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# Integrating LIBS and NIR for detection of heavy metals in perlite ores

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## Abstract

Perlite products are used as a filter aid in the food industry. For such applications, the purity of the material is one of the most significant parameters of control. Early detection of heavy metals is therefore of great industrial interest. In this study, a sensor-based approach for chemical and mineralogical characterization enabled the identification of patterns in the distribution of heavy metals in the perlite ore. Integration of Laser-Induced Breakdown Spectroscopy (LIBS) and Near Infrared Spectroscopy (NIR) was used to determine the presence of heavy metals in perlite ores. The results have direct implications for the development of methods and techniques for material characterization, as well as for the mining of perlite ores.

## Introduction

Perlite is a generic term for a naturally occurring hydrated volcanic glass. For commercial applications, perlite is heated to temperatures between 800 and 1100°C. This causes expansion up to twenty times its original size (Doğan and Alkan 2004). Such treatment allows the production of a light-weight and highly porous aggregate. The exceptional expansion capabilities and chemical inertness of perlite make it a material of economic interest (Barker and Santini 2006). Main applications of perlite include construction products, horticultural aggregates, fillers and filter aids for filtration of water, pharmaceuticals, food products and chemicals. For the filter aid applications, the purity of perlite products is of outstanding importance. The regulations regarding the composition of processing aids, especially in the food industry, set strict parameters that suppliers should fulfill (FAO 2006; FCC 2012). The presence of chemical impurities in excess of those parameters are deleterious penalties for the perlite products.

Perlite is formed by the chemical weathering of volcanic glass present in rhyolitic domes. It is composed mainly of opaline silica and occasionally is associated with clay minerals. The

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geological conditions that lead to the formation of perlite deposits sometimes result in the occurrence of heavy metals. Depending on the physicochemical conditions of the system, perlite adsorbs these elements (Silber et al. 2012). This results in pollution of the ore, with a subsequent impact on the quality of perlite filter aids.

Timely detection of heavy metals is of relevance during mining and mineral processing. However, a comprehensive understanding of the distribution and controls upon their distribution in the ore has not yet been developed. There is strong industrial interest in the development of methods and techniques to permit the detection of heavy metals in perlite ore. A sensor-based approach for in-pit characterization that integrates chemical and mineralogical analysis could provide real-time tools for the detection of the target elements.

Laser-Induced Breakdown Spectroscopy (LIBS) is becoming more used for the identification of major and trace elements in geological samples (Harmon et al. 2013). The growing interest in real-time analysis has prompted the development of LIBS systems for qualitative and quantitative chemical analysis of raw ores in field conditions (Gaft et al. 2007). Determination of heavy metal content using LIBS has been successful for detection of the levels of pollution in soils (Capitelli et al. 2002). This demonstrates the suitability of LIBS as a technique for detection of heavy metals associated with the perlite ore.

Near Infrared (NIR) spectroscopy is a well-known technique for identification of alteration minerals (Clark 1999). Technological developments have led to a broad range of instruments that permit rapid and on-site recognition of minerals (Thompson et al. 1999). The main constituents of perlite, which are opal and clay minerals, have distinctive features in the NIR spectrum. Opal ($SiO_2 \cdot H_2O$) has absorptions related to surface hydroxyl groups, structural water, and Si-OH bonds respectively at 1400nm, 1900nm and 2200nm. Clay minerals are distinctive by strong absorptions at 2200nm, associated with the Al-OH bonds, and other secondary absorptions depending on the type of clay (Hunt 1977).

In this research, integrated LIBS and NIR spectroscopy are used for the characterization and the detection of heavy metals in a perlite mine. The samples were obtained from a deposit affected by hydrothermal alteration. Chemometrical analysis of LIBS, complemented with XRF data, detects the presence of heavy metals and establishes groups of correlated elements. Extraction of NIR spectral parameters determines the dominant mineralogy. The integration of chemistry and mineralogy shows that some of the heavy metals behave accordingly with the mineralogy.

## Materials and Methods

A total of 19 samples were provided for this study from a perlite mine in Turkey. The samples were selected to be representative of an area in the pit that shows the influence of hydrothermal alteration. One of the samples was from a rhyolite dyke that cuts the perlite deposit, causing hydrothermal alteration. The rest of the samples were taken from various distances around this dike. For the analysis, the samples were powdered using mortar and pestle.

