Comparative study of the matrix effect in Cl analysis with laser-induced breakdown spectroscopy in a pellet or in a dried solution layer on a metallic target

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ABSTRACT

Chlorine content brought by salt in a composite powder was determined when the sample was prepared in pellet or first dissolved into solution and then dropped on the surface of a pure metallic target. The purpose is to address the matrix effect when the mixture powders of different kinds of mineral salt are used, and to compare the influence of the matrix effect for two kinds of sample preparation. Three types of powder mixture, $NaCl + KBr$, $NaCl + MgSO_4$, and $NaCl + Na_2CO_3$, were then first prepared with well controlled proportion of salt ($NaCl$) and mineral salt powder. On one hand, pellets were prepared for laser ablation. On the other hand, mixture powder was dissolved in deionized water for analysis with surface-assisted laser-induced breakdown spectroscopy (LIBS) of solution by dropping it on the surface of a pure aluminum target. Calibration curves were established for the pellets and the solutions, respectively. The slopes of these curves provided an assessment of the matrix effect related to the different mineral salt matrix and different forms of the sample preparation. The similar responses from chlorine for the solution samples showed absence of matrix effect for analysis with the surface-assisted solution analysis configuration. This result was further confirmed by the consistence of the measured temperatures and the electron densities of the produced plasmas. In contrast, the slopes of the chlorine calibration curves exhibited significant variation for different pellet samples corresponding to different powder mixtures, which is an indication of matrix effect in the LIBS analysis of the pellet samples.

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1. Introduction

As a promising elemental analysis technique, laser-induced breakdown spectroscopy (LIBS) demonstrates various advantages such as sensitive multi-elemental detection, rapid response for online monitoring, easy sample preparation for *in situ* measurements, high spatial resolution for surface mapping, and stand-off operation capacity for remote sensing. It has attracted great attention in different areas such as industrial application and environmental pollution detection. A lot of work has been done to understand the fundamental physical and chemical processes in the ablation plasma and to develop instrumentation and applications of the technique [1–3]. However, the matrix effect is in general, considered as a limitation of the LIBS technique, especially for its use in quantitative analysis [4]. Such an effect corresponds to the response variation from an analyte with the same given concentration but in different material matrix. Generally speaking, the highly

nonlinear laser-material interaction, which occurs during laser ablation and analyte vaporization can be considered as the origins of such variation of analyte response as a function of the sample matrix. When the matrix effect becomes significant, calibration curves should be, in principle, established according to the matrix of the sample to be analyzed, *i.e.* matrix matching calibration, which can lead to complicated analytical procedures, even bottleneck difficulty in analytical science.

Various normalization methods can help to reduce the influence of the matrix effect. Emission signals have been normalized by the ablated mass, electron temperature [5], electron density [6–7], emission lines of internal reference elements [8–9] and powder surface densities [10]. More recently, some statistical methods relying on the principles of artificial neural networks [11], partial least squares and wavelet-transform hybrid model [12], principal component analysis [13] are increasingly used to reduce the influence of the matrix effect. Meanwhile, others have explored the calibration-free approaches [14].

In general, the above matrix effect correction methods correspond to elaborated data processing. Applying to real elemental analysis cases, it is not always easy to guarantee the efficiency and the precision of the matrix effect correction, as many parameters can influence the result.

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Efforts have been made to search solutions which eliminate the matrix effects experimentally rather than mathematically or statistically with as posterior data correction process. Recently, a method called laser ablation-LIBS (LA-LIBS) [15] has been put forward to overcome the matrix effect, which consists in separating sampling with laser ablation of solid target and excitation process of the analyte species. In such a configuration, laser-induced plasma was produced in a buffer gas mixed with sample particles ablated by a first laser pulse from a solid state matrix. In our previous work, we have demonstrated similar responses from wear metals when they were dispersed in different lubricating oils [16]. The experimental configuration used was that of indirect ablation of a thin oil film coated on the surface of the pure aluminum target [17,18].

