Application of Multi-Energy Calibration for Determination of Chromium and Nickel in Nickeliferous Ores by Laser-Induced Breakdown Spectroscopy

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Abstract

A multi-energy calibration method was applied for the determination of chromium and nickel in nickeliferous ores by laser-induced breakdown spectroscopy. For the optimization of the laser-induced breakdown spectroscopy parameters, such as laser fluence and delay time, an experimental study was conducted. The best results in terms of trueness were observed using a laser fluence and a delay time of 2500 J/cm² and 1.1 μs, respectively. A study of sample matrix effects and the determination of emission lines for calibration and normalization of the spectra were undertaken, and appropriate values of those variables were selected for each analyte. The trueness values for chromium and nickel varied from 89 to 114% when certified reference samples (Nickeliferous Laterite, Rock Phosphate and Contaminated Soil) were analyzed.

Keywords: LIBS, MEC, minerals, ores, nickel, calibration, chromium
Introduction

Considering their diverse chemical composition, ore and soil samples are extremely complex. Typical samples contain several components, such as minerals, fossils, and organic matter. The physical, chemical and biological properties of soils can vary greatly due to human activity or changes to the environment.\textsuperscript{1,2}

Approximately 60% of the global supply of nickel (Ni) is extracted from ores – specifically, nickel laterites. Nickel laterites are found in serpentines, which are formed under specific conditions such as humidity and tropical climate.\textsuperscript{3} Mineral exploration of nickel and chromium reserves is of strategic economic importance in several countries, and Cr and Ni quantification in these samples is a key step for mining industries.

The analytical techniques traditionally employed for inorganic composition analysis are inductively coupled plasma optical emission spectroscopy (ICP-OES) and flame or graphite furnace atomic absorption spectrometry (FAAS and GFAAS, respectively). However, these techniques require solid samples to be converted into homogeneous solutions for analysis.\textsuperscript{4} Converting ore samples into an aqueous solution is not a trivial task. This procedure often requires large amounts of reagents (e.g., nitric, hydrochloric and hydrofluoric acids) and energy, and it is laborious and requires excessive amounts of chemical waste, thereby disqualifying it as a Green Chemistry process.\textsuperscript{5} Green analytical chemistry utilizes procedures that minimize hazardous residue formation and are safer and benign to the environment.\textsuperscript{6}

The development of analytical methods employing techniques that provide fast and robust analysis, a lower relative cost, and are consistent with Green Chemistry principles is very important. Laser-induced breakdown spectroscopy (LIBS) is a technique that enables direct solid sampling with a minimum sample pretreatment.\textsuperscript{1,7-10}
LIBS has been widely investigated in a variety of applications such as environmental analysis and monitoring, industrial analysis, food, and geology.

Calibration is the main challenge for quantitation by LIBS due to strong matrix effects and a lack of representative standards with enough homogeneity for microgram sampling. In 2017, Virgilio et al. described a novel and simple matrix-matching procedure called Multi-Energy Calibration (MEC). That procedure was utilized for the analysis of several liquid samples, namely, green tea, cola soft drink, cough medicine, hard liquor, beer, apple juice, soy sauce, ethanol fuel, vinegar, red wine, and creek water, in comparison to analyses employing microwave-induced plasma optical emission spectrometry (MIP OES), ICP-OES, and high-resolution continuous source flame atomic absorption spectrometry (HR CS FAAS). The use of MEC in solid samples has not yet been reported.

The aim of this paper was to evaluate the MEC procedure as a strategy to minimize the matrix effects in LIBS and to develop a fast and environmentally friendly method for direct determination of Ni and Cr in solid nickeliferous ores.

**Experimental**

**Instrumentation**

All LIBS measurements were carried out using a J200 Applied Spectra commercial system (Fremont, USA). This system is equipped with a Nd:YAG 1064nm laser with a single laser pulse of 8 ns in duration and a repetition rate of 5 Hz, a spectrometer with 6-channel CCD detectors with a wavelength range from 186 to 1042...
nm, and an X-Y-Z translational ablation chamber equipped with a CMOS color camera (1280x1024 pixels) imaging system.

Samples and standards were pressed into pellets with a diameter of 12 mm by applying a pressure of 10 tons in a hydraulic press, GS15011 Specac (Swedesboro, USA), for 2 minutes.

Reagents and samples

Ni(NO$_3$_)$_2$·6H$_2$O (Ecibra, São Paulo, Brazil) and Cr(NO$_3$_)$_3$·9H$_2$O (Vetec, Rio de Janeiro, Brazil) were used as analyte standards, and Na$_2$CO$_3$ (Mallinckrodt, Missouri, USA) was used for pellet formation, for MEC calibration.

