Standoff Detection of Geological Samples of Metal, Rock, and Soil at Low Pressures Using Laser-Induced Breakdown Spectroscopy

Jae-Jun Choi, Soo-Jin Choi, and Jack J. Yoh

Abstract
Categorized certified reference materials simulating metal, rock, soils, or dusts are used to demonstrate the standoff detection capability of laser-induced breakdown spectroscopy (LIBS) at severely low pressure conditions. A Q-switched Nd:YAG laser operating at 1064 nm with 17.2–50 mJ energy per pulse was used to obtain sample signals from a distance of 5.5 m; the detection sensitivity at pressures down to 0.01 torr was also analyzed. The signal intensity response to pressure changes is explained by the ionization energy and electronegativity of elements, and from the estimated full width half-maximum (FWHM) and electron density, the decrease in both background noise and line broadening makes it suitable for low pressure detection using the current standoff LIBS configuration. The univariate analyses further showed high correlation coefficients for geological samples. Therefore, the present work has extended the current state-of-the-art of standoff LIBS aimed at harsh environment detection.

Keywords
Laser-induced breakdown spectroscopy, LIBS, standoff, low pressure, certified reference material, CRM

Introduction
In laser-induced breakdown spectroscopy (LIBS), a sample is irradiated with sufficient light energy to generate the surface plasma for generation of high intensity emission for subsequent signal detection. This is quite attractive when accessing samples that are physically inaccessible or potentially harmful for in situ handling.

In Cremers et al., various metal samples were analyzed at a standoff distance in the range of 0.5–2.4 m. With growing interest in using LIBS for space exploration starting early 2000, various experimental efforts have been reported for remote detection via LIBS. Salle et al. performed qualitative analysis of metals and rocks at distances 3–12 m under the Martian atmosphere and reported that signal intensities decreased exponentially with increasing sample distances. In addition, the capabilities of detecting chlorine and sulfur were discussed in comparison to the results obtained from the atmospheric condition. In Salle et al., a report of standoff LIBS on a set of certified soils at distances of 5.3 m under Martian conditions was provided. The results showed useful spectra and calibration curves obtained with a standoff setup without an intensified detector. Moreover, more recently Cousin et al. developed a laboratory model to construct a database of reference lines on Martian rocks and soils. They have recorded more than 1300 LIBS lines of 32 elements that are of direct interest to the Martian exploration via a rover. With recent interest on exploring the Moon, Lasue et al. reviewed the capabilities of standoff LIBS for lunar crater analysis at a distance of 1.5 m using a set of powdered basalts. Detection of both major and minor elements were discussed using partial least squares (PLS) and various methods of estimating limit of detection (LOD).

The first utilization of LIBS as a space payload is ChemCam, mounted on the Mars exploration rover, Curiosity. ChemCam instruments that are composed of body unit and mast unit can perform remote detection at a distance of up to 7 m from a target using a telescope at ambient pressure (7 torr). It showed remote LIBS analysis capability in more than 5000 different locations including Gale Crater and obtained over 200 000 spectra.
Apart from the influence of pressure on standoff LIBS, several other parameters are also studied. Palanco et al. tested a field-deployable standoff LIBS system in the hundreds of meter ranges for Al and Ti samples and showed that LIBS performance was dependent on distance, peak power, beam quality, and laser wavelength. Laserna et al. studied the effect of beam propagation through atmospheric turbulence on standoff measurements up to 120 m. It was found that beam wander effects of incident laser beams caused by turbulence in the atmosphere can cause uncertainty in obtaining LIBS signals that leads to signal fluctuations in measurements.

Significantly separate and progressing from the previous attempts with standoff LIBS, we have considered lower pressure conditions down to 0.01 torr for the geological sample analysis. Three categories of certified reference materials (CRMs) are selected that represent metal, rock, and sand for standoff measurements. Signal intensity, signal-to-noise (S/N) ratio, and electron density are analyzed to investigate the characteristics of laser-induced plasma to a pressure change, and results are analyzed using the physicochemical properties of elements. Quantitative analysis is also performed using the univariate method. The work presented here is intended to extend the feasibility of the standoff LIBS in harsh environments.

