

Quantitative Determination of Chlorine Concentration by Measurement of Sodium Deposited on Steel via Laser-Induced Breakdown Spectroscopy

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Accurate measurements of chlorine contained in salts deposited on steel surfaces at low concentrations, frequently in challenging environmental conditions and in areas with limited access, are of significant interest for dry cask storage monitoring due to the potential role of chlorine in enhancing stress corrosion cracking. Laser-induced spectroscopy (LIBS) enables such measurements, but can suffer from the interference of the intense atomic emission lines of iron with the much less intense atomic emission lines of chlorine. In this work, homogeneous sea salt standards have been created using a nebulizer and LIBS measurements of chlorine concentration in the range of 0.0025-0.25 g/m² have been performed to detect and quantify sodium contained in this artificial sea salt deposition, as a benchmark for future field tests.

I. INTRODUCTION

LIBS is a rapid *in-situ* chemical analysis technique that involves focusing a pulsed laser onto the sample surface, generating ionized and excited particles in luminous plasma, and resolving emission lines from the plasma that are characteristic of the elements of interest.¹ Although extensive studies have been performed to improve its analytical performance, characterization of chlorine on stainless steel is still challenging due to the high excitation energy of Cl of over 10 eV and the potential for interference from iron emission lines when the spectrometer resolution is limited.^{2,3}

In order to use this technique in the venting system of a dry cask storage facility located in coastal areas where airborne salt could deposit on the canister, Eto *et al.*⁴ recently demonstrated a fiber-coupled LIBS system and a coaxial focusing configuration for detection of Cl on steel in confined space. However, reliable detection remains challenging, especially when quantitative concentration measurements are sought at low concentrations. One possible alternative is to use the detection of Na as a surrogate to infer the presence of salt (and thus, chlorine), since no significant variation of the ratio of alkali elements to Cl has been observed in oceans and major seas⁵ and alkali metals could be readily measured by LIBS with a typical detection limit of a few ppm.⁶

In this work, samples with homogeneous distribution of sea salt on steel substrates have been prepared with Cl concentrations in the range of 0.0025-0.25 g/m². The ability to detect and quantify the Na emission line in LIBS

and correlate it with Cl concentration is demonstrated in this study.

II. EXPERIMENTAL SETUP AND METHODS

Figure 1 shows the experimental setup for LIBS measurements. A Q-switched Nd:YAG laser (Spectra Physics Quanta-Ray) with 10 ns pulse duration was operated frequency doubled to 532 nm. The laser pulse energy was attenuated to around 40 mJ and focused onto the sample surface. The emission light was collected in standard atmospheric conditions and diverted through an optical fiber into a Czerny-Turner spectrometer (Horiba Jobin Yvon iHR 550) and an Intensified CCD camera (Andor iStar 334T). A LabVIEW-based data acquisition system was developed to provide proper timing between shutter and ICCD through a delay generator (Stanford Research Systems DG645).

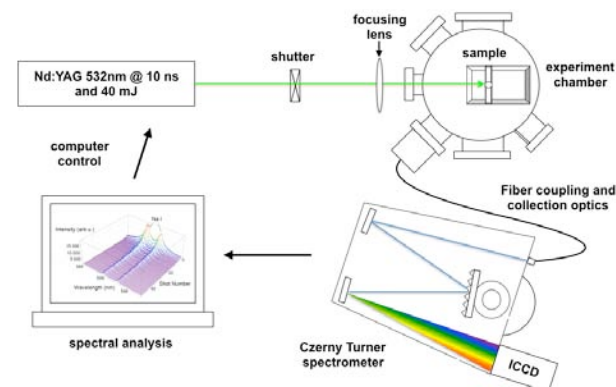


Fig. 1. Experimental setup for LIBS measurements

Reliable standards were created by spraying nanoscale droplets of diluted artificial seawater solution (Lack Product Company LLC) onto heated (~500 K) steel substrates using a Perkin Mira-mist nebulizer. With this procedure we obtained samples with high homogeneity as well as precisely known concentrations by considering the concentration of the diluted seawater solution, the well-controlled flow of the nebulizer, and the exposure time of the samples.

III. RESULTS

III.A. SEM Sample Characterization

Scanning electron micrographs (SEM) of the samples are shown in Fig. 2 a-e. Uniformly distributed salt deposits are observed on the samples with Cl concentration greater than 0.0125 g/m^2 . These clusters are homogenous over the scale of the laser focal spot size ($\sim 200 \mu\text{m}$). In contrast, circular shapes are shown on 0.0025 g/m^2 and 0.0125 g/m^2 standards because of different dilutions used in sample preparation process, but which are also homogenous over the scale of the focal spot size. Thus, these samples can serve as standards for LIBS measurements.