In this paper, we studied the analysis with LIBS of chlorine brought by salt in composite powder. We compared the matrix effect for the samples prepared with different mineral salts in the forms of pellet or solution. For the solution samples, they were first dropped on the polished surface of a pure aluminum target, and then the dried surface was ablated by laser. Such configuration has been introduced to enhance the sensitivity of LIBS analysis of solution and presents high performance [19]. Our results showed negligible matrix effect for the solution samples, while the results for pellets exhibited strong matrix effect as expected. The electron density and temperature of the induced plasmas were further determined, which confirmed again the reduced matrix effect for solution sample with surface-assisted LIBS configuration. Finally some remarks were made about the choice of chlorine as the analyte in this work. A large amount of salt samples in pellet form or in solution form with a high concentration was required to evaluate the matrix effect brought by salt. It is hard to control the low concentration of a metal analyte due to fluctuation caused by the contamination during the sample preparation and the minor impurity from the chemical regeant sample. Meanwhile, the chlorine as a nonmetal element can be analyzed at much higher concentrations without severe self-absorption than metal elements under the same experimental conditions. In this work, the analyzed content of chlorine ranged from 5% to 50.3% in salt mixtures, providing an easier way to control.

2. Experimental

2.1. Sample preparation

In this experiment, four mineral salts with analytical reagent grade, NaCl, KBr, MgSO$_4$, and Na$_2$CO$_3$ (Sinopharm Chemical Reagent Co., Ltd) were used to prepare the powder mixtures without further purification. The four kinds of powders were first dried and ground to suitable mesh size of less than 50 μm. The NaCl powder was then mixed with the rest

of the powders respectively at different NaCl percentages. Each mixture obtained was manually homogenized for 10 min in an agate mortar. The mixing ratios and the corresponding concentrations for chlorine in the final mixtures are as given in Table 1.

With the above mixture powders, pellets of 13 mm diameter were prepared with 0.5 g of powder using a hydraulic press with a pressure of 10 ton in 3 minutes. No further treatment was necessary before laser ablation. In parallel, a set of powder solutions were prepared with deionized water as solvent. As shown later in §3.2, the percentage of the powder in solution was optimized for obtaining a uniform dried solution layer on the target surface and for high efficient emission from chlorine. An amount of 0.3 ml of the prepared solution was then deposited on the polished and cleaned surface of a pure aluminum target. A homogeneous layer of solution was first obtained on its whole surface (49×43 mm^2) by spreading the liquid with a glass stick with much care. Mild warming with a hot plate was used to facilitate the drying process. The aluminum target was put on the hot plate. When the plate was heated to 30 ºC, a thin layer of dried solution was formed on the target surface. It is important to note that if the plate was set at a higher temperature, the homogenous layer could not be formed because of the surface tension. To remove the crystalliferous water, which may affect LIBS signal, the plate could be further heated after the dried layer was formed. Under such a condition, the plate was kept at a temperature of 180 °C for 3 min. Crystallization could be observed when the percentage of powder in solution becomes high enough as shown later in §3.2. The surface-contaminated target was then cooled down to the room temperature and mounted to the sample holder for ablation.

2.2. Experimental setup and measurement protocol

A standard LIBS experimental setup was used in the present investigation. The ablation source was a Q-switched Nd:YAG laser (Quantel Brillant) operating at 1064 nm with a repetition rate of 5 Hz, a pulse duration of 5 ns, and a pulse energy of 60 mJ. The laser beam was focused slightly into the sample surface using a lens of 5 cm focal length to generate the plasma. The laser spot on the target surface was estimated to be 400 μm in diameter, which resulted in a laser fluence of 47.3 J/cm^2 and a maximum irradiance of 9.5 GW/cm^2, without considering the absorption by the plasma. The pellet as well as the aluminum target was mounted on a motorized 3-D micrometric displacement stages in order to provide a fresh sample surface during the spectral accumulation for each laser shot. The lens-to-sample distance was maintained constant during the detection using a monitoring system combining a laser pointer in oblique incidence on the target surface and a CCD camera. The plasma emission was collimated by a

Table 1
NaCl percentage in composite powders and the corresponding Cl concentration in these powders.

Percentage of NaCl (% in weight)	Concentration of Cl (% in weight)		
	NaCl + MgSO$_4$	NaCl + KBr	NaCl + Na$_2$CO$_3$
8.3	5.1	5.1	-
16.7	10.1	10.1	-
25.0	15.2	15.2	15.2
33.3	20.2	20.2	20.2
50.0	30.4	30.4	30.4
66.7	40.5	40.5	-
83.4	50.6	50.6	50.6
100.0	60.7	60.7	-