Quantitative analysis of arsenic in mine tailing soils using double pulse-laser induced breakdown spectroscopy

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A double pulse-laser induced breakdown spectroscopy (DP-LIBS) was used to determine arsenic (As) concentration in 16 soil samples collected from 5 different mine tailing sites in Korea. We showed that the use of double pulse laser led to enhancements of signal intensity (by 13% on average) and signal-to-noise ratio of As emission lines (by 165% on average) with smaller relative standard deviation compared to single pulse laser approach. We believe this occurred because the second laser pulse in the rarefied atmosphere produced by the first pulse led to the increase of plasma temperature and populations of exited levels. An internal standardization method using a Fe emission line provided a better correlation and sensitivity between As concentration and the DP-LIBS signal than any other elements used. The Fe was known as one of the major components in current soil samples, and its concentration varied not substantially. The As concentration determined by the DP-LIBS was compared with that obtained by atomic absorption spectrometry (AAS) to evaluate the current LIBS system. They are correlated with a correlation coefficient of 0.94. The As concentration by the DP-LIBS was underestimated in the high concentration range (>1000 mg-As/kg). The loss of sensitivity that occurred at high concentrations could be explained by self-absorption in the generated plasma.

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1. Introduction

Mine waste materials from abandoned mine sites without proper management were reported to cause severe pollution to the surrounding environment with increasing heavy metal concentrations [1–3]. Among metals, arsenic (As) has been of special concern due to its high toxicity level to animals and human beings [4]. At sites where the As concentration level in soils was high, populations of indigenous plant and animal species were significantly reduced or even completely disappeared, leaving the sites biologically barren [5]. In Korea, out of the total 906 metal mines, 894 mines were abandoned, and 127 abandoned mines among them were reported to have severe As contamination [6]. Thus, continuous monitoring of As in such sites is essential to determine As contamination level and to establish a control strategy to mitigate As exposure to humans and environments.

To determine concentration of As in soils, atomic emission spectrometry (AES) via inductively-coupled plasma (ICP), atomic absorption spectrometry (AAS) via graphite furnace, or X-ray fluorescence (XRF) has been used [78]. These off-line conventional analytical methods require complicate sample preparation steps such as collection, transport, extraction, and dissolution, which are expensive and time-consuming. For real-time measurements of As, a Laser Induced Breakdown Spectroscopy (LIBS) can be used [79]. It provides less-destructive, rapid, and highly selective analysis. The LIBS technique uses a powerful pulsed laser to generate microplasma on a sample. As the plasma cools down, the excited atomic, ionic, and molecular fragments within the plasma emit light with specific wavelengths which are signatures of elements in the sample [10–12].

Several previous works have been conducted to quantify As concentration in various samples (soil, aerosol, liquid, and etc.) by using LIBS technique as summarized in Table 1. In spite of a great potential of the LIBS, the sensitive detection of the As by the LIBS was limited due to its high excitation energy levels (~6 eV) [13] and the existence of strong As emission lines in the UV spectral range (180–200 nm), resulting in the limited optical system response [14]. The minimum limit of detection (LOD) of As in soils that has been reported is around 400 mg/kg, which must be further lowered considering the level of current regulatory As concentration (50 mg/kg suggested by the Ministry of Environment, Korea). One of the possible approaches to improve the LIBS sensitivity and to lower the LOD of As in soils is to use of double pulse laser which may lead to enhance the LIBS signal due to higher ablation rate [15–20]. It was reported that the use of double pulse-LIBS provided enhanced emission intensity, lower detection limit, and longer sustained emission. Sattmann et al. [15] demonstrated that the ablated mass increased 8 times with the use of...
2. Experimental

2.1 Sample preparation

Aerosols emitted from rotary kiln incinerator
Aerosols generated from standard aqueous solutions of metals
Aerosols emitted from municipal waste incinerator
Soils collected from Los Alamos, USA
Soils collected from Los Alamos, USA
Liquid solution of metals
Paint pigments
Wood waste contaminated with metals
Mine tailing soils

