Correction of Self-absorption Effect in Laser-induced Breakdown Spectroscopy Analysis for Sea Salt Aerosols Using a Duplicating Mirror

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ABSTRACT: Sea salt aerosols significantly impact marine ecosystems and climate change; however, self-absorption effects unavoidably occur in the detection of sea salt aerosols via laser-induced breakdown spectroscopy (LIBS). This work illustrates the application of a renowned replica plasma method for self-absorption correction in the detection of sea salt aerosols via LIBS. Two sets of spectral data were obtained by adding a duplicating mirror behind the plasma, and the self-absorption correction factor was calculated using a previously described method. Consequently, the experimental results show a marked improvement in the linearity of the calibration curve. The determination coefficients of linear fitting were above 0.99, and the root mean square error of the cross-validation RMSECV was negligible. The duplicating mirror method for self-absorption correction in the detection of sea salt aerosols via LIBS can thus achieve high accuracy and stability within a certain range and therefore can prove useful for sea salt aerosol, aerosol, and gas detection.

INTRODUCTION

Sea salt aerosols (SSAs) released from sea spray droplets are directly produced at the air-sea interface and constitute a major component of the natural aerosol mass.1 SSAs are one of the most important natural sources of aerosols in the atmosphere, especially in coastal areas, and are the largest source of particulate matter in the troposphere. SSAs are hydrophilic and consist of NaCl, KCl, CaSO4, and Na2SO4, which directly and indirectly affect the climate. The direct effect is the absorption or scattering of solar radiation by aerosol particles, which reduces the intensity of solar radiation on the surface. The indirect effect is the aerosol particles acting as cloud condensation or ice nuclei, hence changing the microphysical and optical properties of clouds and affecting the climate by absorbing, scattering, and reflecting solar radiations.2 SSAs also play a vital role in the marine ecosystem. The nutrients that enter the ocean through the atmospheric deposition of SSAs enhance the primary productivity of the ocean and even accelerate the eutrophication of water bodies. Meanwhile, the presence of other heavy metal elements and organic pollutants can lead to water pollution.3

Laser-induced breakdown spectroscopy (LIBS), which has been praised as the “future superstar” in analytical chemistry, has the advantages of simple or no sample preparation, as well as online and multi-elemental detection; consequently, the method
has received considerable attention from scholars.\textsuperscript{4, 5} It has been utilized in various fields, such as coal analysis\textsuperscript{6, 7}, nuclear industry, aerosols\textsuperscript{8}, biomedicine\textsuperscript{9, 10, 11} and Mars exploration.\textsuperscript{12, 13} The analytical detection of SSAs via LIBS can quantify the main components of SSAs and thus detect marine ecosystems and climate change in real time. However, the complexity of spatial and temporal evolution of plasma leads to matrix effects, spectral fluctuations, and self-absorption effects. Self-absorption also affects the quantitative performance of LIBS in SSAs. These problems restrict the large-scale application and industrial development of LIBS\textsuperscript{14}. The self-absorption effect is a result of the uneven distribution of plasma temperature and electron number density in space. The laser interacts with the object to be measured, forming a temperature difference that leads to outward radiation of energy in the form of photons from particles in the high-energy state of the inner layer of the plasma. The photons are absorbed by particles of the same element in the outer layer of the plasma at a lower, resulting in distortion of the LIBS spectrum, which can lead to "self-etching" of the spectrum in severe cases.\textsuperscript{15}

Since the first use of LIBS for aerosol detection in 1983\textsuperscript{16}, the self-absorption effect has been widely discussed, and several solutions have been proposed. However, the self-absorption correction method for SSA detection has not yet been investigated. The existing experimental results conclusively prove the effectiveness of the "duplicating mirror" method in detecting the self-absorption effect of solids via LIBS;\textsuperscript{17} however, there is no experimental proof of whether the self-absorption effect of aerosols can be corrected using this method. In particular, to the best of our knowledge, no study has addressed the detection and correction of the self-absorption effect of SSAs using the "duplicating mirror" method.

