Quantitative analyses of glass via laser-induced breakdown spectroscopy in argon

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ABSTRACT

We demonstrate that elemental analysis of glass with a measurement precision of about 10% can be performed via calibration-free laser-induced breakdown spectroscopy. Therefore, plasma emission spectra recorded during ultraviolet laser ablation of different glasses are compared to the spectral radiance computed for a plasma in local thermodynamic equilibrium. Using an iterative calculation algorithm, we deduce the relative elemental fractions and the plasma properties from the best agreement between measured and computed spectra. The measurement method is validated in two ways. First, the LIBS measurements are performed on fused silica composed of more than 99.9% of SiO_2. Second, the oxygen fractions measured for heavy flint and barite crown glasses are compared to the values expected from the glass composing oxides. The measured compositions are furthermore compared with those obtained by X-ray photoelectron spectroscopy and energy-dispersive X-ray spectroscopy. It is shown that accurate LIBS analyses require spectra recording with short enough delays between laser pulse and detector gate, when the electron density is larger than 10^{17} cm^{-3}. The results show that laser-induced breakdown spectroscopy based on accurate plasma modeling is suitable for elemental analysis of complex materials such as glasses, with an analytical performance comparable or even better than that obtained with standard techniques.

1. Introduction

Glasses are complex materials with a wide variety of chemical compositions [1]. Typically composed of a large number of elements, strong variations of minor and major element concentrations characterize glasses, making their analytical investigations particularly difficult [2]. Standard techniques of glass analysis are energy-dispersive X-ray (EDX) spectroscopy, X-ray fluorescence (XRF) spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) [3–5]. Compared to analysis of alloys, the analytical performance on glasses is typically much lower [6]. Due to the large dispersion of glass compositions, standard samples are generally unavailable and the measurement accuracy is consequently often lower than 10 or 20% [7].

In the last decade, glass analysis via laser-induced breakdown spectroscopy (LIBS) has attracted growing interest. LIBS analyses of various glasses and glassy materials have been investigated in different fields of applications, such as quality control in industrial production [8], material recycling [9,10], art conservation [4,11,12], archaeometry [3] forensic research [13–15] and nuclear waste management [2,16,17]. LIBS was also applied to characterize minor element concentrations in optical glasses [18]. Most of these applications do not require high measurement accuracy, and LIBS takes advantage over the standard techniques because of its unique features: measurements can be performed in real-time, in situ, they are almost non-destructible and do not require particular sample preparation [19].

The main objective of analyzing historical glasses, or glass splinters from a crime scene, is the identification of the glass origin. Thus, the measured chemical composition is compared to a database to classify the glass type. Here, LIBS analyses were mostly performed using calibration curves generated via concentration measurements with the standard techniques of glass analyses [4,5,13]. In some particular applications, standard samples were available and used to calibrate the LIBS measurements [3,20]. The use of standards is efficient when the glass matrix is known and minor or trace elements have to be measured [16,17]. Some authors prepared the standard samples themselves by synthesizing the glass composing oxides with well defined composition ratios [10].

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Despite the particular difficulties of calibrating the LIBS measurements, only a few authors report on calibration-free laser-induced breakdown spectroscopy (CF-LIBS) analysis of glass. To improve the measurement accuracy, Panne et al. [8] performed calculations based on local thermodynamic equilibrium (LTE) to correct calibration curves. Burakov et al. [6] applied the standard CF-LIBS method [21] to analyze optical glasses. The authors report on difficulties to measure the concentrations of alkali elements for which only strongly self-absorbed resonance lines are observable. In a later work, Burakov and Raikov [22] performed CF-LIBS analysis of glasses using an improved experimental arrangement. However, the spectra recorded without time-resolution were not appropriate for CF-LIBS as the plasma temperature and electron density decrease during the time-evolution of the expanding plasma [23]. The measurement accuracy remained therefore moderate.

Among the numerous LIBS analyses of glass, none of the former investigations include the measurement of the oxygen concentration. Usually, LIBS is performed in ambient air and oxygen is ignored as its quantification is difficult due to the contribution of air to the plasma emission. Thus, the relative fractions of silicon and mineral elements are measured and the oxygen content is assumed to equal the value expected from the stoichiometric contribution of the glass composing oxides [2,3,22]. The latter assumption is valid for most glasses [23]. However, the explicit measurement of the oxygen content is of interest. On one hand, it is useful to compare the measured oxygen fraction with the value expected from the stoichiometric contribution of the glass composing oxides in order to verify the measurement result and to evaluate its accuracy [24]. On the other hand, the reliable determination of the oxygen content within optical glass networks is crucial for a number of applications such as glass recycling [10] or the novel field of atmospheric pressure plasma-induced modification of optical properties based on chemical reduction of silicon dioxide to silicon suboxide [25,26]. Furthermore, the measurement of oxygen is of interest from the fundamental point of view. Oxygen neutral atoms and ions are characterized by large maximum energy gaps between excitation levels. The Boltzmann equilibrium distribution of excitation level number densities is therefore hardly established for the most abundant oxygen species in the plasma and calibration-free LIBS analysis based on LTE modeling may fail [27]. It is noted that CF-LIBS measurements generally ignore elements composing organic matrices. For example, the analyses of organic materials such as hair [28] or food [29,30] via calibration-free LIBS were performed by measuring the relative fractions of minerals only.

