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Chemometrics and theoretical approaches for evaluation of matrix effect in laser ablation and ionization of metal samples

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ABSTRACT

Matrix effect is one of the shortcomings of direct solid analysis which makes the quantitative analysis a great challenge. All of the physical properties of solid and laser parameters could make contributions to the matrix effect. For better understanding and controlling laser ablation process, it is of great importance to investigate how and to what extent these factors would affect matrix effect, through simulation and chemometrics works. In this study, twenty-three solid standards of six types of metal matrices were analyzed, including aluminum, copper, iron, nickel, tungsten and zinc. The influence of laser pulse duration was investigated by applying nanosecond (ns) and femtosecond (fs) lasers to a buffer-gas-assisted ionization source coupled with an orthogonal time-of-flight mass spectrometer. After relative sensitivity coefficients (RSCs) of each element in different matrices were calculated, they were combined with the physical property values of the matrices to form a dataset which was analyzed by the chemometrics tool of orthogonal partial least-squares (OPLSs). The S-plot result reveals that thermal properties of solid play vital roles in the matrix effect induced by ns-laser ablation, while fs-laser could significantly reduce the thermal effect. Additionally, a theoretical model was figured out to simulate the RSCs by combining the laser–solid interaction process and plasma expansion process. The model prediction shows a relatively close agreement with experimental result, revealing that the model could reasonably explain the process of matrix effect.

1. Introduction

Laser ablation (LA) is a convenient and versatile technique which has been applied in various fields, such as chemical analysis [1–3], micromachining [4,5], nanoparticle manufacturing [6], pulsed laser deposition [7–9] and so on. Based on LA, many excellent analytical techniques have been developed, including Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) [10], Laser Microprobe Mass Spectrometry (LMMS) [11], Laser Induced Breakdown Spectrometry (LIBS) [12], Matrix-assisted Laser Desorption/Ionization Spectrometry (MALDI) [13] and Laser Ionization Mass Spectrometry (LIMS) [14]. By utilizing LA, time-consuming and complicated sample pretreatment procedures can be eliminated, and less contamination is supposed to be introduced into sample in comparison with solution methods [15]. Moreover, little amount of sample is needed [16]. Despite its wide range of application, it suffers from several shortcomings, including limitation in spatial and depth resolution induced by melting and resolidification, fractional evaporation, matrix effect and so on [17,18]. Among them, matrix effect was claimed to be one of the most intractable drawbacks [19].

Matrix effect is the matrix dependence of analytical signal. It was discussed by Whitehead et al. for the first time in 1968 and was claimed to be originated from vaporization process [20]. As more and more investigations went on, it was revealed that laser–solid interaction process could also make an impact on matrix effect, and all of the solid physical properties and laser parameters would make contributions to it [21–23]. As to solids, influencing factors may be crystal structure, laser absorption efficiency, melting point, boiling point and so on; while for laser, influencing parameters include laser pulse duration, wavelength, laser irradiance and incident angle [24–26].

It was claimed that the utilization of ultra-short pulsed laser would be helpful to minimize matrix effect compared to that of long-duration laser [18,27,28]. Many studies have been reported about the matrix effect during laser ablation process by comparing nanosecond (ns) laser with femtosecond (fs) laser [12,21,29–31]. One of the reasons may be that the high irradiance and short duration of fs-laser could extensively minimize heating of the lattice [32,33].

Since matrix effect makes direct quantitative analysis of solid a great challenge, it is indispensable to investigate how and to what extent the factors involved in laser–solid interaction would influence matrix effect. In the present study, twenty-three solid standards of six types of metal

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matrices (samples that possess a common major component element belong to the same type of metal matrix), including aluminum, copper, iron, nickel, tungsten, zinc, were employed to study matrix effect by applying ns- and fs-lasers to a buffer-gas-assisted ionization source coupled with an orthogonal time-of-flight mass spectrometer. The relative sensitivity coefficients (RSCs) of the elements in different matrices were measured experimentally. By combining the RSCs values with the physical property values of the matrices, the newly formed datasets were analyzed by the chemometrics tool of orthogonal partial least-squares (OPLSs). The S-plot result of the statistical model was further analyzed to figure out the vital factors that contribute to matrix effect under different laser pulse durations. Moreover, a theoretical model was worked out by combining the laser–solid interaction and plasma expansion processes to predict the RSCs involved in the study. An acceptable agreement between the experimental and theoretical outcomes may indicate that the model could reasonably explain the process of matrix effect.

2. Experimental

2.1. Instrumentation

The experiments were done within a buffer-gas-assisted high-irradiance laser ionization orthogonal time-of-flight mass spectrometer (LI-O-TOFMS) [34]. An fs-laser (S-pulse HP, Amplitude System, France) with wavelength of 1030 nm and pulse width of 500 fs and a ns Nd:YAG laser (NL303G, Ekspla) with wavelength of 1064 nm and pulse duration of 4.4 ns were employed in the same conditions. The laser energies could be adjusted through a continuous laser beam splitter (ABSO-6.35-1030, CVI Melles Griot). Both laser beams were focused on the samples via the same optical apparatus, and the ablated spot diameter was measured to be 40 μm. The background gas in the ionization source was high-purity helium whose pressure was 800 Pa. Other ionization parameters were pre-optimized, as shown in Table 1. All the electronic parameters of the time-of-flight mass spectrometry were optimized and adjusted to be the same for both lasers. The interference of polyatomic ions was minimized by applying the pulse train data acquisition mode with pulse width of 3 μs and pulse frequency of 40 kHz [35]. In order to collect the ion packets of all the elements, a digital storage oscilloscope was utilized with a recording length of 500 μs.

