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Correlation between laser-induced breakdown spectroscopy signal and moisture content

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ABSTRACT

The possibility of using Laser-Induced Breakdown Spectroscopy (LIBS) for measuring the moisture content of fresh food samples is studied. The normalized line emission of oxygen is highly correlated with the moisture content of the sample, cheese in our case, and can be used as a moisture marker in situations where oxygen interference from the matrix is not a critical issue. The linear correlation between the oxygen signal and the moisture content in the sample shows great potential for using LIBS as an alternative spectroscopic method for moisture monitoring.

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) [1,2] is an elemental spectroscopic technique considered a serious candidate to solve analytical issues linked to time consumption and in-situ operation. As a consequence, it becomes an attractive option for applications such as material analysis [3], quality control [4], forensic science [5], homeland security [6], and environmental safety monitoring [7]. In LIBS, laser pulses are focused on the sample surface and create micro-plasmas. The spectrum of the plasma emission provides information about the elemental composition of the sample. The major advantages of using LIBS for these applications are: (i) the minimal sample preparation required, (ii) its potential for rapid analysis, (iii) its advantage of providing in-situ examination, (iv) concurrent multi-element analysis and (v) the high spatial resolution that is produced. LIBS is an all-optical, non-contact detection technique (laser power delivery and optical emission spectroscopy), not requiring system or personal contact with the sample, therefore lessening dramatically external contamination of the analysis.

A diagnosis that requires such advantages is the measurement of moisture content. Moisture content is one of the most important factors in food product quality, as water-related physical or chemical reactions during or after the manufacturing process affect the quality and stability of the food product. In addition, the moisture level of the food affects the choice of food packaging and shipping methods [8,9]. Space exploration is also interested in such diagnostics. A criterion for habitability of some planets is the presence of liquid water. Thus, the detection of water-formed materials and hydrated minerals is of importance [10].

Spectroscopic techniques such as near-infrared spectroscopy and microwave attenuation [4] are traditionally used to measure water content in samples. However, infrared spectroscopy requires preparation of solid samples prior to analysis, and spectral interference and calibration error can lower the accuracy. Microwave attenuation is based on the measurement of the modification of the microwave propagation in the sample due to its water content. Although this technique is often used in industry, the accuracy of the results depends on material properties such as density and temperature.

LIBS can be an alternative for moisture quantification, since atomic emission from hydrogen and oxygen as well as molecular emission from OH radicals can be used as proxy indicators of water [11]. However, early studies mentioned that the water concentration negatively affects the LIBS spectra [12], and a systematic study on moisture monitoring using LIBS has never been reported. The work presented here examines the feasibility of LIBS as a tool for moisture measurement. The experimental results showed that the LIBS spectrum could be well correlated to the water content in cheese samples. After optimization of the laser energy to minimize the oxygen influence from the air, the oxygen emission lines normalized by the CN emission as an internal standard were used as an indicator of the cheese sample moisture. By measuring the intensity change of the normalized oxygen emission lines as a function of sample dryness measured by the mass loss of the sample, this work shows that LIBS is a candidate for quantitative moisture monitoring in fresh samples.

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2. Experimental

2.1. LIBS setup

A schematic diagram of the LIBS moisture monitoring system is shown in Fig. 1. A 10 Hz Nd:YAG laser (Brilliant, Quantel) with 5 ns pulse duration at 532 nm (frequency doubled by a KD*P crystal (SHG) from 1064 nm) was focused with a 36 mm lens (L1) to create plasmas on the sample. A laser light valve comprising a combination of a half-wave plate and a cube polarizer controlled the laser energy at the sample. The beam diameter was about 240 μm on the sample surface, measured via a knife-edge scan. The sample was mounted vertically and clamped to an XYZ automated translation stage (PT3-Z8, Thorlabs) and was moved after each spectrum was taken, to ensure a clean surface. Two lenses (L2 and L3) with focal length 35 mm (front) and 60 mm (back) were used to collect the plasma emission and match the numerical aperture of the 0.22 NA fiber that was connected to the Czerny-Turner spectrometer (2300i, Acton) with a 1800 l/mm grating. A 512×512 pixels iCCD camera (PIMAX 2, Princeton Instruments) was used for recording the spectrum, providing a pixel resolution of 0.04 nm in the vicinity of 770 nm. The acquisition window was optimized for the oxygen lines and the CN band emission simultaneously. The camera was triggered 100 ns after the laser pulse. The short delay was aimed to catch the short-lived O lines and remove the most intense continuum emission. The exposure time (gate width) was 10 μs to capture the intensity of the long lasting CN emission. Each spectrum was the result of 10 accumulations. Ten spectra, taken at different positions on the sample, were used for statistical analysis.