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Limit of detection (LOD)</th>
<th>Wavelength of As emission lines (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosols emitted from rotary kiln incinerator</td>
<td>400 μg/m³</td>
<td>278.0, 286.0</td>
<td>[36]</td>
</tr>
<tr>
<td>Aerosols generated from standard aqueous solutions of metals</td>
<td>400 μg/m³</td>
<td>228.81</td>
<td>[14]</td>
</tr>
<tr>
<td>Aerosols emitted from municipal waste incinerator</td>
<td>1.32 μg/m³</td>
<td>235.0</td>
<td>[37]</td>
</tr>
<tr>
<td>Soils collected from Los Alamos, USA</td>
<td>440 mg/kg</td>
<td>189.0</td>
<td>[38]</td>
</tr>
<tr>
<td>Soils collected from Los Alamos, USA</td>
<td>705, 1512 mg/kg</td>
<td>234.984, 286.044</td>
<td>[39]</td>
</tr>
<tr>
<td>Liquid solution of metals</td>
<td>5 ppm</td>
<td>274.50, 278.02, 286.04</td>
<td>[40]</td>
</tr>
<tr>
<td>Paint pigments</td>
<td>N/A</td>
<td>274.50, 278.02, 286.04</td>
<td>[23]</td>
</tr>
<tr>
<td>Wood waste contaminated with metals</td>
<td>15 ppm</td>
<td>234.984, 287.020</td>
<td>[41]</td>
</tr>
<tr>
<td>Mine tailing soils</td>
<td>85 mg/kg</td>
<td>188.979, 200.335, 228.812</td>
<td>Current study</td>
</tr>
</tbody>
</table>

A schematic of the DP-LIBS system.

Fig. 1. A schematic of the DP-LIBS system.

using a plano convex lens (focal length = 70 mm). For a single pulse measurement, the laser pulse with energy of 90 mJ/pulse was employed with a power density of $26.5 \times 10^9$ W/cm² at the focal point. Gate delay time and integration time in the spectrometer were optimized to 2.7 μs and 16 μs, respectively, having the maximum intensity of the As emission line. For a double pulse measurement, we extracted two laser pulses from one flash lamp pulse by opening the Pockels cell twice in rapid succession. The separation of the two pulses (i.e., inter-pulse delay time) is adjustable from 1 μs to 180 μs with 1 μs step. Two laser pulses have the same energy and the total energy (pulse 1 + pulse 2) is equal to the energy of the single pulse (90 mJ/pulse) in this study. The optimum inter-pulse delay time in the double pulse approach providing the greatest LIBS signal intensity of the As emission line was found to be 20 μs. Argon gas with a flow rate of 0.25 l/s was supplied into the region of the sample surface where the plasma is generated. The argon buffer gas is known to increase the plasma lifetime [21] and to reduce self-absorption [22], producing a stronger emission. The emitted light was measured by the f/10 Echelle spectrograph (LTB Inc., ARYELLE) having a 50 μm slit width and a 12,000 resolving power ($\lambda/\Delta\lambda$). A CCD detector (2048 × 512 pixels) with a spectral wavelength of 180–310 nm in which most of As emission lines were detected was used in the spectrometer [23,24].