**METHODS**

The derivations in this study are based on the results of previously reported studies available in the literature.\textsuperscript{18} In the derivation of the spectral radiation of the optical leap, assuming that the atoms are uniformly distributed in space and integrated along the emission line direction, the relation after the introduction of self-absorption can be written as:\textsuperscript{19}

\[
B_\lambda(\ell) = \frac{A_u n_u \hbar c}{4 \pi l_0} S_\lambda(\ell) \left( \frac{1 - \exp[-k_\lambda(\ell)\ell]}{k_\lambda(\ell)} \right) \tag{1}
\]

where \(B_\lambda\) is the spectral irradiance of the emission line (W cm\(^{-1}\) sr\(^{-1}\) cm\(^{-1}\)), \(A_u\) is the transition probability, \(\hbar\) is Planck’s constant, \(c\) is the speed of light, \(n_u\) is the overall number of excited states, \(S_\lambda(\ell)\) is the spectral profile of the line, \(\ell\) is the length of the emission (absorption) path in the observation direction, and \(k_\lambda(\ell)\) is the net absorption coefficient.

The ratio in the last term of Eq. (1) is the self-absorption term divided by \(\ell\), which can be obtained as:

\[
B_\lambda(\ell) = \frac{A_u n_u \hbar c}{4 \pi l_0} S_\lambda(\ell) \left( \frac{1}{k_\lambda(\ell)} \right) \tag{2}
\]

where \(K_\lambda\) is defined as:

\[
K_\lambda = \frac{k_\lambda(\ell)\ell}{(1 - \exp[-k_\lambda(\ell)\ell])} \tag{3}
\]

If the excited emission is negligible, a condition that is valid for most of the analytical plasma feats and spectral transitions used, \(k^*\) can be substituted with \(k\).

Further, the optical depth \(\tau\) is defined as:

\[
\tau_\lambda(\ell) = k_\lambda(\ell)\ell \tag{4}
\]

The last term of Eq. (1) can thus be rewritten as:

\[
\frac{1 - \exp[-\tau_\lambda(\ell)]}{\tau_\lambda(\ell)} \tag{5}
\]

Finally, when Eq. (2) is integrated over the entire wavelength range, the renowned expression for thermal emission given by the radiation theory is obtained using the relationship between the Einstein coefficient of the leap and Boltzmann ratio of the absorption oscillator intensity and atomic booster, which is valid under the local thermodynamic equilibrium (LTE) condition.

\[
B_{\text{thermal}}(\ell) = \int_{\lambda_0}^{\lambda_f} \frac{1}{1 - \exp[-k_\lambda(\ell)\ell]} S_\lambda(\ell) \, d\lambda \tag{6}
\]

\[
B_{\text{thermal}}(\ell) = \int_{\lambda_0}^{\lambda_f} \frac{1}{1 - \exp[-k_\lambda(\ell)\ell]} S_\lambda(\ell) \, d\lambda \tag{7}
\]

where \((B)_{\lambda_0}(T_P)\) (W cm\(^{-2}\) sr\(^{-1}\) nm\(^{-1}\)) is the spectral irradiance of blackbody radiation given by Planck’s law or Wien’s law at \(T_P\), and the integral is the total absorption factor (in nm). Under LTE conditions, with the optical thickness over the entire wavelength range of the line profile and negligible self-absorption conditions (\(k\lambda\ell \ll 1\)), we obtain

\[
B_{\text{thermal}} = \int_{\lambda_0}^{\lambda_f} k_\lambda(\ell) S_\lambda(\ell) \, d\lambda \tag{8}
\]

Under optically thin conditions, \(B_{\text{thermal}}\) increases linearly with the wavelength-integrated absorption coefficient, which in turn is directly related to the atomic number density.

However, at the other extreme (optically thick) condition, for \(k\lambda\ell \gg 1\), we obtain:

\[
B_{\text{thermal}} = (B)_{\lambda_0}(T_P) \tag{9}
\]

To describe the self-absorption correction, we start with the radiation intensity \(I_\alpha\) of the uniform plasma layer (length \(\ell\)) under LTE:
When a reflector is placed behind the plasma to determine the line profile to that of an optically thin case, the self-absorption coefficient is equal to:

\[ K_\lambda = \frac{k_\lambda \ell}{1 - \exp(-k_\lambda \ell)} \]  

This can be obtained by dividing Eqs. (10) and (11).

Under the influence of very strong self-absorption, the observed line intensity reaches blackbody radiation at temperature \( T_p \), and the line loses its characteristic shape; as a result, the observed line intensity is no longer linearly related to the absorption coefficient and the line profile cannot be recovered. For the intermediate case, that is, if the influence of the optical depth \( k_\lambda \ell \) is not too strong, the line profile observed in the optically thin case can be obtained using \( K_\lambda \) as a correction factor, as defined in Eq. (3). The observed line profile can be multiplied by the correction factor \( K_\lambda \).