Five samples of nickeliferous ores provided by Ana Teresa Acebal Ibarra from Elio Trincado Laboratory, Geominera Oriente Enterprise (Santiago de Cuba, Cuba) were used throughout the experiments. These samples are primarily composed of Al (1 to 27% w/w), Fe (7 to 52% w/w) and Mg (0.4 to 21% w/w).

For accuracy evaluation, one certified reference material (CRM) was used, namely, 2701 Hexavalent Chromium in Contaminated Soil (High Level) from the National Institute of Standards and Technology (NIST, Gaithersburg, USA), and two reference materials (RM) were used, namely, L-1 Nickeliferous Laterite manufactured by Central Laboratory of Minerals José Isaac del Corral (La Habana, Cuba) and CRM-AGRO E2003a Rock Phosphate manufactured by Embrapa Pecuária Sudeste (São Carlos, Brazil).
Multi-energy calibration

The MEC procedure applied to the analysis of liquid samples, required two solutions per sample: Solution 1 was a mixture of sample and standard solutions (1:1 ratio by volume), and Solution 2 was a mixture of sample and blank solutions (1:1 ratio by volume). The MEC linear model is plotted using the analytical signal intensity for Solution 1 (x-axis) vs. the analytical signal intensity for Solution 2 (y-axis) at several different emission lines, and the analyte concentration in the sample is calculated using Equation 1:

\[
[\text{Analyte}] = \frac{\text{slope} \times [\text{Analyte standard}]}{1 - \text{slope}} \quad \text{Equation 1}
\]

In this study, MEC was applied in Cr and Ni determination by LIBS. Solid samples were used directly with no aqueous workup, as acid mineralization was utilized. Therefore, two pellets were prepared from each solid sample: a) Pellet A was composed of 250 mg sample plus 250 mg salt mixture (77 mg Cr(NO\(_3\))\(_3\) \cdot 9\text{H}_2\text{O} + 173 \text{ mg Na}_2\text{CO}_3) and b) Pellet B was composed of 250 mg sample plus 250 mg Ni salt mixture (50 mg Ni(NO\(_3\))\(_2\) \cdot 6\text{H}_2\text{O} + 200 \text{ mg Na}_2\text{CO}_3). For Cr determination, Pellet A was plotted as Solution 1 (sample plus standard), and Pellet B was plotted as Solution 2 (sample plus blank). For Ni, Pellet A was plotted as Solution 2 and Pellet B as Solution 1.

The application of the MEC strategy required that the different emission lines belonging to each element be determined. For this, the 30 most sensitive emission lines for Cr and Ni were pre-selected according to the NIST database. For the final selection of the emission lines used in the calibration, 7 pellets that contain the major components of nickeliferous ores were prepared: (1) 10% Mg, (2) 10% Fe (3) 5% Mn (4) 5% Al (5)
5% Cr \((6)\) 5% Ni \((7)\) and the Na\(_2\)CO\(_3\) matrix. These pellets were analyzed via LIBS, and each of the 30 pre-selected emission lines for Cr and Ni were evaluated to verify possible overlap from the major components, analytes and matrix spectra.

\textit{Laser-induced breakdown spectroscopy instrument parameter optimization:}

\textit{Experimental design}

For Cr and Ni determination by LIBS, the instrument parameters (laser fluence and delay time) were optimized using a central composite design augmented with a group of axial points and a desirability function. An experimental design with 12 analyses was employed, where 3 analyses were replicates at center points, 4 analyses were at axial points \((-\sqrt{2}\) and \(+\sqrt{2}\)), 4 were at points -1 and +1, and 1 analysis was at points -0.73 and 0. With this model, the variables can be tested at different levels simultaneously. The laser fluence variable (J/cm\(^2\)) was tested from 701 (coded as \(-\sqrt{2}\)) to 4227 (coded as \(+\sqrt{2}\)); and delay time (\(\mu\)s) was tested from 0.1 (coded as \(-\sqrt{2}\)) to 2.0 (coded as \(+\sqrt{2}\)). Once central points were determined, it was possible to estimate the pure error of the proposed model.

