*. John Wiley & Sons: Hoboken, NJ, USA, pp. 321–343
Harmon and Senesi	2021	Laser-Induced Breakdown Spectroscopy-A geochemical tool for the 21st century	*Appl. Geochem.*, 128, 104929
Lemière and Harmon	2021	XRF and LIBS for field geology.	In *Portable Spectroscopy and Spectrometry 1: Technologies and Instrumentation*. John Wiley and Sons: Hoboken, NJ, USA, pp. 455–497
Balaram and Sawant	2022	Indicator Minerals, Pathfinder Elements, and Portable Analytical Instruments in Mineral Exploration Studies	*Minerals*, 12, 394
Senesi and Harmon	2023	Application of LIBS to Terrestrial Geological Research	In *Laser-Induced Breakdown Spectroscopy (LIBS): Concepts, Instrumentation, Data Analysis and Applications, Volume 2*, 1st Edition. John Wiley & Sons Ltd., pp. 593–614
Harmon	2024	Laser-Induced Breakdown Spectroscopy in Mineral Exploration and Ore Processing	*Minerals*, 14, 731
Harmon and Senesi	2024	Laser-Induced Breakdown Spectroscopy (LIBS)	In *GGR Handbook of Rock and Mineral Analysis*, Chapter 13. *Geostand. Geoanal. Res.*, 48, 763–792
Harmon et al.	2025	Laser-Induced Breakdown Spectroscopy (LIBS)	In *Treatise on Geochemistry* (3rd edition), Elsevier, pp. 607–644

The aim of this perspective paper is to focus on the potential future application of recent promising advanced hLIBS instrumentation to the analysis of mine waste in view of their safe and sustainable recovery/recycling/reuse.

2. Basic Principles of the LIBS Process and Instrumentation

The LIBS technique is a kind of atomic emission spectroscopy, which is simple, dependable, and adaptable, and allows the rapid, in situ chemical analysis of the elemental composition of almost any material (gas, liquid, or solid) by measuring the light emitted by its plasma [13]. The broadband LIBS spectrum generated by a single laser shot can detect in real time any element present in the sample above its intrinsic limit of detection (LOD), which is determined by the instrument design and sample matrix. Furthermore, analysis conducted in a plasma confined in an inert He or Ar atmosphere can remarkably improve the elemental emission intensities and the overall analytical performance of the technique.

A typical LIBS equipment includes a laser, a spectrometer, several lenses and optical fibers, a data acquisition system, and a system for controlling and synchronizing the laser and spectrometer. The garnet yttrium doped neodymium (Nd:YAG) solid-state laser featuring a characteristic wavelength of 1064 nm is the most widely used laser in LIBS. When the sample is exposed to a high-power laser beam, a tiny amount of matter, of the order of nanograms, is ablated and generates a plasma plume. A charge-coupled device (CCD) detector reveals the evolution of the light emitted by the plasma, thus yielding a spectrum containing distinct atomic and ionic emission lines typical of the various elements present in the sample analyzed (Figures 1b and 2).



C 0.0578% +/-0.0116%
Na 0.1947% +/-0.0955%
Mg 8.2543% +/-0.2681%
Si 1.9087% +/-0.6183%
Ca 1.1261% +/-0.1630%
Cr 0.0812% +/-0.0157%

Figure 1. Example of an hLIBS instrument (**a**); onscreen display of the instrument which shows the spectrum acquired and the chemical information on the elements detected (**b**); example of microscale

mapping of the distribution of Fe, Ni, and Cr elements in an iron meteorite achieved using a single laser shot by raster scanning over a 2-mm^2 area and shown in a gradient of colors that varies from red for high relative abundance to blue for low relative abundance. The spectral lines used to construct these microchemical maps are Fe = 404.58 nm; Ni = 227.01 and 338.06 nm; Cr = 428.97 nm (**c**).