2.2. Sample preparation

Yellow American cheese purchased at the supermarket was used as the sample in this study. The original cheese slices were 8.7 cm by 8.5 cm by 2.4 mm thick. One slice was cut into 2×1 cm pieces which made the sample easier to handle and allowed the same sample to be used for the entire study. The small pieces were placed on weighed microscope glass slides. With a little pressure by a stainless steel ruler, the cheese remained on the glass for the duration of the experiment. No other sample preparation was made. Each sample set included a small piece of cheese and the glass slide, and the sample sets were weighed before taking the LIBS data using an electronic scale with 0.1 mg precision. The weight of the sample was tracked by subtracting the weight of the glass slide. The loss of weight of the cheese was considered to be mainly due to water loss [13]. Therefore, the weight of the cheese sample could be linked with the water concentration in the sample. A formula for calculating the moisture ξ at certain time t in the cheese is

$$\xi(t) = \frac{m(t) - m(\infty)}{m(0)} \times 100 \quad (1)$$

where $m(t)$, $m(\infty)$ and $m(0)$ are respectively the mass of the cheese at time t, the mass when it is completely dry (stayed in air for more than one day), and the mass when the cheese is just out of the package. Cheese samples were left in a laboratory environment and dried naturally in air between measurements.

3. Results and discussion

3.1. Emission spectrum and choice of analytical spectral lines

The emission from the hydrogen Balmer H_α line at 656 nm and the oxygen ($2s^22p^3(4S°)3s–2s^22p^3(4S°)3p$ triplet around 777 nm are shown in Fig. 2. The oxygen emission was considered to be more correlated to the water content in the cheese sample than the hydrogen line emission. Both water and organic molecules are rich in hydrogen. However, one third of the atoms in water are oxygen, while in organic molecules such as protein and fat, which are the majority constituents in cheese besides water, oxygen atoms are present in a much lower proportion. Therefore, the change of moisture in the cheese sample would affect the oxygen intensity more than the hydrogen intensity. Some factors can affect the oxygen line intensity, such as the laser energy fluctuation and surface roughness differences that can change the ablation efficiency from shot to shot. It is also easier to ablate drier samples as less energy is consumed in vaporizing the water. In order to obtain a more stable oxygen intensity that reflects the oxygen concentration, a normalization procedure was applied to reduce the shot-to-shot signal fluctuation [14,15]. The signal from the cyanide radical CN at 774 nm (in the second diffraction order due to the 1–1 transition of the Violet system at 387.14 nm) was used as an internal standard for three reasons.

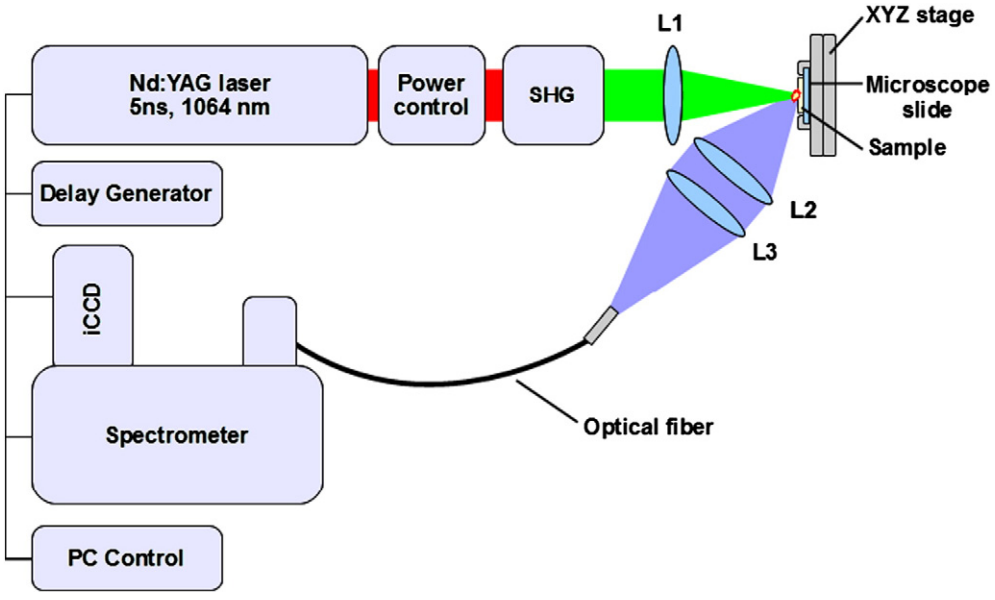

Fig. 1. Setup for LIBS moisture monitoring system.

