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Revealing discriminating power of the elements in edible sea salts: Line-intensity correlation analysis from laser-induced plasma emission spectra

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ABSTRACT

We have investigated the discriminating power of the elements in edible sea salts using Laser-Induced Breakdown Spectroscopy (LIBS). For the ten different sea salts from South Korea, China, Japan, France, Mexico and New Zealand, LIBS spectra were recorded in the spectral range between 190 and 1040 nm, identifying the presence of Na, Cl, K, Ca, Mg, Li, Sr, Al, Si, Ti, Fe, C, O, N, and H. Intensity correlation analysis of the observed emission lines provided a valuable insight into the discriminating power of the different elements in the sea salts. The correlation analysis suggests that the elements with independent discrimination power can be categorized into three groups; those that represent dissolved ions in seawater (K, Li, and Mg), those that are associated with calcified particles (Ca and Sr), and those that are present in soils contained in the sea salts (Al, Si, Ti, and Fe). Classification models using a few emission lines selected based on the results from intensity correlation analysis and full broadband LIBS spectra were developed based on Principal Component Analysis (PCA) and Partial Least Squares-Discriminant Analysis (PLS-DA) and their performances were compared. Our results indicate that effective combination of a few emission lines can provide a dependable model for discriminating the edible sea salts and the performance is not much degraded from that based on the full broadband spectra. This can be rationalized by the intensity correlation results.

1. Introduction

Salt, a mineral primarily composed of sodium chloride (NaCl), provides the essential elements for living organisms and is one of the most important industrial raw materials. The salt production for human consumption dates back even earlier than the Iron Age [1,2]. Salts are generally classified in three groups: sea salt, rock salt, and refined salt [3]. The sea salt is extracted from oceans and saline lakes. The rock salt is formed as underground deposits in the geographical regions that previously enclosed seas, lakes, and playas. These natural salts have been used to produce refined salts with significantly reduced concentrations of the elements outside of sodium (Na) and chlorine (Cl). The refined salts have been popular food additives. However, the unrefined salts extracted from seawater are gaining popularity due to detrimental health effects of high Na consumption on human health and the health benefits provided by rich minerals present in the unrefined sea salts [4–8].

A wide variety of elements comprises typical sea salts. The alkali and alkaline earth metals such as lithium (Li), Sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), and strontium (Sr) are found in most unrefined sea salts [9]. The abundance of these elements in the sea salts can be attributed to relatively high water solubility of the ionic compounds that they form. The nonmetal elements such as chlorine (Cl), sulfur (S), oxygen (O), carbon (C), nitrogen (N), hydrogen (H), and boron (B) are included in the sea salts as counter anions of the metal cations in forms of chlorides (Cl^-), sulfates (SO_4^{2-}), nitrates (NO_3^-), bicarbonates (HCO_3^-), borates (BO_3^{3-}), etc. [9]. The sea salts are usually produced on salt pans that are shallow artificial ponds created to extract salts from the seawater. The salt pans consist of reservoir, evaporation, and crystallization areas. The concentrations of these alkali and alkaline earth metal cations and their counter anions in the sea salts vary with the relative density of seawater in evaporation and crystallization areas [10,11]. Also, relatively high concentration of aluminum (Al) is present in some sea salts [12]. The Al in the sea salts may mainly come from soil particles. The sea salts produced on the natural salt pans

