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Temperature based segmentation for spectral data of laser-induced plasmas for quantitative compositional analysis of brass alloys submerged in water☆

Tomoko Takahashi[a,*], Blair Thornton[a,b], Takumi Sato[a], Toshihiko Ohki[c], Koichi Ohki[c], Tetsuo Sakka[d]

[a] Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro, Tokyo 153-8505, Japan
[b] Southampton Marine and Maritime Institute, University of Southampton, Burgess Road, Southampton SO16 7QF, UK
[c] OK Lab. Co. Ltd., 8-7-3, Shimorenjyaku, Mitaka, Tokyo 181-0013, Japan
[d] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

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ABSTRACT

This study describes a method to quantify the composition of brass alloys submerged in water using laser-induced plasmas. Principal component regression (PCR) analysis and partial least squares (PLS) regression analysis are applied to spectral measurements of plasmas generated using a long-ns duration pulse. The non-linear effects of excitation temperature fluctuations on the signals are treated as systematic errors in the analysis. The effect of these errors on the analytical performance is evaluated by applying PCR and PLS with a temperature segmented database. The results of the analysis are compared to conventional methods that do not consider the excitation temperature and it is demonstrated that the proposed database segmentation improves accuracy, with root-mean square errors of prediction (RMSEP) of 2.7% and 2.8% for Cu and Zn in the PCR model and 2.9% and 1.8% for Cu and Zn in the PLS model, respectively. The results indicate that systematic effects contribute to fluctuation of underwater plasmas, where appropriate database segmentation can improve the performance of the PCR and PLS methods.

1. Introduction

In laser-induced breakdown spectroscopy (LIBS), a high-power laser pulse is focused on a sample to create a plasma and the elemental composition of the target can be determined by analyzing the light emitted from atoms and ions of ablated material. LIBS is suitable for in-situ chemical analysis, since it does not require any sample preparation and targets can be rapidly analyzed. Due to these advantages, LIBS can be applied to in-situ analysis on land and in planetary exploration [1–4]. Whereas LIBS should be essentially applicable to elemental analysis of solids immersed in a transparent liquid, it is often reported that signal degradation is observed when targets are measured in water using a conventional laser pulse [5–7]. Enhancement of signals from solids submerged in water using a double pulse technique has been reported [8], in contrast to single pulse measurements [9,10]. However, the double pulse method is sensitive to external pressure [11,12], and it has been demonstrated that no enhancement in line emission is observed compared with measurements using a single pulse at pressures of more than 14.6 MPa for immersed solids [11] and 10 MPa for liquids [13]. Meanwhile, it has been reported that the use of a laser pulse with long duration of ≥ 100 ns can yield significant enhancements in signal quality for underwater samples [14,15]. It has further been shown that the signal enhancements for both bulk liquids [16] and submerged solids [17] are effective at pressures of up to 30 MPa. This method has been applied to in-situ real-time measurements of seawater and hydrothermal deposits at depths of more than 1000 m, using ChemiCam, a deep-sea LIBS instrument [18]. While in-situ detection of peaks of elements contained in targets in the ocean can be successfully performed using a long-pulse LIBS technique, quantification of compositions of these targets on site is still a challenging task. Since the calibration curves in atomic emission spectroscopy can be affected by the matrix [19,20], matrix matched standards are typically required. In the case of measurements of unknown samples, prior knowledge about the chemical compositions of the samples is required to prepare calibration curves, which is not practical for in-situ measurements in the field. While calibration curves have been demonstrated for specific targets under controlled conditions [21], for most general applications, the shot-to-shot fluctuations of signals

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[*] Corresponding author.

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in underwater long-pulse LIBS can also lead to unreliable calibration curves. Since a plasma created on a target submerged in water is strongly confined, the plasma lifetime is shorter than in air [5,11], and the signals observed exhibit much larger shot-to-shot fluctuations. Calibration-free LIBS (CF-LIBS) has been introduced to determine the elemental composition without preparing calibration curves [22]. In CF-LIBS, matrix effects and signal fluctuations are theoretically corrected based on the Boltzmann distribution law and the quantification of compositions of samples in a gaseous environment has been successfully performed in a number of studies (for example, Refs. [23–25]). The compositions of major elements of brass alloys submerged in water were also determined using a CF-LIBS method with relative errors of less than 10% [26]. It should be noted that several assumptions are made in the CF-LIBS method [20]: 1) ablation is stoichiometric, 2) the plasma is optically thin, 3) local thermodynamic equilibrium of the plasma is fulfilled temporally and spatially (within a short optical window), and 4) the plasma can be modeled as a spatially homogeneous source. Additionally, peaks of all elements contained in the target need to be observed. If any of these assumptions or requirements are not satisfied, the calculation of chemical composition using CF-LIBS can be unreliable. Meanwhile, multivariate analytical techniques have been examined for quantifying compositions of targets in atomic spectroscopy [27,28]. Multivariate analysis is a statistical approach to analyze correlations between the compositions of measurement targets and their spectra. Among the techniques, principal component regression (PCR) analysis and partial least squares (PLS) regression analysis have been successfully applied to LIBS signals of rocks taken in vacuum and gaseous environments [29–32]. PCR and PLS are based on classical multivariate regression analysis, such as the classical least squares (CLS) method or the inverse least squares (ILS) method, but they extract a few latent variables from the original training dataset by finding redundancy [27]. Using these methods, statistical errors can be removed from signals in the process of reducing the dataset's dimensions. It should be noted, however, that systematic errors cannot be removed using these techniques. The fluctuations in LIBS signal intensities observed in underwater measurements can occur systematically. In fact, it was reported that variation of experimental parameters leads to fluctuation of electron temperature, electron number density, and ablation mass, which have systematic relations with signal intensity based on the Saha-Boltzmann distribution law [33]. It was also suggested in the Ref. [33] that the performance of quantification of the compositions of metal alloys from simulated spectra using artificial neural network (ANN), which is a natural computing multivariate analytical method, improved when these parameters were added to the input data for ANN. Since PCR and PLS are more sensitive to systematic errors than ANN, it is necessary to remove the significant sources of any systematic error.