**Experimental Setup**

Figure 1 shows both the in situ and standoff detection layout. As illustrated in Figure 1a, a pulsed nanosecond Nd:YAG laser (Quantel, Ultra 50) operating at 1064 nm at 20 Hz with 17–50 mJ/pulse is irradiated at the surface of samples. The laser beam passes through Lens 1 (plano-convex, focal length 350 mm, fused silica, Thorlabs) and is focused on the sample surface. Once plasma is generated by the laser, it is captured by Lens 2 (plano-convex, focal length 300 mm, fused silica) and sent to the spectrometer by a 200 μm single custom fiber optic cable (FOC). An intensified charge-coupled device (ICCD)-coupled echelle grating spectrometer (Mechelle and iStar, Andor) covering a wavelength range of 200–975 nm is used as a detector. The laser is focused on the sample surface and five shots are fired at each of the same location of three different points for measurements. The time delay is fixed at 1 μs for pressure above 7 torr, while it is 0.1 μs for measurements below 1 torr, and gate width is set to 20 μs. The flash lamp and Q-switch of the laser were connected to the pulse generator for time synchronization and the output signal of pulse generator lets the spectrometer to start collecting the data. Using a sample holder, samples can be placed inside the vacuum chamber so that the location of the sample is not moved during the process of depressurization and measurement. Pressure conditions varied from 760 torr to 0.01 torr by using a rotary pump connected to vacuum chamber. A digital pressure gauge is also connected to the vacuum chamber, so that the gauge of pressure could be checked in real time. Each measurement is taken after pressure has been stabilized at room temperature.

Figure 1b shows the schematic of a configured standoff LIBS system. We used the same experimental condition as...
that for the in situ system. The 4× beam expander is used for a higher beam collimation and focused on sample surface through Lens 3 from the distance of 5.3 m. Standoff measurements are taken at 5.5 m distance by using a 3.5 inch Maksutov–Cassegrain type of telescope. The telescope is located behind the laser and set at a higher position for proper detection.

Results and Discussions

Standoff Detection of Alloy Samples

We demonstrated the performance of a configured standoff system by using alloy samples listed in Table 1. Pulse energy of 40 mJ is used for comparison between in situ and standoff measurements.

For standoff measurements, we employed a beam expander to reduce the total divergence of the beam, which is proportional to the beam diameter which in turn caused a smaller beam diameter, so that the configured system would deliver sufficient energy for surface plasma generation at the distance of 5.5 m. In addition, the depth of focus (DOF) must be well defined:

$$\text{DOF} = \frac{\lambda}{\pi} \left( \frac{r}{D} \right)^2 M^2$$

where, $\lambda$ is the beam wavelength, $r$ is the distance between the optical paths, $D$ is the diameter of the beam, and $M$ is the parameter determined by beam quality. From Eq. 1, as the optical path $r$ becomes longer, DOF becomes significant, which can lead to undesirable breakdown of the surrounding air due to elongated focal spot. To minimize such effect, the location of samples is adjusted and optimized by moving the sample along the beam axis.

Regarding the position of standoff detection, all our standoff detections are performed near the beam axis, since the plasma moves towards the laser beam axis upon the sample ablation. Therefore, central direction is preferred for proper detection when the signal is especially weak as it is in low pressure. Additionally, a Maksutov–Cassegrain type telescope is used to minimize the effect of chromatic aberration that can significantly affect the signal detection.

For demonstrating the configured standoff LIBS system, Al signals from one alloy sample (654 b) are acquired in both in situ and standoff system. For both detections, intensity of Al 396.15 nm is normalized and analyzed as shown in Figure 2. From Figure 2a, maximum intensities are obtained at 100 torr and signal intensities are decreased at 7 and 760 torr. Pressure conditions below 1 torr result in significant decrease in the intensity; however, the standoff measurements remained strong enough for detection in comparison to the in situ case, even at those unfavorable low pressure conditions.

The S/N ratios are obtained in both detecting conditions, which are shown in Figure 2b. Signal-to-noise ratios are enhanced significantly, especially at below 1 torr region. Signal-to-noise ratios are increased up to an order of hundreds in those regions, whereas S/N ratios remain only at orders of few tens at high pressures. It is quite encouraging that performance of standoff detection below 1 torr retained strong enough S/N ratios to detect signals compared to in situ measurements.