For the chemical characterization, XRF data were used as a reference for the LIBS study. One XRF measurement per sample was made using XRF Pro-Trace. Analyses comprised forty trace elements, $Fe_2O_{3,}$ and $TiO_2$. The LIBS measurements took place at an experimental set-up at TNO (the Netherlands Organization for Applied Scientific Research). The instrument specifications included a Litron laser Nd:YAG at 1064nm and a spectral range between 200 to 800 nm. For each sample, sixteen scans in a 4x4 grid were recorded. The NIST database (Kramida et al. 2014) assisted in the selection of specific emissions for the determination of elements. The data was processed in Matlab®. The XRF and LIBS analyzes were done in LatentiX, which is a specialized software for chemometrics.

The NIR reflectance spectra were measured using an ASD LabSpec, from PANalytical. The spectral range covered both the visible and near infrared ranges, from 350 to 2500 nm. Three measurements were made for each sample to ensure quality of the data. The spectral pre-processing included splice correction and continuum removal. Use of The Spectral Geologist software (TSG) assisted in the extraction of spectral parameters for mineral identification. The USGS spectral library was used as reference (Clark et al. 2007).

The selection of the analytes was based on the parameters established by the legislation regarding food processing aids (FAO 2006; FCC 2012), and the general purity acceptance criteria set by perlite customers for food, wine, and cosmetic applications. The heavy metals of high interest are arsenic (As), lead (Pb), cadmium (Cd), mercury (Hg). The metals of secondary interest are antimony (Sb), neodymium (Nd), cobalt (Co), chromium (Cr), nickel (Ni), iron (Fe), copper (Cu), selenium (Se), zinc (Zn) and barium (Ba).

The data analysis approach consisted first of a chemical characterization of the selected analytes using the XRF dataset, followed by interpretation of the LIBS data. The mineralogical characterization was conducted with NIR spectroscopy. Finally, the results of chemistry and mineralogy were integrated. A chemometrical analysis of the XRF and LIBS datasets using Principal Component Analysis (PCA) assisted in the identification of possible correlations between heavy metals and the definition of parameters for analysis. The basis of the mineralogical characterization was the extraction of depth, width and wavelength position of the spectral absorptions as main parameters. This led to the identification of the mineral content, and to the establishment of mineral relationships. The correlation between chemistry and mineralogy was assessed with an integrated interpretation of the XRF-LIBS and NIR results.

# Results

## Chemical characterization

### *XRF analysis*

To characterize the heavy metal content of the samples, a PCA analysis was performed for the elements of interest (twelve elements and two oxides). The objective of the analysis was to identify patterns in the distribution of the heavy metals, which would serve as a basis for the further LIBS analysis. The first and the second PCA components gave the most relevant information. According to the loadings of these components, displayed in Figure 1, some of the heavy metals were correlated along the sample-set, meaning that their concentration in the samples varied similarly. Based on this, three groups could be described. The first component suggested a good correlation among As, Rb, and Ba, and among $TiO_2$, $Fe_2O_3$ and Zn. The loadings suggested that there was a negative correlation between these two groups. The second component indicated that Pb, Nd, and Cu were also associated. The other elements did not have any clear pattern.

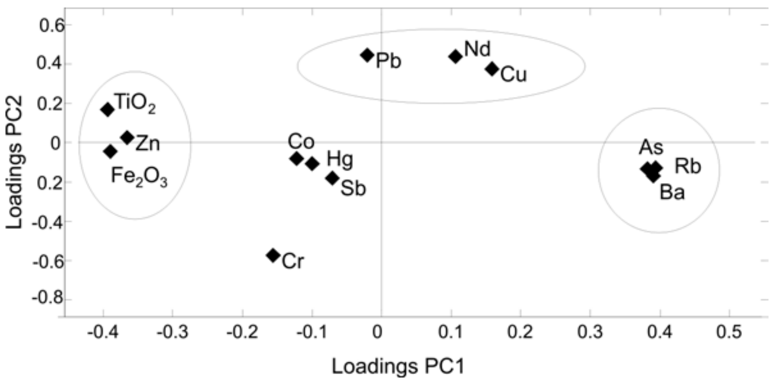

Figure 1 Loadings of the 1st and 2nd component of the heavy metals PCA analysis. Three groups of elements are identified: As-Rb-Ba, $TiO_2$-$Fe_2O_3$-Zn, and Pb-Nd-Cu,

The definition of three groups of correlated elements, plus a fourth group with the remaining ones, constituted the basis of the LIBS analysis. For this, the groups are labeled as *Group 1*: As, Ba, Rb; *Group 2*: Zn, $TiO_2$, $Fe_2O_3$; *Group 3*: Pb, Nd, Cu; and *Group 4*: Co, Hg, Sb, Cr.