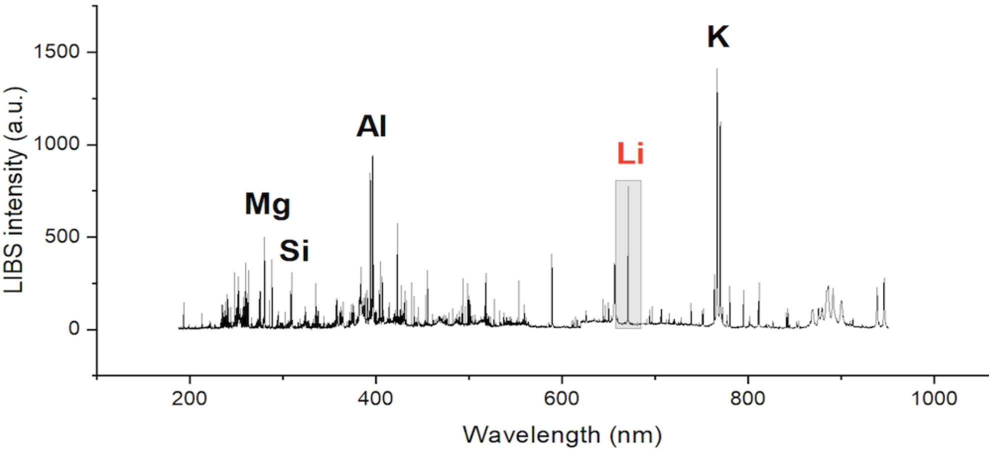


Figure 2. Averaged broadband LIBS spectrum acquired from a metamorphic rock. Some specific emission lines of the elements Mg, Si, Al, and K are detected, together with that of Li at 610.79 nm, which highlights the capacity of hLIBS to detect light elements.

An hLIBS instrument consists of a compact, lightweight, self-contained unit (Figure 1a) that can be comfortably used whilst being held in the hand of the operator features that make it a very attractive analytical choice for many applications [11]. The smaller size and weight of the instrument assume special importance as it can be easily transported across the field for extended periods of time and/or when analysis must be performed in constricted or otherwise inaccessible areas.

3. Attributes/Advantages of hLIBS for On-Site Analysis of Mine Wastes

The hLIBS instrument features several attributes that make it an attractive tool for the on-site analysis of mine wastes. These include:

- real time (<1 s) analysis;
- simultaneous capture of the full elemental composition of a sample with a single laser pulse, as any element in the periodic table has one or more emission lines in the spectral regions between 190 and 950 nm;
- particular sensitivity to light elements such as H, Li, Be, B, and C, which cannot be readily analyzed by many other analytical techniques;
- small analytical laser spot size diameter, typically around 100 s μm;
- requirement of only picograms (pg)/nanograms (ng) of material for an analysis;
- little to no sample preparation involved in the analysis;
- use of the initial laser shots to efficiently “cleaning” the sample surface from dust, burning contamination, and oxidation layers;
- availability of a miniature camera in the nose of the instrument that enables the view and optimization of the correct location of the analyzed sample points and the documentation/archiving of samples;
- as a point source detector, the capability of analyzing mineral and rock surfaces at a sub-millimeter spatial resolution of individual particles, mineral grains, and solid inclusions;

- capacity of using multiple additional laser shots at any location in order to achieve the stratigraphic composition profile down to a depth > 100 µm, especially in the case of the presence of a surface-weathered coating/patina;
- possibility of beam rastering by firing the laser beam across a 2-mm segment of the sample and configuration of the pattern of the raster grid in order to optimize the number of laser spots on the sample surface;
- possibility to achieve microscale mapping (Figure 1c) by a single laser shot at a fixed laser firing rate of 10 Hz at 256 locations over a 16 × 16 grid over 2 mm^2 areas at 12.5 µm steps with mg/kg-level sensitivity;
- safe design that avoids any laser operation in the air if no sample is positioned in front of the nose, so allowing the operator to perform analyses safely;
- power supplied by one/two lithium-ion battery(ies), which allow between six and eight hours of operation;
- availability of a GPS receiver that facilitates analysis and the efficient finding of location, so allowing real-time decisions to be taken with reasonable confidence.