In this context, the present work is motivated by two main objectives: (i) the validation of calibration-free LIBS measurements that include oxygen and (ii) the development of a LIBS measurement procedure for quantitative standard-less analyses of glasses. The present investigations were therefore performed under argon. We apply a calibration-free LIBS measurement procedure based on the calculation of the spectral radiance of a plasma in LTE. The method takes into account self-absorption and may consider temperature and density gradients [31,32]. The calculations are self-consistent and do not use any freely adjustable parameters. They take advantage of the calculation of the precise spectral line shapes that, compared to the measured line profiles, present an efficient feedback for measurement control.

The paper is organized as follows: The calculation algorithm of the LIBS measurement procedure is presented in Section 2 while the experimental details are given in Section 3. The results presented in Section 4 are organized in 3 sub-sections. First, the laser ablation characteristics and the time evolution of the plasma properties are analyzed, followed by a sub-section dedicated to the spectroscopic database. In the third sub-section, the LIBS measurement procedure is validated on fused silica and applied to the analyses of heavy flint and barite crown glasses.

2. Plasma modeling and calculation algorithm

2.1. Calculation of plasma composition

The composition of a plasma in LTE composed of N elements depends on $N + 1$ parameters: the temperature and the atomic number densities of the N elements. In the temperature range of interest the formation of polyatomic molecules can be neglected and the atomic number density of an element x is given by

$$n_x = \sum_{z=0}^{z_{max}} n_x^z + 2\sum_{z=0}^{1} n_{x_2}^z + \sum_{z=0}^{1} n_{xy}^z \quad , x, y = 1, \ldots, N. \tag{1}$$

Here, n_x^z and $n_{x_2}^z$ are the number densities of atomic and diatomic species of charge z, respectively, and n_{xy}^z is the number densities of diatomic species of charge z formed by chemical reactions with element y. The sum includes all species of significant abundance up to the maximum charge z_{max}. Thus, for given values of temperature and atomic number densities n_x of the N elements, the number densities of all plasma species can be calculated by numerically solving the equations that govern the LTE plasma [33]. Once the number densities of all species are calculated, the electron density is obtained from the equation of charge neutrality by summing the densities of all charged particles,

$$n_e = \sum_{x=1}^{N} \sum_{z=1}^{z_{max}} z\, n_x^z. \tag{2}$$

For practical applications, the atomic number densities n_x of the N elements can be replaced by an equivalent set of input parameters: the electron density and the relative atomic fractions of $N - 1$ elements. The relative atomic fraction of each element C_x is obtained by dividing its atomic number density by the sum over the atomic number densities of all elements, $n_{tot} = \sum_{x=1}^{N} n_x$, according to:

$$C_x = n_x / n_{tot}. \tag{3}$$

A useful parameter for the characterization of the plasma is the kinetic pressure P. According to Dalton's law, P is the sum over the partial pressures associated to the different plasma species:

$$P = \left[n_e + \sum_{x=1}^{N} \sum_{z=0}^{z_{max}} \left(n_x^z + n_{x_2}^z + \sum_{y=1}^{N} n_{xy}^z \right) \right] kT - \Delta P_D. \tag{4}$$

Here, ΔP_D is the Debye correction that accounts for the potential energy of charged species in the plasma.

Thus, for given values of temperature, electron density and relative fractions of elements, the plasma composition is fully defined. The calculation is performed using an iterative loop. First, the plasma composition is calculated for given values of T and the $N - 1$ atomic fractions assuming a total number density or pressure. Then, the electron density is determined from the equation of neutrality [Eq. (2)] and compared to the n_e input value. The total number density or pressure is adjusted until the electron density obtained from the neutrality equation equals the n_e input value [33].

The number densities of the most abundant species computed for a silicon-dioxide plasma in LTE are presented in Fig. 1 as functions of temperature. In Fig. 1(a), the pressure was maintained constant to 1.8×10^5 Pa. This value was deduced from the spectra recorded for $t = 500$ ns during laser ablation of fused silica (see Section 4.1.2). In Fig. 1(b), we assumed the pressure dependence $P(T)$ (black curve) that matches the pressure evolution deduced from the measurements in the temperature range from 8800 to 16,400 K [Fig. 7(c)]. In addition to the number densities of plasma species, the upper level