Table 1. Concentrations of Al in alloy samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>654b</td>
<td>6.34%</td>
</tr>
<tr>
<td>1128</td>
<td>3.06%</td>
</tr>
<tr>
<td>1243</td>
<td>1.23%</td>
</tr>
</tbody>
</table>

Figure 2. In situ versus standoff detection of alloy 654b: (a) signal intensities of Al I 396.15 nm, (b) signal-to-noise ratio of Al I 396.15 nm.
Furthermore, using a standoff system, we measured Al signals of two other alloy samples in which a relatively smaller amount of Al is contained, compared to the alloy of 654b. As shown in Figure 3, intensities obtained from alloys are varied according to different concentrations of Al contained in samples. Overall behaviors of intensities according to pressure changes are similar regardless of its different Al concentrations. As a result, it was possible to detect 1.23% of Al, which is the least amount of Al concentration considered in alloy samples even at 0.01 torr using relatively small amount of energy of 17.2 mJ/pulse. Therefore, a configured standoff system seems quite promising for low pressure remote sensing for elements other than Al.

**Standoff Detection of Basalts and Powders at Low Pressures**

Two different sets of samples containing various major and minor elements are introduced to study the effect of remote sensing at low pressure down to 0.01 torr; their chemical compositions are listed in Table 2.

A set of basalt samples are analyzed that are abundant in oxides that include aluminum oxide (Al$_2$O$_3$), calcium oxide (CaO), iron(III) oxide (Fe$_2$O$_3$), sodium oxide (NaO), potassium oxide (K$_2$O), silicon dioxide (SiO$_2$), magnesium oxide (MgO), and more. These unique chemical compositions of basalt samples are similar to those of chemical compositions of the lunar surface, and therefore the importance of analyzing these samples is well reviewed by many authors.$^{12-14}$ Therefore, it is important to demonstrate the feasibility of standoff detection of such unique elements contained in the samples.

Powder samples contain relatively small amount of elemental concentrations in orders of parts per million (ppm). Due to such low concentration, the laser energy was raised to 50 mJ/pulse. On the other hand, it is a quite high energy for space missions that require increased mass and size of the laser. However, we are expecting to enhance the LIBS performances using tight focusing of the laser beam or larger diameter of the telescope for reducing the laser energy in the future work. Powder samples were mixed with paraffin binder at a proportion of 90 % concentration and were pelletized with 10 tons of pressure, 2.5 min of dwell time, and 1.5 min of release time. The paraffin binder consisted only of hydrogen and carbon ($C_nH_{2n+2}$) to ensure easy concentration adjustment and bonding of the powder samples. One of the characteristics of powder samples is that they could easily be scattered which sometimes leads to a difficulty in detection of signals, particularly when pressure is low.

Using the standoff set-up, we successfully obtained emission signals of various elements from both sets of samples at low-pressure conditions. The emission lines of Al(I) 396.15 nm, Ca(II) 396.84 nm, Ca(II) 422.01 nm, K(I) 769.89 nm, Mg(I) 518.36 nm, Na(I) 588.89 nm, and Si(II) 518.36 nm are shown in Figure 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al$_2$O</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-2G</td>
<td>13.5 %</td>
<td>7.12 %</td>
<td>13.8 %</td>
<td>1.79 %</td>
<td>3.59 %</td>
<td>3.16 %</td>
<td>54.1 %</td>
<td>2.26 %</td>
</tr>
<tr>
<td>BHVO-2G</td>
<td>13.5 %</td>
<td>11.4 %</td>
<td>12.3 %</td>
<td>0.52 %</td>
<td>7.23 %</td>
<td>2.22 %</td>
<td>49.9 %</td>
<td>2.73 %</td>
</tr>
<tr>
<td>BIR-1G</td>
<td>15.5 %</td>
<td>13.3 %</td>
<td>2.06 %</td>
<td>0.030 %</td>
<td>9.70 %</td>
<td>1.82 %</td>
<td>47.96 %</td>
<td>0.96 %</td>
</tr>
</tbody>
</table>