### *LIBS analysis*

For the evaluation of the LIBS data set, two main parameters were taken into consideration. The first one refers to the groups defined by the XRF-PCA analysis. The second parameter was given by the actual concentration of the heavy metals in the samples, the industrial standards for purity criteria and the limit of detection of the LIBS instrument. Table 1 shows all these considerations and reveals that not all the elements were suitable for a successful LIBS analysis. However, based on the established correlation by XRF, the detection of at least one element per group could be used as a proxy for the remaining heavy metals. In Group 1, arsenic was far below the detection limit, and rubidium is close to it, although LIBS could easily detect barium. In Group 2 all the elements were detectable; nevertheless, the complex spectra of iron and titanium hindered their reliable identification, whereas detection of zinc was simpler. In Group 3, lead was the element with the most accurate detection. In this way, LIBS analysis of Ba, Zn and Pb was considered as representative of their respective groups. Given the lack of correlation of the elements in Group 4, the selection of a single element as group representative was not valid. Moreover, the heavy metals in this group were either below or close to the LIBS limit of detection; in other elements the concentration was below the purity criteria. For these reasons, Group 4 was excluded from the LIBS analysis.

Table 1 Parameters for the selection of analytes for LIBS. The selected analytes per group are in bold letters

| Group | Heavy metal | Samples content* (ppm) | Purity criteria (ppm) | LIBS detection limit (ppm) | Suitable for LIBS analysis |
|---|---|---|---|---|---|
| **1** | As | 2-10 | <5 | 100-500 | No |
| | **Ba** | 618-1259 | Only detect | 1-10 | Yes |
| | Rb | 16-130 | Not reported | 10-100 | Probable |
| **2** | Fe** | 0.649-1.585 | <300 | <1 | Yes |
| | Ti** | 0.108-0.159 | Not reported | 1-10 | Probable |
| | **Zn** | 32-69 | Only detect | 1-10 | Yes |
| **3** | **Pb** | 34-58 | <5 | 1-10 | Yes |
| | Cu | 1-21 | Only detect | 1-10 | Probable |
| | Nd | 17-33 | <20 | Not reported | No |
| **4** | Co | 1-3 | <1 | 10-100 | No |
| | Hg | 0.002-0.14 | <1 | <1 | Yes |
| | Sb | 4-6 | <2 | >500 | No |
| | Cr | 1-3 | <5 | <1 | Probable |

* Sample content range corresponds to the minimum and maximum values reported by XRF

** Sample content for Fe and Ti are reported as oxides in Wt%

For the analysis of Ba, Zn, and Pb, the three strongest LIBS lines were selected. Table 2 lists the LIBS lines utilized in the analysis.

Table 2 Selected LIBS emissions for the identification and analysis

| | **Ba** | **Zn** | **Pb** |
|---|---|---|---|
| 1st strongest emission | 493.56 | 637.23 | 363.28 |
| 2nd strongest emission | 456.52 | 334.84 | 404.76 |
| 3rd strongest emission | 553.73 | 250.81 | 357.71 |

A PCA analysis intended to assess if the relationship among these elements was comparable to the XRF-PCA results. The LIBS-PCA loadings, displayed in Figure 2, showed that the second component differentiates Zn from Ba and Pb. It indicates that the variation in the concentration of Zn had an opposite pattern than the other two elements. The third component separated Pb and Ba, due to their negative correlation. Due to the nature of the dataset, the LIBS loadings are inverted in relation to the XRF loadings. In this case, high loads represent low concentrations.