When a reflector is placed behind the plasma to determine the value of \( K_\lambda \), two spectral lines (with and without a reflector) are obtained:

\[ B_{\lambda,1} = B_{\lambda} \exp[1 - \exp(-k_\lambda \ell)] \]  

\[ B_{\lambda,2} \equiv B_{\lambda,1} + G B_{\lambda,1} \exp(-k_\lambda \ell) = B_{\lambda,1} [1 + G \exp(-k_\lambda \ell)] \]  

\[ R_\lambda = \frac{B_{\lambda,2}}{B_{\lambda,1}} = 1 + G \exp(-k_\lambda \ell) = \frac{I_2}{I_1} \]

In the above expressions, subscripts 1 and 2 represent an operation with and without the reflector, respectively, and parameter \( G \) represents the reflection and absorption losses of the reflector, as well as the incomplete matching of the stereo angles, that is, \( k_\lambda = 0 \):

\[ R^c = \frac{B_{\lambda,2}^c}{B_{\lambda,1}^c} = 1 + G = \frac{I_2^c}{I_1^c} \]

where \( I_2^c \) and \( I_1^c \) indicate the spectral intensities with and without the reflector, respectively, and \( R^c \) can be determined, with high accuracy, at the plasma plume with weaker self-absorption.

Using Eqs. (13-1) and (14), the optical depth (see Eq. 4) can be expressed as

\[ k_\lambda \ell = \ln \left( \frac{(R^c - 1) (R_\ell - 1)}{(R_\ell - 1)(R^c - 1)} \right) \]  

Finally, by substituting Eq. (15) into Eq. (12), the experimental correction factor \( K_{\lambda,corr} \) can be calculated from the experimental ratios \( R^c \) and \( R_\ell \) as:

\[ K_{\lambda,corr} = \ln \left( \frac{R_\ell - 1}{R^c - 1} \right) \]

To obtain the line profile for the optically thin case, the recorded profile \( I_1 \) must be multiplied by the correction factor \( K_{\lambda,corr} \).

**EXPERIMENTAL**

The plasma emission acquisition device is shown in Fig. 1. An aerosol generator was used to transform the aqueous solutions into aerosols. The aerosol generator consisted of an atomizer and air pump. The aerosols passed through a 10 cm long drying tube...
Table 1. Concentrations of aerosols samples used for experiments

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration gradient (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca, K, Mg, and Na</td>
<td>2.5 5 10 17.5 25 50 100 150 250</td>
</tr>
</tbody>
</table>

(containing silica gel particles) and then entered the chamber. The entrance and outlet of the chamber consisted of two stainless-steel tubes. The former had an inner diameter of 1 mm and an outer diameter of 2 mm, whereas the latter had an inner diameter of 5 mm and an outer diameter of 7 mm. In the chamber, a Nd: YAG laser (Quantel Q-smart 850 with maximum energy of 430 mJ@532 nm, spot diameter of 9 mm, and beam divergence angle of <0.5 mrad) was passed through a 3x Galilean beam expander and focused using an aspherical plano-convex lens (F=50 mm) to interact with the aerosol flow and produce plasma. In this experiment, the laser frequency was 10 Hz, energy was 198 mJ, relative standard deviation was 2.8%, and pulse width was 6 ns. The laser-induced plasma emission light was passed through the acquisition lens (spherical plano-convex lens, UV-fused quartz, focal length of 50 mm) for collection and was subsequently coupled into the fiber. The other part of the plasma light was passed through a reflector (spherical mirror with a focal length of 25 mm, coated with UV-enhanced aluminum film, highly reflective at 200-800 nm) and was reflected to the focusing lens and coupled into the optical fiber, which was connected to a spectrometer (avantes multichannel fiber spectrometer, covering a range of 200-900 nm, resolution of 0.1 nm) at the other end, and the spectral signal was recorded for transmission to a computer. A digital signal generator (Stanford Instruments, DG645) was used to ensure that the laser and the spectrometer worked simultaneously. MATLAB 2019b was used for data processing under the existing experimental conditions.

The measured samples were a series of aqueous solutions containing CaCl₂, KCl, MgCl₂, and NaCl at graded concentrations (the liquid atomization rate was 50 μL/min and the gas flow at the outlet of the atomizer bottle was 2 L/min), which were calculated and converted into SSA-specific content, as shown in Table 1. The atomizer converted the aqueous solution into aerosols via compressed air produced by the air pump, and the excess water was absorbed by the drying tube. The dried aerosols were then delivered through a rubber tube into the chamber. Another air pump, connected to the outlet tube, was used for aerosol pumping. Notably, the currently available experimental data show that in East Asia, SSA concentrations are in the range of 50–60 μg/m³ in spring, lowest recorded SSA concentrations are in the range of 40–45 μg/m³ (in summer) and 40–50 μg/m³ (in autumn), and highest recorded SSA concentrations are in the range of 100–110 μg/m³ (in winter), with an average mass concentration of 14.69 μg/m³.²⁰ In the global distribution of the SSA seasonal variation analysis, the results showed that the SSA concentration was three times higher in winter than in summer.²¹ These SSA concentrations were used in this experiment.