2.2. Sample preparation

In this study, twenty-three solid standards of six types of metal matrices were involved which were obtained from either Chinese National Standards Centre (GBW series) or National Institute of Standards and Technology (SRM series). The six types of metal matrices were as follows: aluminum (GBWE921b, GBWE922b, GBWE923b, GBWE925b and GBWE926a), copper (SRM 1112, SRM 1114, SRM 1116 and SRM 1117), iron (SRM 1762, SRM 1264a, GBW01396, GBW01398, GBW01399, GBW01400, GSBH-40115-2, GSBH-40115-5 and GSBH-40115-6), nickel (SRM 1244 and SRM 1248), tungsten (GBWQB200335 and GBWQB292436) and zinc (SRM 629). All of these bulk samples were cut into discs of 1.5 mm thickness and 6 mm diameter and polished before being loaded into the ionization source.

Table 1
Ionization parameters of ns- and fs-LI-O-TOFMS in the study.

Ionization parameters	ns-Laser	fs-Laser
Laser wavelength (nm)	1064	1030
Laser pulse duration	4.4 ns	500 fs
Laser pulse frequency (Hz)	10	10
Laser irradiance ($W \cdot cm^{-2}$)	9×10^{10}	9×10^{13}
Laser incident angle (deg)	0	0
Aperture diameter (mm)	4	4
Spot diameter (μm)	40	40
Source pressure (Pa)	800	800
Shots per sample	50	50

The term relative sensitivity coefficient (RSC) was utilized to evaluate the matrix effect [15]. Owning to the fact that iron could be detected in all the solid standards, it was selected as the reference element to calculate the RSCs of other elements:

$$RSC_i = (I_i/C_i)/(I_{Fe}/c_{Fe})$$

where I_i and I_{Fe} are the signal intensities of a particular element and iron, while C_i and c_{Fe} are the concentrations of them. After that, the RSCs of a specific element in different solid standards that belong to the same matrix were averaged.

2.3. Chemometrics works

After the RSCs of a particular element in different matrices were calculated, they were combined with the solid property values to form a new dataset, including atom number density (N), absorption coefficient (α), electron work function (Φ), first ionization potential (IP^1), fusion heat (ΔH_{fus}), vaporization heat (ΔH_{vap}), melting point (T_m), boiling point (T_b), Mohs hardness (*Mohs*), specific heat capacity (C_p) and coefficient of heat conduction (k). The values of the above physical properties of the six types of metal matrices were obtained from ref. [36] and listed in Table 2. The newly formed dataset was introduced to SIMCA-P v12.0 (Umetrics AB, Sweden) to perform orthogonal partial least-square (OPLS) analysis. The RSCs were regarded as Y matrix and the physical properties were regarded as variables in X matrix. The RSCs and variables were centered and scaled to "Unit Variance" [37]. The OPLS models with $Q^2{}_{cum}$ larger than 0.5 were deemed to have good prediction abilities and were adopted to be further analyzed [38]. The S-plot results of these selected models were picked out, and the farther the variables stay away from the origin in the S-plot, the more importantly they contribute to the model [39]. Hence, for each variable its distances to the origin in the S-plots of different models were averaged to evaluate its importance. Finally, the absolute value of the averaged distance of each variance was adopted for the purpose of better comparison, and a higher value represents that the variable contributes more to the model.

3. Theoretical model

When a laser beam is focused on the surface of a solid to an energy density above the damage threshold of the solid, the laser energy will be absorbed and reflected. As a result, the solid surface layer will be instantly heated to a high temperature. By solving the one

Table 2
Physical properties of the six types of metal matrices involved in this study. The data are obtained from ref. [36].

	Al	Cu	Fe	Ni	W	Zn
N (10^{23} cm^{-3})	0.60	0.85	0.85	0.91	0.63	0.66
α (10^5 cm^{-1})	12.21	10.34	5.19	6.22	4.44	4.01
Φ (eV)	4.12	4.76	4.74	5.22	4.55	3.63
IP^1 (eV)	5.99	7.73	7.90	7.64	7.86	9.39
ΔH_{fus} ($KJ \cdot mol^{-1}$)	10.71	13.04	13.76	17.48	35.30	7.32
ΔH_{vap} ($KJ \cdot mol^{-1}$)	293.4	300.3	349.6	370.4	824.0	115.3
T_m (K)	934	1356	1808	1728	3660	692.73
T_b (K)	2792	2835	3023	3186	5828	1180
Mohs	2.75	3	4.5	4	7.5	2.5
C_v ($J \cdot cm^{-3} \cdot K^{-1}$)	2.42	3.45	3.53	3.93	2.55	2.77
C_m ($J \cdot mol^{-1} \cdot K^{-1}$)	24.20	24.44	25.10	26.07	24.27	25.39
k ($W \cdot cm^{-1} \cdot K^{-1}$)	2.37	4.01	0.80	0.91	1.74	1.16
A	0.05	0.02	0.36	0.28	0.41	0.44