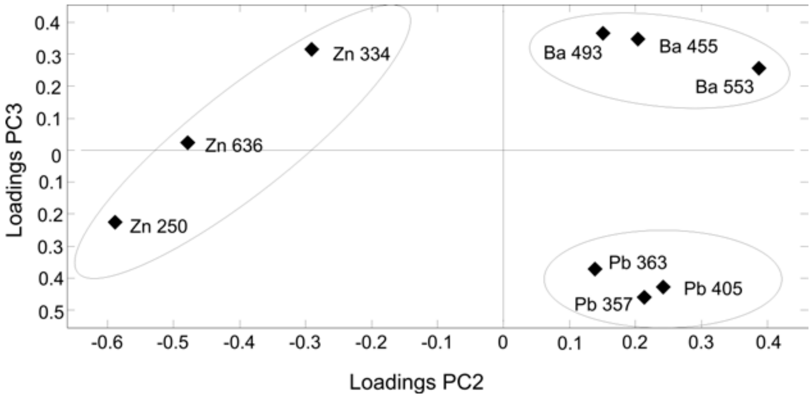

Figure 2 Loadings of the 2nd and 3rd component of the selected elements for LIBS-PCA analysis. The 2nd component differentiates Zn, whereas the 3rd component differentiates Ba from Pb.

## Mineralogical Characterization

### *NIR analysis*

The near-infrared spectrum of a common perlite is usually dominated by the fingerprints of opal, which is its main component. Three absorptions characterize the opal spectra: 1400 nm, 1900 nm, and 2200 nm. Since the mineral structure of opal is nearly amorphous, the spectral absorptions tend to be weak. This produces shallow and broad features for the hydroxyl-related features. The water absorption is always dominant. However, the NIR spectra of the studied samples showed variations in the shape of these absorptions, indicating the presence of another mineral. The main differences were present in the depth and width of the 1400 and 2200 nm absorptions, respectively. According to the USGS spectral library, the most likely mineral to be present in these samples was montmorillonite. In contrast with opal, montmorillonite produced a stronger absorption at 1400 nm, and a narrower feature at 2200 nm, as Figure 3 shows. XRD data confirmed the presence of montmorillonite.

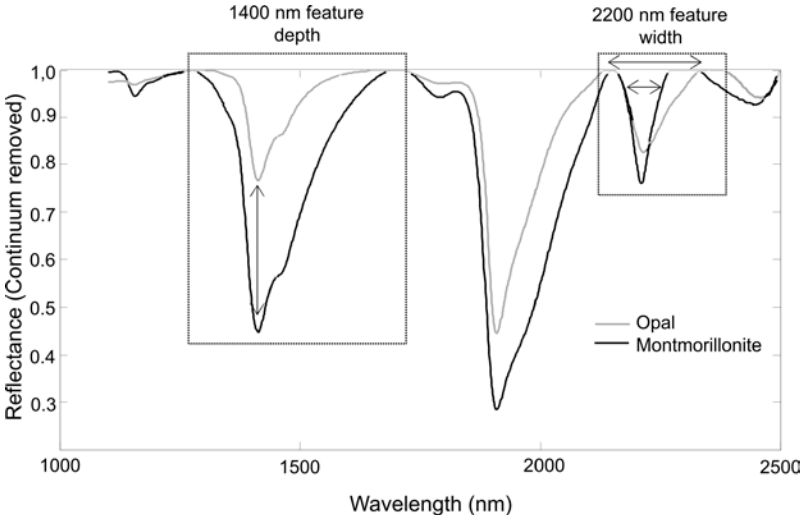

Figure 3 Spectral profiles of opal-like and montmorillonite-like spectra in the studied samples. The depth at 1400 nm and the width at 2200 nm are the main differences between opal and montmorillonite.

To be able to automate the identification of the dominant mineralogy, it was necessary to create a method that differentiates opal from montmorillonite. Figure 4 shows the relationship between the spectral features of the target minerals. Absorptions that are deep at 1400 nm and narrow at 2200 nm were distinctive of montmorillonite. In contrast, opal was characterized by shallow 1400 nm and broad 2200 nm features. This relationship was the basis to develop the Opal-Montmorillonite (OM) Index, shown in Equation 1. In this equation, 2200w refers to the width and 1400d to the depth at the corresponding features. The OM Index favors high values for opal-like spectra, aiming to detect montmorillonite-free perlite.