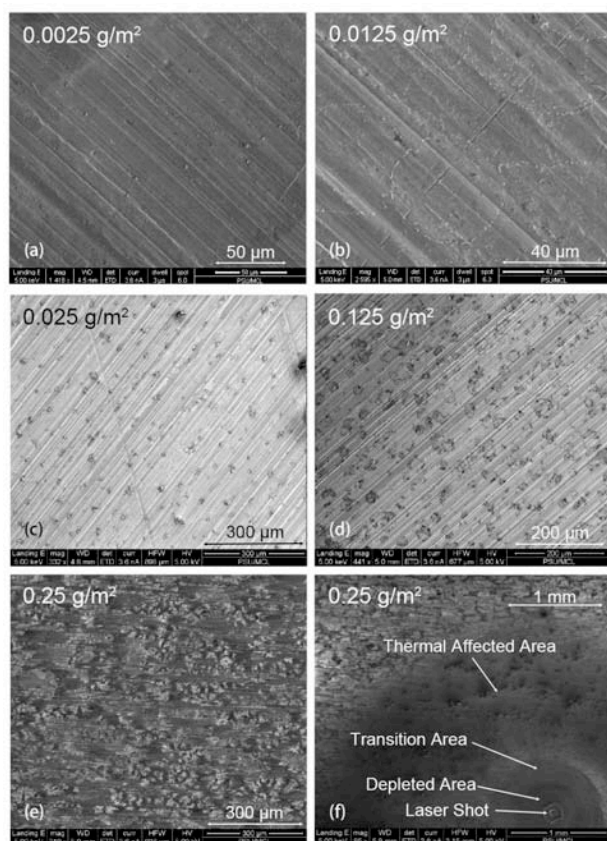


Fig. 2. SEM of surfaces after salt deposition with a Cl concentration of (a) 0.0025 g/m^2 (b) 0.0125 g/m^2 (c) 0.025 g/m^2 (d) 0.125 g/m^2 (e) 0.25 g/m^2 and (f) LIBS laser shot (2 accumulated pulses) on 0.25 g/m^2 standard

A typical laser shot imprint on a 0.25 g/m^2 standard can be seen in Fig. 2f. The laser shot imprint is directly surrounded by a depletion area on which no salt is observed and by a thermal affected area on which the salt layer begins to melt under the high substrate temperature produced by the deposition of laser energy, without affecting the overall concentration. Depleted and thermal

affected areas are separated by a transition area within which a gradient of concentration could be observed. The diameter of the depletion area is approximately 0.5 mm . The thermally affected area is $\sim 6 \text{ mm}$ in diameter.

III.B. LIBS Spectral Analysis

III.B.1. Na I Emission Lines Identification

In LIBS measurements, the gate delay and gate width of the ICCD camera were set to $1 \mu\text{s}$ and $0.1 \mu\text{s}$, respectively. Emission spectra were obtained at 20 different locations (1.27 mm apart to account for the thermally affected area of the neighboring spot), with accumulation of two laser pulses on each spot. The emission spectrum of the standards at chlorine concentration of 0.0025 - 0.25 g/m^2 is shown in Fig. 3. Two Na I emission lines at 589.0 nm and 589.6 nm are detected. Multiple peak fitting using Lorentz distributions was adopted in spectral analysis. The Na I emission line at 589.0 nm was used for quantification.

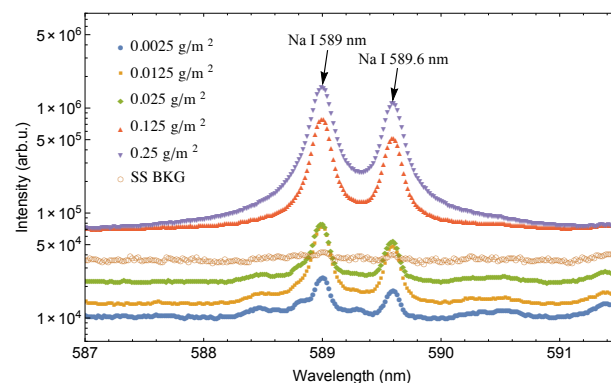


Fig. 3. Na I accumulated emission spectrum (20 position averaged) of the standards at the Cl concentration of 0.0025 - 0.25 g/m^2 on stainless steel and the background spectrum of blank steel substrate

No evidence of significant environmental Na speciation can be seen from the background spectrum of blank steel substrate in Fig. 3. Instead, the Na I emission peak increases corresponding to the increase of the sea salt concentration (Cl concentration).