After the experiments were carried out, a desirability model was constructed to evaluate the best conditions for analysis. For this, a reference material, L-1 Nickeliferous Laterite, was analyzed via LIBS using the MEC strategy. Recovery determinations for Cr and Ni were used as response functions in order to construct the desirability model. The most appropriate conditions should present recovery (trueness) values near 100\% for both analytes simultaneously. After the calculation of the trueness for both analytes, these values were converted to individual desirability \((di)\). In this case, the lowest and the trueness values equal to 100\% were converted to 0 and 1, respectively. This calculation
was performed for both analytes (Cr and Ni). Later, a global desirability value (D) was obtained after geometric mean calculation\textsuperscript{26}.

Spectral acquisition for step optimization was performed in-line (raster) for all experiments and a total of 32 spectra were collected for each experiment. After analysis and spectra collection, twelve signal normalizations were utilized to verify and correct signal variations and matrix effects. Signal normalizations are explained by Castro and Pereira-Filho\textsuperscript{27} and Sperança, et al.\textsuperscript{21}

\textit{Chromium and nickel determination}

After LIBS parameter optimization and emission line selection, the method was applied to the determination of Cr and Ni in five nickeliferous ore samples. Three pellets (n=3) were prepared for each sample, and approximately 130 spectra were collected for each pellet. Accuracy was checked by analyzing the three reference materials described in the Reagents and Samples section.

\textbf{Results and discussion}

The initial attempt was to prepare pellets in a similar manner as the MEC procedure originally proposed by Virgilio et al.\textsuperscript{23}. Pellet A contained 50\% sample plus 50\% standards (similar to Solution 1), and Pellet B contained 50\% sample plus 50\% blank (similar to Solution 2). However, due to hydrated Cr and Ni salts used in the experiments, different sample stability was observed in Pellets A and B, affecting the plasma formation. The stability problem was resolved by using Cr salt in Pellet A and Ni salt in Pellet B.
Thus, for Cr determination, the Pellet A was used as Solution 1 and Pellet B was used as solution 2, but for Ni, Pellet A was used as Solution 2 and Pellet B as Solution 1.

To apply MEC, several emission lines for each element are required. For this, the 30 most sensitive emission lines for Cr and Ni were pre-selected according to the NIST database. The interference-free emission lines used for MEC calibration in this study were evaluated by overlaying the major components (Fe, Mg, Mn an Al), analytes (Cr and Ni) and matrix (Na₂CO₃) LIBS spectra as described before. The emission lines selected for Cr and Ni were Cr II 205.55, Cr II 283.56, Cr I 434.45, Cr I 435.17, Cr I 540.97 and Ni II 217.46, Ni II 220.55, Ni II 221.64, Ni I 341.47. The identification I and II indicates atomic and ionic emission lines, respectively.

The results obtained from desirability model were not consistent and resulted in a lack of fit. The explanation for this is that nickeliferous ores are complex matrices and contain several non-spectral interferences. To correct for this problem, an experimental design was used, applying only the extreme values for each variable (-1 and +1). The normalizations that provided the best results for the experimental design were averaged and summed, and the normalization to the average was selected for the development of the optimized ranges. A graph of the optimum conditions of delay time vs laser fluence was generated using the extreme values of the variables and the final condition used for delay time and fluency was, 1.1 μs and 2500 J/cm², respectively. Fig. 1 shows the contour plot obtained for the calculated model.

**FIGURE 1**

Utilizing the optimized operating parameters, MEC plots for Cr and Ni were obtained, and an example for Nickeliferous Laterite is shown in Fig. 2. For Cr and Ni, 5
and 4 emission lines were selected, respectively. In both cases, the correlation coefficients were higher than 0.92. The analyte concentration ([Analyte]) was calculated according to Equation 1. In this case, it is necessary to determine the slope value (see Fig. 2) and the standard concentration ([Analyte standard]) added to the sample. Error bars were not displayed in this figure because two error sources are present: (1) mass differences among the pellets and (2) aleatory error. In this case, the final analyte concentration was averaged after calculation. As implied in equation 1, the analyte concentration depends on the slope and not the correlation. A poor correlation does not necessarily indicate a poor result.

FIGURE 2

The accuracy of the MEC method was checked by analyzing two RMs (Nickeliferous Laterite and Rock Phosphate) and one CRM (Hexavalent Chromium in Contaminated Soil) for Cr and one RM (Nickeliferous Laterite) for Ni, the results are shown in Table 1.

All determinations for Cr and Ni were in concordance with the certified values at the 95% confidence level (t-test). The calculated t value in all cases was lower than the tabulated one with 95% confidence level.