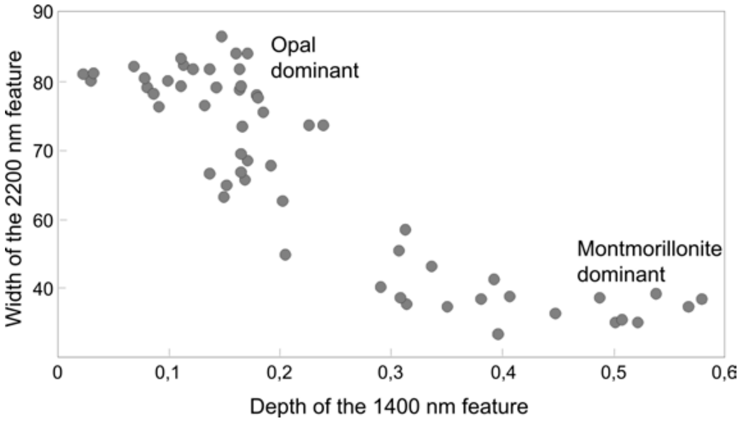

Figure 4 Relationship between the opal and montmorillonite features. Opal dominant phase is wide at 2200 nm and shallow at 1400nm. The montmorillonite-dominant phase is narrow at 2200nm and deep at 1400nm.

Equation 1 Formulation of the OM Index. 2200w = width at 2200nm, 1400d = depth at 1400nm. The logarithm expression is used to simplify the units.

$$OM\ Index = log_{10}\left(2200w * \left(\frac{1}{1400d}\right)\right)$$

In the studied sample-set, the lowest OM values were from the rhyolite, which was expected. The samples collected close to the rhyolite dyke also showed low OM values. In contrast, samples gathered farther away had the highest OM values. This showed that the hydrothermal alteration gave rise to the increasing montmorillonite content.

## Integration of chemistry and mineralogy

In order to identify whether there is a correlation between chemistry and mineralogy, the PCA scores of the XRF and LIBS analysis were compared with the OM Index.

The XRF-PCA scores plot colored by OM index, shown in Figure 5, revealed that high $TiO_2$, $Fe_2O_3$, and Zn corresponded to a low OM index. In contrast, high As, Rb and Ba were more likely to have high OM index. The third group, Pb, Nd, and Cu, did not seem to have any correlation with the mineralogical content.

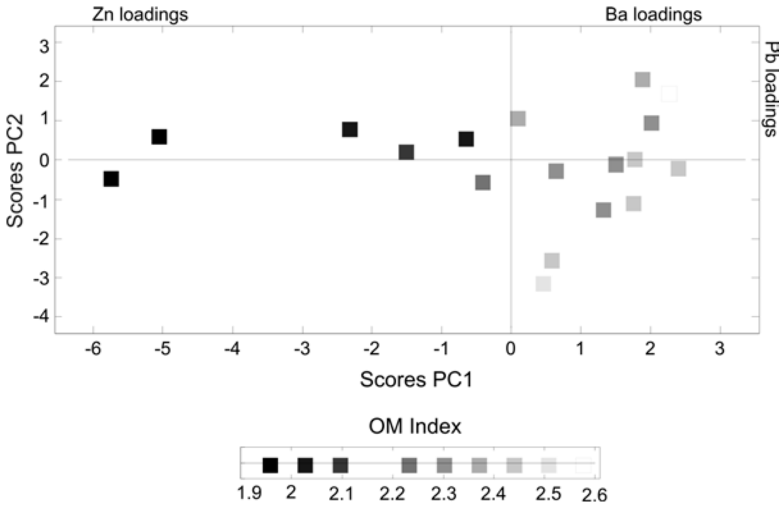

Figure 5 Scores of the 1st and 2nd component of the heavy metals XRF-PCA analysis, colored by OM Index. The montmorillonite-dominant phase has the highest $Fe_2O_3$-Zn concentrations, whereas the opal-dominant phase is richer in As-Rb-Ba

To verify whether the correlation with mineralogy was also evident in the LIBS data set, the LIBS-PCA scores for the second and third component were also plotted (Figure 6). The correlation between mineralogy and the second component, that described the correlation between Ba and Zn, was not as clear as in the XRF analysis, but the pattern remained. The differences in the nature of the XRF and LIBS data results in inversion of the loadings, nevertheless, the meaning is the same. The concentration of Ba tended to be low in low OM index, whereas Zn decreased with high OM index.