RESULTS AND DISCUSSION

After the spectral signal was acquired using the spectrometer, the laser energy and acquisition time were adjusted to achieve the highest signal-to-noise ratio, as shown in Fig. 2 (parameter optimization using a 25 μg/m³ sample).

Experimentally, in the delay time SNR plots of Ca II 396.36 nm, K I 766.49 nm, and Na I 588.99 nm, all three analysis lines reached the highest SNR at 4 μs. In contrast, in the integration time SNR plots, Ca II 396.36 nm reached the highest value at 50 μs, while Na I 588.99 nm and K I 766.49 nm did so after 350 μs; 300 μs was taken as the integration time for this experiment to ensure the maximum SNR is achieved.

Owing to the inhomogeneity of aerosol particle distribution, some experimental results were the sum of plasma emission spectra formed by several particles at different positions, whereas some experimental results were of cases with no breakdown of particles. To avoid this discrepancy, the spectra of particles with spectral intensities that deviated from the mean by more than three times the standard deviation were treated as outliers for rejection during the data analysis. The spectra were obtained after averaging, as shown in Fig. 3, and the lines of the four elements (K, Ca, Na, and Mg) were selected for analysis, referring to the National Institute of Standards and Technology database in Table 2. A total of 200 spectra were taken, 10 spectra were averaged in a single...
Evaluation of concentration of the sample with a lower and the collected spectral signal satisfying the $3\sigma$ rule was selected as the no self-absorption point (the background noise in plasma emission spectra is believed to conform to a normal distribution; when the spectral intensity ratio is greater than three times the standard deviation of the background noise $\sigma$, the spectral signal is considered reliable with a 99.74% confidence level); the $R^2$ of the four elements along the concentrations with weaker self-absorption are shown in Table 3. The different $R^2$ values for various elements may be due to the different distributions of various elements in the plasma. Therefore, the size of the distribution range affects the enhancement multiplier of the reflector, which in turn leads to different minimum concentrations for determining $R^2$.

As shown in Fig. 4(a), the intensity of the spectrum after the addition of the reflector is nearly twice that without the reflector due to a combination of the weak absorption and the use of a highly reflective UV-enhanced reflector at 200-800 nm. This also verifies that the previous method of determining $R^2$ at a lower concentration using the signal satisfying $3\sigma$ is indeed correct.

### Evaluation of $R^2$ and self-absorption correction

After determining $R^2$, $R_\lambda$ for each concentration was determined based on the ratio of the spectral intensity with and without the reflector each time (see Eq. (13-3)), and ultimately, the correction factor $K_{corr}$ was calculated according to Eq. (16).

$$R_\lambda = \frac{B_{\lambda,2}}{B_{\lambda,1}} = 1 + G exp(-k_\lambda \ell) = \frac{I_2}{I_1}$$  \hspace{1cm} (16)

The relationship between $R_\lambda$ and $K_{\lambda,corr}$ for each analyzed element is shown in Fig. 4(b). After $R^2$ was determined, $K_{\lambda,corr}$ and $R_\lambda$ exhibited an inverse relationship, which also indicates a stronger degree of self-absorption. The experimental results show that the slope of $K_{\lambda,corr}$ vs $R_\lambda$ for the same element is similar, indicating that the degree of self-absorption in different atomic or ionic emission lines of the same element is also similar.