Following the method accuracy validation, MEC was applied to Cr and Ni determination in five nickeliferous ores samples (Table 2). Determined values ranged between 2.1 – 3.0% and 1.12 – 2.69% for Cr and Ni, respectively. These concentrations represent the typical concentration range of Ni and Cr expected in the variety of samples potentially analyzed by the proposed method. The RSDs calculated for 12 successive measurements of a sample containing 2.3% m/m Cr and 1.12% m/m Ni were 9% and 6%, respectively.
Conclusions

Herein, the possibility of using MEC as an efficient alternative calibration method for LIBS analysis of solid samples was demonstrated. The MEC procedure is a simple matrix-matching procedure with the convenience of only requiring the preparation of two calibration standard pellets per sample analysis. The method showed good precision (9% Cr and 6% Ni) and accuracy for the determination of Cr and Ni in nickeliferous ore samples. The use of LIBS in combination with MEC is an effective approach to reducing analysis time, waste generation, and sample consumption and is in concordance with Green Chemistry principles.

Acknowledgements

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References


Tables Caption

Table 1 Results (mean ± standard deviation) for chromium and nickel determination (n=3) in reference materials and certified reference materials (% m/m) using multi-energy calibration and Laser-induced breakdown spectroscopy.

Table 2 Mean concentration ± standard deviation (n=3) for chromium and nickel in laterite ores samples (% m/m) using multi-energy calibration and Laser-induced breakdown spectroscopy.
**Figure Captions**

Fig. 1 Optimal conditions graph using extreme values for each variable. Delay time: 0.0 to 2.0 (µs) and Laser fluence: 701 to 4227 (J/cm²). Optimal conditions: 1.0 µs and 2500 J/cm², for delay time and Laser fluence, respectively. Subtitle represents the desirability values.

Fig. 2 Multi-energy calibration plots for Cr (a) and Ni (b) for replicate 1 of the Nickeliferous Laterite sample.
Tables

Table 1. Results (mean ± SD) for chromium and nickel determinations (n=3) in reference materials and certified reference materials (% m/m) using multi-energy calibration and laser-induced breakdown spectroscopy.

<table>
<thead>
<tr>
<th>Certified reference material</th>
<th>Chromium</th>
<th>Nickel</th>
<th>Calculated $t$ value from an unpaired $t$ test$^b$</th>
<th>Chromium</th>
<th>Nickel</th>
<th>Calculated $t$ value from an unpaired $t$ test$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Certified</td>
<td>Determined</td>
<td></td>
<td>Certified</td>
<td>Determined</td>
<td></td>
</tr>
<tr>
<td>Nickeliferous</td>
<td>1.97 ± 0.09</td>
<td>1.79 ± 0.09</td>
<td>3.46</td>
<td>1.15 ± 0.05</td>
<td>1.32 ± 0.09</td>
<td>3.27</td>
</tr>
<tr>
<td>Laterite</td>
<td>288.78 ± 18.91</td>
<td>259 ± 13$^a$</td>
<td>3.97</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rock Phosphate*</td>
<td>4.26 ± 0.12</td>
<td>4.1 ± 0.1</td>
<td>2.77</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Contaminated soil*</td>
<td>18.91$^a$</td>
<td>19.76 ± 1.23</td>
<td>3.27</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ mg/kg  *Ni concentrations were not available.

$^b$ Tabulated $t$ value with 95% of confidence level and 2 degree of freedom = 4.303
Table 2. Mean concentration ± SD (n=3) for chromium and nickel in laterite ore samples (% m/m) using multi-energy calibration and laser-induced breakdown spectroscopy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chromium</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.6 ± 0.2</td>
<td>1.12 ± 0.07</td>
</tr>
<tr>
<td>2</td>
<td>2.5 ± 0.3</td>
<td>1.65 ± 0.06</td>
</tr>
<tr>
<td>3</td>
<td>2.1 ± 0.2</td>
<td>2.69 ± 0.07</td>
</tr>
<tr>
<td>4</td>
<td>2.79 ± 0.08</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>3.0 ± 0.2</td>
<td>2.65 ± 0.07</td>
</tr>
</tbody>
</table>
Figure 1
Figure 2a

Cr emission intensity (Sample + Blank)

Cr emission intensity (Sample + Standard)

\[ y = 0.3695x + 35 \]

\[ R^2 = 0.9983 \]
Figure 2b

![Graph showing Ni emission intensity vs. wavelength (λ) for different wavelengths: 221.64 nm, 351.50 nm, 220.55 nm. The graph includes a linear regression line with the equation y = 0.3437x + 0.899 and R² = 0.9215.](image-url)