**Figure 3.** Standoff detection of alloys (a) signal intensities of Al I 396.15 nm, (b) S/N ratio of Al I 396.15 nm.
634.71 nm are analyzed as shown in Figures 4 and 5, where the strongest emission lines are obtained for both samples of basalt (BCR-2G, BIR-1G) and powder samples (1573a, 1575a; Table 3). The highest signal intensities of most of the elements are observed when pressure is in the range of 7–100 torr. The emission intensity of analyzed elements starts decreasing as pressure further reduces below 7 torr regardless of their different chemical matrices. Noticeably, the intensity of silicon in basalt samples is very weak although the concentration of silicon oxides is high. Perhaps high ionization potential and the electronegativity of silicon as listed in Table 4 has caused such intensity and concentration differences. In the selection of analytical lines of silicon, it was more appropriate to choose the strong first ionized silicon emission line appearing at 634.72 nm rather than the neutral silicon emission lines near the ultraviolet (UV) range for analysis due to a fast extinction of the LIBS plasma at low pressures where plasma shielding effects are diminished at lower electron density. On the other hand, pressure dependency of K and Na shows a bit peculiar when compared to those of other elements at high-pressure regions specifically above 100 torr; whereby the maximum intensities are obtained at 760 torr. This behavior of K and Na can be explained again by their physico-chemical properties. They have relatively small electronegativity as well as ionization potential compared to other elements, therefore they are more likely to be ionized and less likely to go through

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
<th>Ca</th>
<th>K</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1515</td>
<td>286 ppm</td>
<td>1.526 %</td>
<td>1.61 %</td>
<td>24.4 ppm</td>
</tr>
<tr>
<td>1547</td>
<td>249 ppm</td>
<td>1.56 %</td>
<td>2.43 %</td>
<td>24 ppm</td>
</tr>
<tr>
<td>1573a</td>
<td>598 ppm</td>
<td>5.05 %</td>
<td>2.70 %</td>
<td>136 ppm</td>
</tr>
<tr>
<td>1575a</td>
<td>580 ppm</td>
<td>0.25%</td>
<td>0.417%</td>
<td>63 ppm</td>
</tr>
</tbody>
</table>

Table 3. List of powder samples and its concentrations of elements (concentrations are in mg/kg, otherwise it is in ppm).

Figure 4. Signal intensities of basalts samples with various elements: (a) BCR-2G, (b) BIR-1G.

Figure 5. Signal intensities of powder samples: (a) 1573a, (b) 1575a.
recombination process which gives rise to sustaining the high intensities even at atmospheric pressure.

This pressure dependence of the emission intensities of LIBS is closely related to the laser plasma interaction. At high pressures above 100 torr, the energy is lost to the surrounding during the expansion of plasma and the plasma shielding effect becomes significant so that the laser energy cannot be delivered to the target, causing a decrease of ablated mass, which in turn results in lower signal intensity. For low pressures, plasma is disordered which results from the lack of sufficient atmosphere to provide adequate confinement, therefore a steep loss in intensity is induced that can be seen at pressures below 7–100 torr from both sets of our samples. It seems the optimal pressure for signal detection exists in the range of 7–100 torr for those tested samples, whereby plasma is still ordered and shielding effect is less effective. However, this optimal pressure may vary with parameters such as pulse duration, sample physical properties, chemical matrix of samples, and laser energy used in experiments.

The analytical emission intensity itself cannot provide useful information, since it does not provide any information on the quality of detection and the existing noise in the signal is still unknown. Therefore, S/N ratios should be examined, which can provide more useful information, and from which we can estimate the quality of LIBS spectra from remote sensing at low pressures.

Signal intensity is calculated by integrating each emission peak area, which is then divided by the area of the noise peaks to estimate the S/N ratio. The S/N ratios of each sample are estimated and are shown in Figure 6. It is seen that S/N ratios of various elements are either sustained or increased as pressure decreases, even though signal intensity was significantly reduced as pressure decreased (Figures 4 and 5). One of the possible reasons for a decrease in noise with the pressure decrease would be the decrease in electron density, since electron density affects the background noise in the LIBS plasma.