To identify As emission lines, we used As-spiking kaolinite (aluminum silicate, H₂Al₂Si₂O₈·H₂O) by adding 0.5% sodium arsenate heptahydrate solution (Na₂HAsO₄·7H₂O) into the kaolinite. Soil samples tested in this study (16 soil samples) were obtained from 5 abandoned mine tailing sites in Korea as shown in Table 2. A soil sample from the Myeongbong mine tailing site (MB-3) that had the highest As concentration (approximately 4000 mg/kg) resulting from AAS measurements was used to obtain a calibration curve for the quantification of As by the LIBS. The MB-3 sample was diluted by uncontaminated soils (Speyer 2.3, Germany) to make As-containing soils having a concentration level of 40, 76, 112, 148, 184, 220, 256, 292, 328, 364, or 400 mg-As/kg. For LIBS measurements, all soil samples were mixed with lactose anhydrous (Fluka, Germany) as the cohesive for soil particles at the ratio of 3:1 by a mechanical press under 250 kg/cm² for 5 s and prepared as pressed pellets. This leads to minimize shot-to-shot variation of LIBS signals resulting from the small differences in the position of the spark on the sample surface. The target sample was mounted on the sample stage which was rotated to avoid any inhomogeneity and crater effect of the sample. 250 spectra (50 spectra at each spot) were used to obtain the average LIBS spectrum.

As concentrations in different mine tailing soils by using the LIBS were compared with those determined by the atomic absorption
spectrometer with graphite furnace (AAS-GF) (PE model 5100 PC, Perkin Elmer, Foster City, CA). For AAS-GF analysis, a soil sample (0.5 g) was digested with a 4 ml solution of HCl and HNO₃ (3:1), and heated at 70 °C in a shaker for 1 h [25]. The digested solution was diluted with de-ionized water (6 ml) and filtered through a 0.45-µm polytetrafluoroethylene membrane filter. All reagents used were analytical grade, and all analytical procedures were repeated in duplicate. Acid blanks and standard reference material (Montana soil, SRM 2710, National Institute of Standard and Technology, USA) were digested under the same conditions and analyzed in parallel with the samples in order to verify the accuracy and precision of the AAS.

3. Results and discussion

3.1. Comparison of As detection by the SP-LIBS and DP-LIBS

As emission lines for 4000 mg-As/kg mine tailing soils determined by the SP-LIBS (solid line) and DP-LIBS (dotted line) at wavelengths of 188.979, 200.335, and 228.812 nm are compared in Fig. 2(A), (B), and (C), respectively. When the double pulse mode was used, the average As signal intensity increased by 15% (188.979 nm), 12% (200.335 nm), and 13% (228.812 nm) and the relative standard deviation (RSD) decreased by 19% (188.979 nm), 23% (200.335 nm), and 22% (228.812 nm) compared to those obtained by single pulse. The As signal intensity was the strongest at the wavelength of 228.812 nm that will be used for further quantification of As concentration in soils in this study.

To compensate any fluctuation of the absolute signal strength caused by the laser shot-to-shot variation, we used a signal-to-noise (S/N) ratio of As emission line for quantification purpose instead of its absolute intensity [26,27]. The S/N ratio is calculated by dividing peak intensity at the specified wavelength by a root mean square value of the noise near the interference-free baseline region (20–30 pixels) of the analyte peak [28]. Fig. 3(A) compares the S/N ratios of As emission lines for 4000 mg-As/kg mine tailing soils determined by the SP-LIBS and DP-LIBS at wavelengths of 188.979, 200.335, and 228.812 nm. The error bar represents the standard deviation. With the use of double pulse approach, the S/N ratio increased by 47% and its RSD decreased by 13%. The use of the S/N ratio showed more improvements than the absolute signal intensity when the DP-LIBS was used. Fig. 3(B) compares the S/N ratios of the As emission line (228.812 nm) among soil samples having different concentrations. A significant improvement of the S/N ratio (by 165% on average) for the As emission line with the DP-LIBS over the given concentration range was observed.

Also, data showed that as the As concentration increased, the S/N ratio of the As emission line measured with the DP-LIBS increased, while that from the SP-LIBS was insensitive to the change of concentration in