Another test for the effectiveness of the calibration method is its application to a case where the standard concentration is

### Table 2. Selected spectral lines of the elements under investigation

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength, $\lambda_{corr}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca I</td>
<td>422.67</td>
</tr>
<tr>
<td>K I</td>
<td>766.49, 769.89</td>
</tr>
<tr>
<td>Na I</td>
<td>588.99, 589.59</td>
</tr>
<tr>
<td>Mg II</td>
<td>279.53, 280.27</td>
</tr>
</tbody>
</table>

### Table 3. Elemental concentrations in the samples with no self-absorption used for the calculation of $R^2$

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Concentration (µg/m³)</th>
<th>Wavelength (nm)</th>
<th>Concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca II 393.36</td>
<td>2.5</td>
<td>Na I 588.99</td>
<td>2.5</td>
</tr>
<tr>
<td>Ca II 396.85</td>
<td>2.5</td>
<td>Na I 589.59</td>
<td>17.5</td>
</tr>
<tr>
<td>Ca I 422.67</td>
<td>10</td>
<td>K I 766.49</td>
<td>17.5</td>
</tr>
<tr>
<td>Mg II 279.53</td>
<td>2.5</td>
<td>K I 769.89</td>
<td>17.5</td>
</tr>
<tr>
<td>Mg II 280.27</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3 Calibration curves with and without a reflector of Ca II 393.36 nm (a), 396.85 nm (b) and Ca I 422.67 nm (c); Mg II 279.53 nm (d) and 280.27 nm (e); Na I 588.93 nm (f) and 589.95 nm (g); K I 766.49 nm (h) and 769.89 nm (i).

As the samples to be measured in this experiment were aerosols produced after atomization by air pumps, all detection was performed in the air, and the matrix effect was negligible. Further, it can be observed that, for more convenient observation, this experiment used exponential fitting, and the observed lines of all four elements were nonlinear, which proved that all the four measured elements (K, Ca, Na, and Mg) had different degrees of self-absorption.

### Evaluation of $R^2$

In this experiment, each sample was collected 200 times. To ensure an accurate determination of $R^2$, the concentration of the sample with a lower and the collected spectral measurement, and the average relative standard deviation for all experiments was 9.47%.
sufficiently high to make the plasma optically thick. In this case, the growth curve shows a classical nonlinear behavior, where the spectral intensity versus concentration curve starts to bend toward the transverse coordinate at a given critical concentration.\(^{22}\) The spectral intensity obtained in the present experiment shows a similar bend toward the transverse coordinate concentration, with the two ionic lines of Ca II 393.36 nm and Ca II 396.85 nm showing self-absorption from approximately 7 \(\mu g/m^3\) and the atomic line of Ca I 422.67 nm doing so from about 30 \(\mu g/m^3\). Additionally, the atomic lines of K I 766.49 nm, 769.89 nm, ionic lines of Mg II 279.53 nm, 280.27 nm, and the atomic lines of Na I 588.99 nm, 589.59 nm also show self-absorption when the concentration is approximately 30 \(\mu g/m^3\). Thus, all four elements analyzed in this study (K, Ca, Na, and Mg) display self-absorption. After the calculation of \(K_\lambda\) and correction, as shown in Fig. 5, the results show that the linearity fit (\(R^2\)) of the four elements after correction exceeded 0.99, and the RMSECV was negligible, which substantially improved the accuracy of quantification, and the analytical lines of all four elements recovered linearity.

Owing to the critical influence of SSAs on marine ecosystems and climate change, this study discusses the application of the duplicating mirror method in LIBS for the detection and correction of the self-absorption effect. Among the four elements that were analyzed, in terms of RMSECV as a standard, the two ion lines of Ca show the best correction effect, and K, Na, and Mg also show good correction effects, proving the effectiveness of the use of reflectors in SSA detection using LIBS. The obtained results show that this method applies to the detection of virtually all aerosols and gases, and can prove useful for large-scale promotion and application of the LIBS technology.

**CONCLUSIONS**

This work aimed to correct the self-absorption effects observed...
when using LIBS for SSA, aerosol, and gas detection. The theoretical considerations and experimental results in this work show that the use of a duplicating mirror for self-absorption correction in the LIBS detection of SSA caused a weak matrix effect, which is a major advantage of this technique. It was capable of rapidly verifying the presence of self-absorption in the aerosol sample using the duplicating mirror without any change in the sample concentration. This study also introduces the concept of considering the aerosol sample with the lowest concentration as a self-absorption-free sample to determine the self-absorption correction factor, with promising results. One disadvantage of using a duplicating mirror for self-absorption correction is that the spectral lines cannot be recovered at large values of self-absorption. However, considering the low SSA concentrations typically encountered in real-world applications, in most cases, the spectral line intensity of the sample will not reach that of blackbody radiation. Finally, a duplicating mirror is a simple yet highly effective device and is hence worth consideration by the wider LIBS scholar community. The experiments showed that the self-absorption correction in LIBS detection of SSA using a duplicating mirror achieved high accuracy and stability in a certain range and therefore could prove useful for sea salt aerosol, aerosol, and gas detection.

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**Notes**

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