We have estimated electron number densities for basalt (BCR-2G) and powder (1573a) samples using line width of Stark broadening by following Eq. 2, since background emission is directly related to electron density.

\[
\Delta \lambda_{\text{FWHM}} = 2w \left( \frac{N_e}{N_r} \right)
\]

where \( \lambda \) is full width half-maximum (FWHM) of the line, \( w \) is the electron impact width parameter relating to plasma temperature, \( N_r \) is the reference electron number density, and \( N_e \) is the electron number density in the plasma. The Stark line widths are calculated by subtracting instrumental line width from the width of observed line peak. Instrumental line width was measured using Hg lines from mercury lamp and was 0.06 nm. In addition, using Lorentz fitting obtains the widths of observed line peaks. Appropriate values for those parameters are given by Griem, and the plasma temperatures are calculated by using the Boltzmann equation below to estimate electron impact width parameter, \( w \),

\[
I = \frac{hc}{4\pi \lambda} N(T) A_k \exp \left( - \frac{E_k}{KT} \right)
\]

Table 4. Physico-chemical properties of test samples.

<table>
<thead>
<tr>
<th>Elements</th>
<th>First ionization potential (eV)</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>5.98</td>
<td>1.61</td>
</tr>
<tr>
<td>Ca</td>
<td>6.11</td>
<td>1.00</td>
</tr>
<tr>
<td>K</td>
<td>4.34</td>
<td>0.82</td>
</tr>
<tr>
<td>Mg</td>
<td>7.64</td>
<td>1.31</td>
</tr>
<tr>
<td>Na</td>
<td>5.13</td>
<td>0.93</td>
</tr>
<tr>
<td>Si</td>
<td>8.15</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Figure 6. Signal-to-noise ratio of various elements: (a) BCR-2G, (b) 1573a.
Here, \( N(T) \) is the total density of neutral atom or ion, \( U(T) \) is the partition function, \( \lambda \) is the wavelength, \( A_k \) is the transition probability, \( g_k \) is the statistical weight for upper level, \( E_k \) is the excited level energy, \( K \) is the Boltzmann constant, and \( T \) is the temperature in Kelvin. All parameters were obtained from NIST Atomic Spectral Base to estimate the plasma temperature.\(^{18}\)

Finally, the electron number density of Ca II 396.84 nm is estimated and summarized in Table 5. Electron densities are decreased in general for decreasing pressure and thus cause a decrease in the background emission that is proportional to electron density;\(^{16}\) this is why the high S/N ratios at low-pressure regions are obtained.

Noticeably, a smaller electron density causes not only a decrease in noise, but also a narrowing of emission lines. This makes it easier for detection and identification of various elements as there is less likelihood of interference between emission lines.

There are other parameters that can affect the line broadening other than electron density in the plasma, which is a pressure condition, namely pressure broadening. This pressure broadening is due to random collisions of particles that lead to random frequency shift in emitted radiation.\(^{15}\) Therefore, pressure on line broadening is less effective when the atmospheric pressure is reduced. For example, mean free path at atmospheric condition is the order of few tens of nanometers and for low-pressure conditions it increases up to the order of few kilometers. This is one of the advantages of low-pressure detection, in which circumstances ambiguity in the identification of peaks arisen from interferences between emissions lines is less likely to occur. With the advantages of low pressures such as narrower line peaks and less noise, the signals of various important elements from basalt samples can be successfully obtained over the whole wavelength regions as shown in Figure 7.

Moreover, these low-pressure environments provide better chance of detecting the low concentration elements that generally result in weak emissions. Thus, emission peaks can be easily overlooked or interfered by the surrounding noise or the other emission peaks. However, a low-pressure environment can reduce the possible interference caused by the adjacent peaks. This is important when the emission lines appear closely within the range of less than 1 nm. Figure 8 illustrates such case where strong emission peaks of Al and Ca appear at 396.15 nm and 396.84 nm, respectively. If the concentrations for emitting those peaks differ by a large amount, identifying the emission peaks may become almost impossible. Therefore, a low-pressure environment seems to be more favorable in the detection of low concentration elements and this can be seen from the spectra obtained from the powder samples shown in Figure 8. In Figure 8, the concentrations of Al and Ca are in orders of a few hundred ppm and 5.05% (50,500 ppm) at maximum, respectively.