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample location</th>
<th>As (mg/kg) by the AAS (average±standard deviation)</th>
<th>As (mg/kg) by the DP-LIBS (average±standard deviation)</th>
<th>AsLIBS/AsAAS</th>
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</thead>
<tbody>
<tr>
<td>DO-1</td>
<td>Deokon mine</td>
<td>547±47</td>
<td>786±161</td>
<td>1.4</td>
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<tr>
<td>DO-2</td>
<td>(Imsil, JeonBuk)</td>
<td>82±2</td>
<td>195±45</td>
<td>2.4</td>
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<tr>
<td>DO-3</td>
<td>35±6</td>
<td>151±16</td>
<td>4.3</td>
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<tr>
<td>DO-4</td>
<td>426±29</td>
<td>321±109</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>DO-5</td>
<td>414±41</td>
<td>339±87</td>
<td>0.8</td>
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<tr>
<td>DO-6</td>
<td>644±28</td>
<td>428±114</td>
<td>0.7</td>
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<tr>
<td>MB-1</td>
<td>Myeongbong mine</td>
<td>86±6</td>
<td>178±22</td>
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<td>MB-2</td>
<td>(Boeung, JeonNam)</td>
<td>114±7</td>
<td>134±14</td>
<td>1.2</td>
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<td>Gwangyang mine</td>
<td>131±19</td>
<td>225±75</td>
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<tr>
<td>GY-2</td>
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<td>141±13</td>
<td>177±47</td>
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<td>GY-3</td>
<td>358±212</td>
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<td>1619±246</td>
<td>1167±119</td>
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<td>GY-5</td>
<td>183±41</td>
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<td>Songcheon mine</td>
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<tr>
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<td>179±31</td>
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<td>(Yeongwol, GangWon)</td>
<td>441±24</td>
<td>38±63</td>
<td>0.9</td>
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</tbody>
</table>

Table 2
List of mine tailing sites in Korea for soil samples examined in this study and As concentrations determined by the AAS and DP-LIBS.

Fig. 2. As emission lines for 4000 mg-As/kg mine tailing soils at wavelengths of (A) 188.979 nm and (B) 200.335 nm and (C) 228.812 nm determined by the SP-LIBS (solid line) and DP-LIBS (dotted line).
### 3.2. Quantitative analysis of As by the DP-LIBS

A relationship between the DP-LIBS signal intensity at the wavelength of 228.812 nm and As concentration in standard soil samples (e.g., 40, 76, 112, 148, 184, 220, 256, 292, 328, 364, and 400 mg-As/kg) was shown in Fig. 5(A). The relationship can be used for quantification of As concentration by the LIBS for unknown soil samples. As not shown here, the DP-LIBS also provided the better relationship between the LIBS signal and As concentration than the SP-LIBS. In addition, we conducted an internal standardization by normalizing the As emission line by using emission lines from other chemical elements to minimize soil matrix effects. As shown in Fig. 5(B), when the internal standardization was employed, the correlation increased significantly. The use of Fe (248.814 nm) showed the best correlation (r = 0.96) with increased sensitivity between the LIBS signal and As concentration among elements (Mg (285.200 nm), Al (309.300 nm), Si (288.200 nm)) used. Note that the Fe is one of major components in our soils and Fe concentration varied not substantially in current soil samples. This suggests that soil matrix effects can be considerably minimized by the normalization of As by Fe which is one of the major elements in soils.

With the DP-LIBS employing the internal standardization method described above, we determined the limit of detection (LOD) for As concentration. The LOD based on the IUPAC (International Union of Pure and Applied Chemistry) method (LOD = 3σn/S) where the σn is the standard deviation of the background and the S is the slope of the calibration line [34]. The calculated LOD for As concentration in soils is 85 mg-As/kg, which is lower than previously reported values.
3.3. Comparison of As determined by the DP-LIBS and AAS