4. Limitations of hLIBS in Practical Operations

The physical properties of the material being ablated, such as its composition, crystallinity, texture, optical reflectivity, optical transmissivity, and surface morphology, as well as the degree of laser energy coupling to the sample surface and the surrounding environment, influence the features of the plasma generated from a solid sample. By principle, the intensity of the LIBS plasma emission is proportional to the concentration of the corresponding element in a sample; thus, the abundance of an element in a sample can be measured by the intensity of light detected at a given spectral wavelength. Although surface asperities may cause a loss of ablation and issues with plasma emission, even in the case of a not perfectly flat sample, the signal is often adequate for element identification by hLIBS.

The dynamic behavior of LIBS plasma and the presence of chemical and physical matrix effects further complicate the quantitative analysis of geomaterials achievable by LIBS [12,14–16]. In particular, chemical matrix effects due to interferences occurring in the plasma between the emission of the element of interest and other ones can be mitigated by optimization of the hLIBS analytical system. Differently, physical matrix effects, which influence the amount of mass ablated by the incident laser pulse, originate from the nature of the sample, i.e., its grain size, porosity, degree of crystallinity and/or induration, texture and roughness, hardness, absorptivity, thermal conductivity, optical transmissibility and reflectivity, water content and presence of organic matter, are much more difficult to eliminate [12,14–16].

Thus, samples must be as homogeneous as possible at the laser beam scale, at least on the area fired by multiple laser shots, especially in cases requiring in-depth analysis. Prior to any geochemical interpretation, the granulometry of the rock must be duly considered, particularly for analyses performed on micrometric areas. In particular, if the bulk composition of the rock is required, the number of analyses must be multiplied. Depending on how smooth the material is, hLIBS analysis can be somewhat destructive, i.e., for every laser shot, a layer of several to dozens of micrometers will be ablated. Finally, depending on the size and physical characteristics of the sample, different minerals may require modifications of the data acquisition procedures.

5. On-Site Data Acquisition and Analysis of Mine Wastes

The LIBS spectra can be directly displayed on the instrument just after the analyses (Figure 1b) and then can be exported either as individual raw spectra or as averaged spectra from the instrument to the user's computer by a USB connection or Wi-Fi. The spectra can be used preliminarily for on-site qualitative analysis in order to identify the emission lines of the detected elements. Then, quantitative analysis can be achieved by means of a set of matrix-matched reference materials using either single-element or multivariate calibration procedures [17,18] and/or using internal calibration-free methods [19]. The total area under a peak, or LIBS area intensity, expressed in arbitrary units (a.u.), is the information needed to develop a calibration curve. Finally, once loaded onto the instrument, the concentrations of the target elements can be calculated using the calibration method selected by the user. Furthermore, when combined with established databases and chemometric methods, LIBS spectral analysis can be used to quickly identify and distinguish unknown materials [20].

Even if the sample is not perfectly flat, the LIBS signal is generally good enough to identify the element, whereas, for example, when using µRaman spectroscopy, various instrumental factors, such as focal plane precision, exposure duration, and field light conditions, may impact the collection and interpretation of spectroscopic data from the specimen. Furthermore, surface conditions and sample heterogeneities often make it difficult to perform real-time chemical and mineralogical analyses of drill cores using portable X-ray fluorescence (pXRF), portable Fourier transform infrared (pFTIR), XRD, and Raman spectroscopy [21].

6. Comparison of hLIBS with Portable X-Ray Fluorescence (pXRF)

The primary rival of hLIBS for the chemical analysis of mine wastes is pXRF [11,20]. Both hLIBS and pXRF are elemental analysis techniques that satisfy the requirements of field use by geoscientists in ambient conditions. Both techniques are basically able to detect, identify, quantify, and classify elements in geological materials in the field. However, each technique implies unique benefits and drawbacks. For example, hLIBS is significantly faster (a few seconds) than pXRF (typically tens of seconds to minutes) for immediate elemental identification. Furthermore, pXRF is incapable of identifying the lightest elements H, Li, Be, B, C, N, and O that may be present in mine waste, whereas hLIBS is very performant in detecting light elements and metallic elements in the middle of the periodic table, but far less efficient in measuring elements of high ionization potential such as S, P, F, Cl, and Br. In particular, pXRF currently performs better than hLIBS in the analysis of rare earth elements and basic metals, thanks to its lower elemental LODs.