Finally, some of the calibration curves are drawn from both samples at 760 and 0.01 torr, respectively, using a linear fit (Figure 9). In general, there are two methods for

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Ca II 396.84 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FWHM (nm)</td>
</tr>
<tr>
<td>0.01</td>
<td>0.203</td>
</tr>
<tr>
<td>0.1</td>
<td>0.300</td>
</tr>
<tr>
<td>1</td>
<td>0.303</td>
</tr>
<tr>
<td>7</td>
<td>0.315</td>
</tr>
<tr>
<td>100</td>
<td>0.369</td>
</tr>
<tr>
<td>760</td>
<td>0.416</td>
</tr>
</tbody>
</table>

Figure 7. Spectra of basalt samples at pressures of 10–2 torr, (a) VIS region, (b) VNIR region.
determining elemental compositions from samples. One method uses a multivariate technique such as partial least squares (PLS) or principal component analysis (PCA) to interpolate compositions from a large number of samples. This multivariate analysis can overcome the matrix effect; however, it is subject to appropriate coverage of the training. Comparably, the univariate analysis cannot provide as high an accuracy as multivariate analysis does; however, it is much simpler to implement and it also allows intuitive comparison with certain accuracy. The wavelengths of spectral lines used throughout the analysis were K(I) 769.89 nm for both set of samples. Higher correlation coefficient, $R^2$ obtained at 0.01 torr showed a better linearity between elemental concentrations and intensities when compared to an atmospheric condition for both cases. In addition, correlation coefficients of other elements such as Ca and Na obtained from basalt and powder samples are 0.97 (basalt), 0.95 (powder) for Ca, and 0.90 (basalt), 0.90 (powder) for Na at 10$^{-2}$ torr. The obtained results also showed better linearity compared to the results obtained from atmospheric pressure. The obtained results suggest that low-pressure environment may provide higher accuracy in obtaining calibration curves, since matrix effects are weakened at low pressure causing a higher linearity. One of the main reasons for such chemical matrix effects comes from a strong interaction between atoms in close proximity such as in the high-pressure condition where it yields dense plasma. Therefore, a decrease in pressure may result in reduced matrix effect since the number of collisions between atoms is significantly reduced at very low pressures, 0.01 torr for instance. To confirm this, further experiments should be conducted since the chemical
matrix effects are dependent on several parameters such as pressure, physical and chemical matrices of samples, wavelength of laser, etc.\(^\text{19}\) Also, the limit of detection (LOD) for K in both samples at 0.01 torr were evaluated using the following formula.

\[
\text{LOD} = \frac{3S}{m}
\]  \(\text{(4)}\)

Here, \(S\) is the residual standard deviation of linear regression and \(m\) is the slope. The evaluated LOD for basalt and powder samples at 0.01 torr are found to be 719 ppm and 2279 ppm, respectively. As expected, basalt samples showed lower detection limit since powder samples are easily scattered particularly at low pressures which in turn causes difficulty in the signal detection. As a result, the combined standoff and low-pressure detection can certainly offer some accuracy, therefore it can be further optimized for minor and trace elements detection using PLS or PCA.

**Conclusion**

In this research, we considered pressure conditions down to 0.01 torr and performed a standoff LIBS analysis on a set of various categorized samples at a distance of 5.5 m. Alloy samples were used to demonstrate the configured standoff system performance for comparison to in situ detection. A set of powder and basalt samples that contain both major and minor elements was used to study the effect of low pressure on the sensitivity of remote sensing. Various emission peaks were successfully obtained and maximum intensities of Al, Ca, Mg, and Si emerged at 7–100 torr, while K and Na seemed to favor 760 torr conditions. This peculiar pressure dependence of K and Na is explained by their low ionization potential and electronegativity. As pressure is further reduced to below 7 torr, signal intensities decreased further significantly. However, high S/N ratios were insensitive to the decrease in background noise. The obtained calibration curves are reasonable for determining concentrations of the unknown samples, suggesting that matrix effects seemed less significant at low pressure. The present results suggest that the combined standoff and low pressure scheme is a promising means for analyzing unknown samples even at harsh pressure conditions and at the same time for detecting the minor trace of elements.

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**References**