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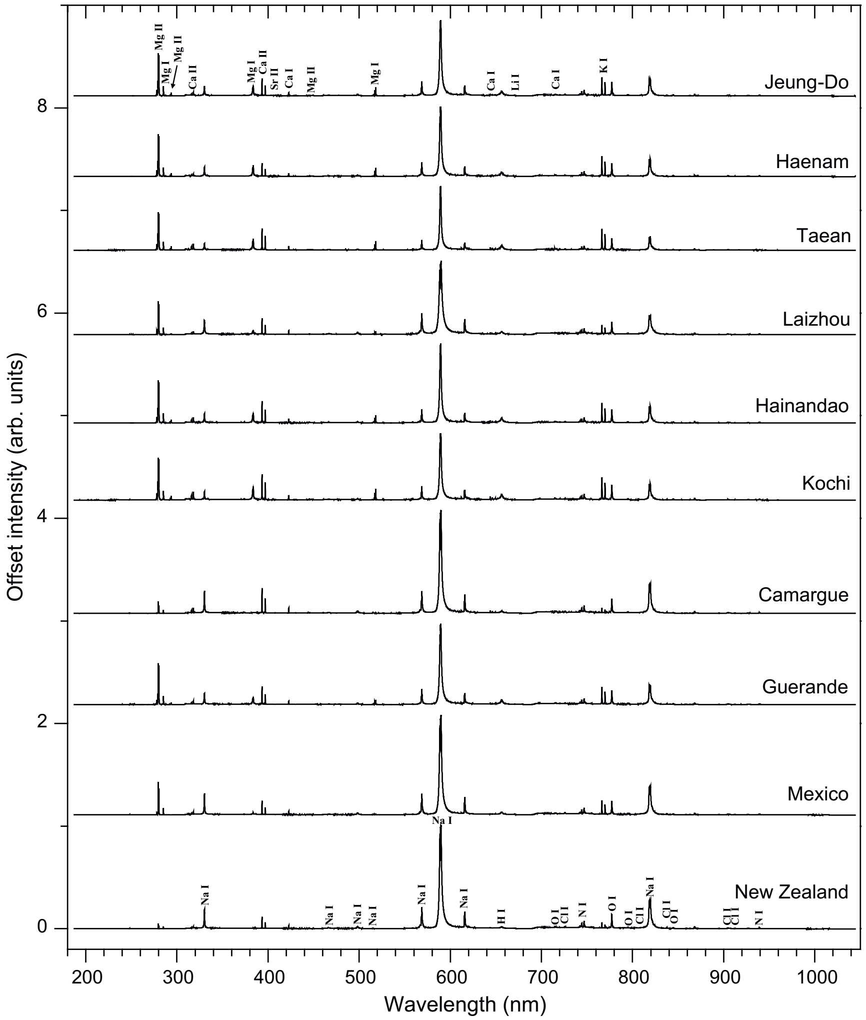

Fig. 1. Typical LIBS spectra of the sea salt samples.

without synthetic building materials tend to contain more soil particles. This probably increases the concentrations of the elements typically found in soils such as silicon (Si), titanium (Ti), and iron (Fe) as well as Al [13,14].

Currently, salt markets in many developed countries are globalized. Various kinds of salts, characterized by their geographical origins, production methods, and qualities, can be found in a single salt market in these countries [15]. Moreover, a growing concern about high Na intake generates much interest in premium salt products from foreign countries. Therefore, a fast reliable methodology for quantitative analysis and classification of salts is highly desirable in regulating salt quality and protecting consumers from counterfeit products. For the quantitative analysis, Singh et al. applied calibration-free LIBS to analyze Na and K in Indian edible salts and discussed their potential role in chronic kidney disease [16]. For the classification of salts, Herrador et al. reported the inorganic indicators of the origin of edible salts marketed in Spain using chemometric analysis [17]. Silva et al. indicated that sea salts contain ~40 volatile organic compounds which can provide information about the geographic origin and salt-pan environment [18]. Galvis-Sánchez et al. demonstrated that near-infrared spectroscopy can be applied as an efficient tool for sea salt quality evaluation [10].

Laser-Induced Breakdown Spectroscopy (LIBS) has been applied to the analysis of various materials including foods and minerals [16, 19–24]. Previously, we demonstrated the feasibility of LIBS for the classification of sea salts [12]. In the previous work, we measured the concentrations of K, Mg, Ca, and Al by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and obtained LIBS spectra for eleven kinds of sea salts using a high-resolution Czerny–Turner spectrometer with a 40 nm spectral window. In the spectral window around 780 nm, K, Mg Ca, and Al were detected using first (K I) and second (Mg I, Ca II, and Al I) order diffraction in the spectrometer. The K I, Mg, I, Ca II, and Al I line intensities from the LIBS spectra were found to be consistent with the K, Mg, Ca, and Al concentrations from ICP-AES. The classification model with the Mg I, Ca II, and Al I lines was developed by Partial Least Squares Discriminant Analysis (PLS-DA) based on principal components (PCs). From the results of our previous work, LIBS was found to be a feasible tool for the classification and discrimination of sea salts. However, sea salts contain a variety of other elements outside those considered in the previous study such as Na, Cl, Li, Sr, Si, Ti, Fe, C, O, N, H, S, B, fluorine (F), and bromine (Br). These elements may play an independent role in classifying a certain group of sea salts or may be only a redundant factor in providing discriminating power with respect to other elements. Therefore, the knowledge about the discriminating power of these elements will be valuable for developing the most effective and robust sea salt classification methodology. The previous study did not address the contribution of these elements to discrimination power due to limited spectral coverage available with the narrowband Czerny–Turner spectrometer.

The aim of this work is to identify the elements in sea salts that provide dominant and independent discriminating power. From broadband LIBS spectra in the spectral range between 190 and 1040 nm we identified the emission lines of Na, Cl, K, Li, Ca, Sr, Mg, C, H, O, N, Al, Ti,