In comparing the performance of the two techniques, it is also critical to take into account the spatial dimension of the area to be analyzed and sample preparation. While hLIBS can use the initial laser shots to ablate and clean the sample surface when needed, pXRF is not able to do this as it is a surface technique, so in some cases, preliminary surface cleaning and/or preparation may be required. However, pXRF is a non-destructive technique, whereas hLIBS is micro-destructive as it forms a small crater on the sample surface. Thus, a hLIBS analysis of a specific spot on a sample cannot be repeated.

Furthermore, an individual hLIBS shot covers a very small area (50 to 600 µm in diameter), whereas the pXRF spot size is usually several mm in diameter; thus, hLIBS features a much higher spatial resolution than pXRF. Additionally, hLIBS usually employs a rastering means to achieve representative data, which offers the possibility to map the sample surface composition on a very small spatial scale.

In general, a hLIBS spectrum is relatively complex, as it may display many characteristic lines for each element present in the sample, which enables the selection of a specific emission line for analysis, thus minimizing or avoiding the occurrence of interferences from spectral lines of other elements. Differently, a pXRF spectrum is much simpler, displaying only two to five distinctive lines per element, which, in the absence of alternative lines, requires the use of fitting algorithms to deconvolute any potential spectral overlaps and interferences that may occur in the case of certain samples.

Another unique advantage of hIBS is the capacity to gain information on a sample composition as a function of depth by shot-by-shot material removal. Differently, the actual depth penetration of XRF is not completely clear as X-rays are thought to penetrate down to a few µm to several mm, depending on the nature of the sample matrix. Although the maximum amount of fluorescent X-rays that can be detected in a sample is a few mm, this value is frequently lowered to a few µm or less, which implies that the use of pXRF for bulk analysis of mine wastes covered by a weathering patina is inappropriate.

Both pXRF and hLIBS can yield accurate quantitative data by making use of suitable matrix-matched standards to construct uni- or multivariate calibration curves for analytical purposes. Finally, unlike pXRF, an hLIBS instrument does not emit ionizing radiation, so it does not require the same special operating and transportation requirements.

In conclusion, although hLIBS would appear to be a technique more widely applicable than pXRF due to its ability to identify light elements and accomplish an analysis more rapidly, it should be regarded as a technique complementary to pXRF to achieve an exhaustive analysis of waste mines.

7. LOD Values Achievable by hLIBS Elemental Analysis

The elemental LODs that can be achieved by hLIBS depend on the type of element, the sample features and its physical properties, the performance of the hLIBS instrument, and the analytical conditions. In general, the LIBS analytical LODs and precision levels are, respectively, of the order of tens of mg/kg and from 5 to 20% RSD, which are often lower than those achieved by some other techniques used in geomaterial analysis. In particular, the LODs of elements with low ionization potentials, such as Li, are relatively low, while those of elements with high ionization potentials, such as F, Cl, and S, are significantly higher. For example, typical LODs achieved for Li, Be, Na, Mg, Ca, Sc, and Y are <10 mg/kg; for H, B, C, O, Si, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Zr, Mo, Rh, Pd, Ag, Cd, Sb, Cs, and Ba are <100 mg/kg; and for F, Al, P, S, Cl, Ga, Br, Nb, In, I, W and, Pt are > 100 mg/kg [22].

According to Ytsma et al. [23], who used more than 2000 rock standards, and Buckley [22], the analytical LODs achieved by hLIBS are very variable but have steadily improved over the past two decades, simultaneously with the technological progress of LIBS instrumentation. Thanks to the possibility of precisely controlling the laser power and optimizing other instrumental operating parameters, the LODs obtained by laboratory LIBS instruments are lower than those typical of field-portable analyzers. However, with the advancement of hLIBS instrument technology, the LODs achieved by hLIBS have been steadily getting better and better over the past 20 years [24].

Furthermore, the inherent connection between spatial resolution and LOD is significant. As the elements present in samples such as soils, rocks, and minerals can be very variable, the concept of LOD may result in very complex and challenging geoscience applications [12]. Therefore, improving LOD may not always be as beneficial as increasing spatial resolution to measure the compositional variations at very small spatial scales.