By using the relationship shown in Fig. 5, we are able to determine As concentration in soil samples from various mine tailing sites in Korea by using the DP-LIBS with an internal standardization method (i.e., As/Fe). The As concentrations determined by the DP-LIBS were compared with those obtained from the AAS as shown in Fig. 6 including a 1:1 line. They are correlated with a linear correlation coefficient of 0.94. Note that the $A_{\text{SLIBS}}$ was underestimated in the high concentration range ($>1000 \text{ mg-As/kg}$) compared to the $A_{\text{SAAS}}$. Although the sensitivity increased with the internal standardization in the DP-LIBS, there was still a saturation region. This suggests that self-absorption in the generated plasma still played a role in the loss of sensitivity at high concentrations in the DP-LIBS. As summarized in Table 2, the ratio of As concentration between LIBS and AAS ($A_{\text{SLIBS}} / A_{\text{SAAS}}$) ranged from 0.5 to 1.7 with an average value of 1.0 except 4 samples (MB-1, DO-2, DO-3, and JC-1). The $A_{\text{SLIBS}} / A_{\text{SAAS}}$ in the soils from MB-1, DO-2, DO-3, and JC-1 mine sites were significantly underestimated. The low As concentration levels in MB-1, DO-2, DO-3, and JC-1 sites (85.5, 81.9, 35.3, and 50.0 mg/kg, respectively), which are near the current LOD value for determination of As by the LIBS, might lead to the observed difference. Also, note that the AAS determined the As concentration from the extracted bulk sample, while the LIBS determined the As concentration from the limited focal area on the sample surface. Thus, any inhomogeneity in the As content on the surface may lead to variation of As concentration although five different spots on the sample surface were used to obtain the average As concentration by rotating the sample. This also led to the higher RSD of As concentrations measured by the LIBS than the AAS. On the other hand, the LIBS is able to provide a very high spatial resolution. Instrumental noise of the LIBS itself and the variation of intensity induced by difference in soil properties among different mine sites might also contribute to the observed difference. It was reported that the existence of different types of constituents and soil properties in the sample were able to change the plasma excitation [35]. Further research would be required to determine the effects of soil properties such as soil texture, soil moisture, soil particle size, and chemical composition on the quantitative performance of the LIBS. We believe that the LIBS technique can be a promising tool to detect As in soils.

4. Conclusions

Comparison of As detection by the SP-LIBS and DP-LIBS showed the enhanced intensity (by 13% on average) and signal-to-noise ratio (by 165% on average), and decreased RSD (by 21% on average) of As emission lines with the use of DP-LIBS. The calculated plasma temperature on the basis of Maxwell–Boltzmann distribution assuming a local thermodynamic equilibrium suggested that the increased plasma temperature in the DP-LIBS plasma led to higher populations of excited levels, producing strong emission lights. The internal standardization by using Fe emission line (248.814 nm) showed better correlation and sensitivity between the DP-LIBS signal intensity and As concentration (i.e., calibration line). Our results suggested that further excitation of species in the plasma by the second laser not only led to the enhancement of emission signals, but also provided better quantification performance by the DP-LIBS. Using the calibration line, we determined As concentration in soils collected from various mine tailing sites in Korea by using the DP-LIBS. The As concentrations determined by the DP-LIBS were compared with those obtained from the AAS. They are correlated with a correlation coefficient of 0.94 although the $A_{\text{SLIBS}}$ was underestimated in the high concentration range ($>1000 \text{ mg-As/kg}$). The loss of sensitivity that occurred at high

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**Fig. 5.** (A) A relationship between the DP-LIBS signal intensity and As concentration in standard soil samples (40, 76, 112, 148, 184, 220, 256, 292, 328, 364, and 400 mg-As/kg) at a wavelength of 228.812 nm, and (B) a relationship between the DP-LIBS signal intensity of As (228.812 nm) normalized by Fe, Mg, Al, or Si and As concentration in standard soil samples.

**Fig. 6.** Comparison of As concentrations in soils determined by the DP-LIBS and the AAS.
concentrations would be due to self-absorption in the generated plasma by the DP-LIBS.

Acknowledgements

The research is collaborated with the Laser-Laboratorium Göttingen e.V., Germany, through the Brain Korea 21 Project, and supported by Korea Science and Engineering Foundation (KOSEF) grant (No. R01-2007-00-010351-0) and Korea Ministry of Environment as “The GAIA Project” (No. G108-17002-0002-0).

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