In order to investigate whether multivariate analysis can be applied to underwater long-pulse LIBS measurements, the effects of systematic errors on the quantification of compositions of solids submerged in water are estimated by comparing conventional PCR and PLS, with the corresponding methods where the reference database is segmented by the excitation temperature (hereafter temperature), which is identified as a possible cause of systematic error.

2. Materials and methods

2.1. Experimental setup

The experimental setup used in this work is shown in Fig. 1. The plasma was generated on a target by a custom-built Q-Switched Nd:YAG laser with wavelength of 1064 nm, pulse energy of 5 mJ, pulse width of 150 ns, and a repetition rate of 1 Hz delivered via a 600 µm fused-silica fiber. A target is submerged in pure water 7 mm away from the face of a custom-made objective lens with 5× magnification. The diameter of the laser beam at its focal point is 120 µm. Spectroscopic measurements were performed by observing the light from the plasma along the same path used for laser delivery. The emitted light passes through a custom-built spectrograph and the spectra are recorded using an intensified charged-coupled device (ICCD, Princeton Instruments, PI-MAX 3 Gen II) from 250 nm to 570 nm at a resolution of 0.8 nm. The wavelength calibration was performed using a standard mercury lamp (Ocean Optics, HG-1). The gate width and the gate delay of the ICCD were set to 500 ns and 400 ns, respectively, where these values were found to achieve the largest signal-to-noise ratio.

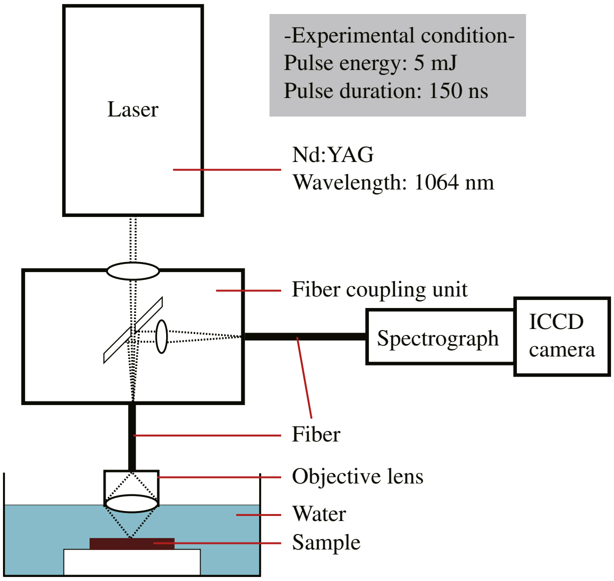

Fig. 1. Experimental setup.

2.2. Materials

A total of 11 certified brass alloys with different mass fractions of copper (Cu) and zinc (Zn) are selected for analysis (MBH Analytical Ltd., 31X7835.5, 31X7835.8, 31XB2, 31XB20, 31XB21 and 31XB23; Japan Copper and Brass Association, C5191, C2600, C6871, C2801 and C3713). The concentrations of Cu and Zn, which are major elements in the brass samples, were examined. The concentrations of Cu and Zn of the samples are shown in Table 1. These are selected to cover a broad range of concentrations (Cu; 59.6% to 93.6% and Zn; 0.02% to 39.2%) where the values for concentrations are spread relatively evenly within these ranges. The irradiation point is moved every 20 measurements in order to limit the effects of target inhomogeneity.

Table 1
Mass fractions of Cu and Zn in the certified samples.

Sample	Cu (%)	Zn (%)	Others (%)
1	91.25	6.23	2.52
2	69.93	24.83	5.24
3	60.13	39.57	0.30
4	58.53	37.03	4.44
5	69.24	29.50	1.26
6	89.57	9.97	0.46
7	93.62	0.02	6.36
8	69.89	30.10	0.01
9	78.08	21.91	0.01
10	60.48	39.50	0.02
11	59.63	39.12	1.25