8. hLIBS as a Promising Means for On-Site Analysis of Mine Wastes in View of Their Possible Recovery/Recycling/Reuse

Mine wastes are very different from wastes from other sources in terms of amount, characteristics, mineralogy, and methods used for their enrichment and processing. The majority of mine wastes are kept in slurry ponds and dump sites, but in certain mineral sites, post-leaching ore piles are present. For example, the release of acidic drainage fluids from iron sulfides, e.g., in coal mines, or sulfur in basic metal mines, which may be exposed to oxidation, are among the most dangerous environmental issues that can arise in these waste sites if waste is disposed of superficially [25].

In some cases, the collection of representative waste samples from disused mine sites may be difficult due to the compositional, spatial, and size heterogeneity of the waste material in which metals of interest generally reside in microscopic phases [7,8]. However, microanalytical techniques, including X-ray mapping, X-ray point analysis, and electron microscopy, can locate as small as 1 micrometer particles containing trace elements and individually analyze them to identify their mineral composition, chemistry, and weathering sequences [7,8]. Usually, mine waste samples are collected from the mining site and transferred to an off-site laboratory, where they are analyzed using appropriate techniques that involve time-consuming and complex sample preparation and analytical processes. Furthermore, rock/mineral surfaces may be subject to significant chemical changes in their composition due to weathering processes, e.g., by the effect of rain and snow. Thus, hLIBS would be the only technique that can guarantee the appropriate sample interrogation on-site if the target rock or mineral face is not present in a fresh, unweathered state.

Metals like Fe, Cu, Ni, and Zn may be found in mine tailings and wastes in relatively high concentrations (0.5–3%), and precious metals like Au and Ag may also be found occasionally. Furthermore, toxic elements like As may be found in concentrations up to 100 mg/kg [26], and metals like Ga, In, and other rare earth elements, which were considered unworthy of extraction during the initial processing of the ores but have since then gained value and application, may also be present in mine wastes at concentrations of interest [26,27]. In general, reusing mine waste consists of using the entire waste for a particular purpose without reprocessing, whereas recycling consists of reprocessing the mine waste as feedstock to extract new valuable resource products [28].

Thus, the amount of time and effort required for the entire recovery, either reuse or recycle, multi-stage process is an important limiting economic factor in the exploitation of mine wastes, which can be potentially reduced drastically by the use of on-site hLIBS analysis. However, currently, hLIBS is not yet used to analyze mine wastes on-site in view of their possible recovery, and, to my knowledge, only one case study is available in the scientific literature on the use of LIBS to analyze mine wastes [29]. For this reason, it is fundamental to investigate the great potential of using hLIBS for this purpose.

On the other hand, nowadays LIBS is a widely used analytical technique in the context of mineral exploration and prospecting, and ore processing [12] and references therein [21] for: (i) real-time chemical analysis in situ with little or no sample preparation at spatial scales down to ~ 10 µm; (ii) analysis of thin coatings and/or surface alterations; (iii) rapid and highly spatially resolved megapixel hyperspectral imaging of chemically zoned rocks and minerals; (iv) downhole compositional interrogation and drill core characterization; and (v) online slurry monitoring during ore processing.

Very often, drill cores are needed for metal resource estimation in mine tailings and ore deposits. With this regard, Kuhn et al. [29] used three drill core meters from the tailings of a former Pb–Zn mine to test two different core scanning techniques in order to acquire chemical data able to identify zones of metal enrichment or depletion, as well as distinct lithological zones in the cores. In particular, a core scanner prototype using LIBS was tested to determine the element concentrations in the tailings, in comparison to a commercially available ITRAX core scanner that uses energy-dispersive (ED) XRF. The phase and mineral distribution maps at larger scales of the drill core, as well as the two-dimensional (2D) element distribution images, could be measured thanks to the high spatial resolution of the LIBS core scanner. Metal-rich layers not visible by the human eye and featuring concentrations up to 2.2% of Pb + Zn + Cu were identified within the analyzed tailing cores by both core scanning methods. However, economically interesting metals, such as Pb, Zn, Cu, Co, and Ni, were not equally distributed within the analyzed mining residues, but they were enriched only in certain layers. This result might be caused by sedimentation processes occurring during the injection of the slurry from (different) spigot points, as well as by the deposition of different residues from different ore processing steps. Furthermore, the weathering of the waste material might have led to the depletion or enrichment of metals in certain zones.