III.B.2. Quantification of Cl concentration on Steel

Figure 4 shows the dependence of the Na I line intensity at 589 nm on chlorine concentration. Since self-absorption of Na I emission lines was not expected to be severe at such low salt concentration, a linear relationship was used to fit the mean values of the Na I emission intensities. The error bars of Na emission intensities are primarily due to the assumed Gaussian-shaped distribution of salt on the sample surface (error bars of

0.0025-0.025 g/m² standards are too small to be observed in Fig. 4.). A good correlation of the measured Na peak intensity with the calculated Cl concentration is found, suggesting that the measurement of Na can be an appropriate surrogate for the measurement of salt concentration.

Although the assumption has been made that the Cl-to-Na ratio remains constant during transport and deposition, it is necessary to examine the possibility that environmental reactions during transport or by exposing the samples to high temperature over prolonged periods could cause this ratio to change. Nevertheless, the technique appears to be a promising path that allows the use of LIBS on steel while avoiding the concerns of the convolution of the Fe and Cl lines and thus enables the investigation of low salt concentration samples.

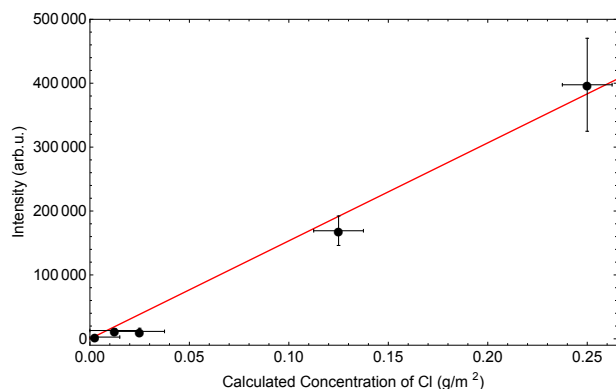


Fig. 4. Intensity of the Na I emission (589 nm) versus calculated chlorine surface concentration.

IV. CONCLUSIONS

Sample preparation procedures have been standardized in our experiment to create homogeneous salt deposits on stainless steel substrates, which were later analyzed using LIBS measurements. The ability to quantify Cl on stainless steel in the concentration range of 0.0025-0.25 g/m² has been investigated in this study by means of a surrogate Na measurement. For future work, other alkali metals such as Mg and K will be examined simultaneously with Na in the salt deposits to increase confidence in the results. Fiber-coupled LIBS and coaxial focusing configuration will be developed to increase the flexibility of the LIBS system and to reduce the impact of misalignment of the focus. Experimental parameters (i.e. laser energy, gate width, gate delay) will be optimized for this configuration. Calibration curves for these specific experimental parameters will be constructed. Ultimately, this project aims to provide a reliable way to measure salt deposition on dry-storage casks and will be implemented on a multi-sensors robot able to assess the absence of salts that could potentially promote stress corrosion cracking and hence ensure the safety of those casks.

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REFERENCES

1. K. HARTIG, J. COLGAN, D. KILCREASE, J. BAREFIELD II, I. JOVANOVIĆ, "Laser-induced breakdown spectroscopy using mid-infrared femtosecond pulses," *J. Appl. Phys.*, **118**, 043107 (2015).
2. S. ETO, J. TANI, K. SHIRAI, T. FUJII, "Measurement of concentration of chlorine attached to a stainless-steel canister material using laser-induced breakdown spectroscopy," *Spectrochim. Acta B*, **87**, 74 (2013).
3. K. SUGIYAMA, T. FUJII, T. MATSUMURA, Y. SHIOGAMA, M. YAMAGUCHI, K. NEMOTO, "Detection of chlorine with concentration of 0.18 kg/m³ in concrete by laser-induced breakdown spectroscopy," *Appl. Opt.*, **49**, C181 (2010).
4. S. ETO, T. FUJII, "Laser-induced breakdown spectroscopy system for remote measurement of salt in a narrow gap," *Spectrochim. Acta B*, **116**, 51 (2015).
5. F. CULKIN, R. COX, "Sodium, potassium, magnesium, calcium and strontium in sea water," *Deep Sea Res.: Oceanogr. Abstr.*, **13**, 789 (1976).
6. M. M. TAN, S. CUI, J. YOO, S. H. HAN, K. S. HAM, S. H. NAM, Y. LEE, "Feasibility of laser-induced breakdown spectroscopy (LIBS) for classification of sea salts," *Appl. Spectrosc.*, **66**, (3), 262 (2012).