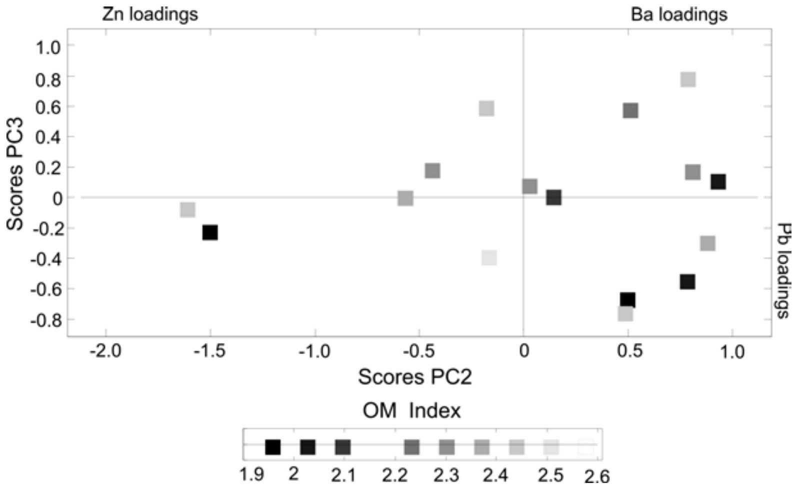

Figure 6 Scores of the 2nd and 3rd component of the group representatives LIBS-PCA analysis, colored by OM Index. The montmorillonite-dominant phase is poor in Ba, whereas the opal-dominant phase is poor in Zn.

# Discussion

The integration of two sensor technologies, LIBS and NIR for the detection of heavy metals in the perlite ore permitted the identification of correlations between heavy metals and their relation to the ore mineralogy. These relationships are significant from a sensor-based point of view since they lead to a simplification of the approach for data collection and data analysis.

The use of LIBS, complemented with XRF data, resulted in a qualitative analysis of the heavy metal content in the perlite. Various groups of elements were defined according to their correlations. Elements that had similar variations among the set of samples constituted a group. This classification is important since it eases the interpretation of the results and enables the integration of the chemical data with other datasets. Moreover, the classification can be utilized for the extrapolation of observations within a certain group. The use of an element as a representative of its group implies that it is not always necessary to perform a comprehensive analysis. Regarding sensor development, this means that for certain applications, simplified systems that focus on specific targets is a viable option, provided there is not a requirement for detailed and quantitative information. In this case, the LIBS detection of Ba, Zn, and Pb can be used as an estimate of the abundance of the elements in their respective groups that would be otherwise difficult to detect. Nevertheless, calibration of the method with reference data is always needed.

The mineralogical analysis with NIR spectroscopy allowed the detection of the mineral mixtures present in the perlite ore. The developed the *OM Index*, which gives an estimation of the opal-montmorillonite proportion, can be used for automation in the identification of the mineral phase that is dominant in a particular sample. Furthermore, the determination of a dominant phase can be used as a proxy for the abundance of some heavy metals. In this sense, samples with low OM index are montmorillonite-dominant and are more likely to have high levels of Zn, $Fe_2O_3$, and $TiO_2$. Likewise, samples with high OM index are opal-dominant and probably have high concentrations of Ba, As and Rb.

LIBS and NIR spectroscopy have proved to be complementary techniques for the detection of heavy metals. Their integration provides not only with more robust information, but it also enables to perform smarter data analysis. This integrative approach could be used for implementing selective mining in the perlite ore. A method for in-pit detection of heavy metals would include the collection of NIR spectra, followed by calculation of the OM index for identification of dominant mineralogy. Based on this, the most likely heavy metal group can be determined. Later, collection of LIBS data and analysis can be focused on the group representative (Ba, Zn, Pb) to check for abundance. Lastly, selection areas to mine according to the NIR-LIBS results, preferring the lowest concentrations of heavy metals.

## Conclusions

The integration of LIBS with NIR spectroscopy has shown to be an appropriate approach for the determination of heavy metals in the perlite ore. The determination of groups of elements that co-exist in the ore enabled a simplified detection of the representatives of their groups using LIBS. The development of the OM index with NIR spectroscopy permitted the rapid identification of the dominant mineralogy in the samples. The integration of the groups of elements with the OM index showed the relationship between the concentration of heavy metals and the mineralogical content in the perlite.

Regarding sensor-based characterization, the results of this work indicate that the integration of technologies provides not only with robust and relevant information but also eases the interpretation of the acquired data. The implementation of this approach in the mining of perlite ores would lead to selective extraction of raw material based on the heavy metal content. As a consequence, it would result in the generation of high-quality perlite products.

## Acknowledgments

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