9. Future Perspectives of hLIBS Application to Mine Waste Analysis

The availability of commercial hLIBS instruments in the last 20 years has facilitated on-site geochemical analysis in the field by filling the gap with respect to other field-portable technologies, such as short-wavelength infrared spectrometers and pXRF analyzers whose detection capabilities are limited by technical constraints, and also providing an unparalleled capability for light element ($Z < 13$) analysis. Furthermore, the initial investment in the instrumentation and the operator's time account of hLIBS involve low and very affordable costs.

Based on the above discussion, the robust promising potential for hLIBS use in mine waste exploration and recovery is evident. The analysis by hLIBS conducted during a field campaign can rapidly identify and quantify elements of economic importance that cannot be recognized by other techniques; also, hLIBS can be used for on-site analysis of pathfinder minerals. Furthermore, hLIBS can also achieve the micro-scale analysis necessary to understand the elemental distribution and complex mineral paragenesis in a set of samples. By screening the sample compositional variation on site, it is possible to infer the most significant elements of interest and concentrate on the most crucial portions of concentration ranges, thereby reducing the number of repetitive, useless samples to be transferred to the laboratory for further analysis. Thus, the screening process that can be performed by hLIBS reduces laboratory expenses and analyses while lowering the cost of sample transportation to the analytical laboratory. Furthermore, the use of hLIBS may be expected to encourage the field operator to map and extend the investigation in areas where abandoned mine wastes are present instead of waiting for laboratory results and returning to the field area after achieving results from the analytical laboratory. In conclusion, the results of hLIBS analysis can provide a robust basis for further sampling and contribute to reducing the number of samples and, therefore, the costs for further investigations in the laboratory, also favoring management decision-making. Time benefits for exploration of mine waste sites can be weeks or months, and the savings extend beyond field campaigns and logistics to include the cost of the ensuing laboratory work.

Furthermore, the use of hLIBS allows the production of datasets much bigger than those achieved by laboratory analyses, which leads to a significantly denser spatial coverage of a study area. Even if the inherent quality of field analytical data is not as good as that of top-notch laboratory data, the total amount of pertinent data in the set could be significantly higher. As a result, the global dataset quality will frequently be significantly higher because of the lower possibility of missing important geochemical observations [20]. When decisions need to be taken about a prospecting mine waste field, a dataset, even of lower quality but achieved on a high number of samples, may have a higher degree of confidence than a high-quality laboratory dataset with significantly fewer samples.

The use of chemometrics, machine learning, and artificial intelligence algorithms in conjunction with cutting-edge data processing can further improve the usefulness of hLIBS data. However, it is rare that a single technique can fully characterize the minerals present in mine waste; thus, most researchers prefer to employ a combination of techniques to characterize the minerals in mine wastes and slurries [30]. For example, the combined use of hLIBS, µRaman, and UV/VIS/NIR spectroscopy results very performant in identifying minerals at the sub-millimeter spatial scale and characterizing rock textures and coatings, hydrated components, and biomolecules in mine wastes. Another example is the integration of pXRF and hLIBS, which together, provide a powerful complementary capability for rapid chemical analysis in the field, which is not currently possible with either analyzer individually. Trained geologists and environmental scientists with a sufficient understanding of geochemistry can use both pXRF and hLIBS analyzers efficiently.

The most suitable portable instrumentation must also be evaluated based on the type of chemical elements to be identified and the ambient conditions. Nowadays, little research and development are in the course of the chemical composition and geotechnical characterization of mine tailings; thus, more studies are required in view of their possible sustainable recycling and recovery [2], which, in terms of volumes, are still in their infancy in the majority of countries. However, in wealthy and environmentally conscious countries, local regulatory pressures are the primary forces behind action [3].

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