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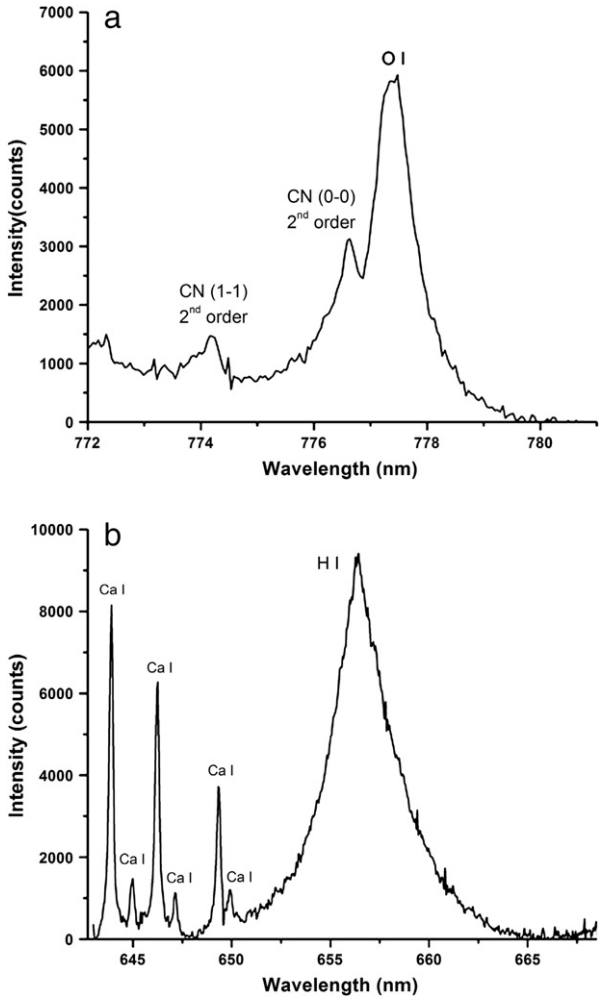

Fig. 2. Spectra of (a) oxygen and CN emission and (b) hydrogen from a cheese sample.

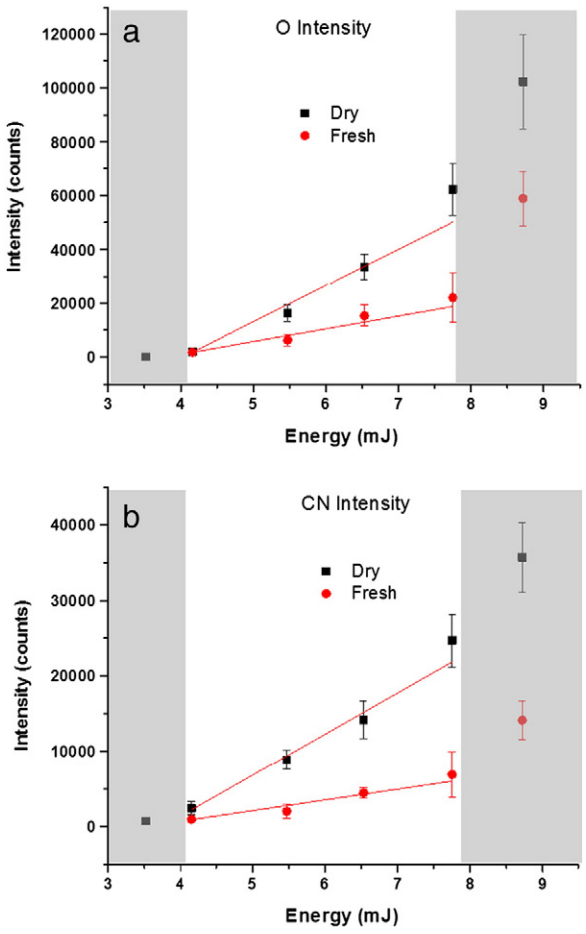

Fig. 3. Oxygen (a) and CN (b) intensity as a function of laser energy for fresh (disk symbol) and dry (square symbol) cheese samples. Shaded regions indicate either too low or too high laser energy used for moisture monitoring. Error bars correspond to 1 standard deviation over 10 measurements.

First, it is closely related to the carbon content in the plasma which reflects the ablation of the cheese sample. Regardless of whether the CN radicals were native to the sample or formed in the plasma by reaction between carbon and nitrogen species [16,17], they can be used as an indicator of the carbon content of the sample. Second, with the second order at 774 nm, both oxygen and CN signals can be detected at the same time and within the same spectral window. Third, other elements in the same spectral window such as potassium showed a less stable signal in this study compared with the CN intensity. Hence the CN signal was chosen as the ideal internal standard. After baseline correction, the oxygen intensity at 777 nm was then divided by the CN peak intensity at 774 nm to generate normalized oxygen intensity.

3.2. Optimization of the laser parameters

The laser energy used in this study was optimized for maximization of the signal as well as minimization of the influence from air before acquisition of the data. The major concern was that both the CN and the oxygen emission could be influenced by the air surrounding the plasma and the sample. The intensity of the oxygen and CN emission lines from both fresh and dry cheese samples are plotted as a function of laser energy in Fig. 3. Three regimes were noticed. At low energies, close to the breakdown threshold, the line intensities were low, and atomization might not be complete which could affect the stoichiometry of the plasma [18]. On the other hand, for energy above approximately 8 mJ, a clear deviation from the linear trend could be observed, which indicated a stronger influence from the air on the plasma emission. This was due to the high laser energy causing air breakdown and excitation of the surrounding air background which increased the oxygen intensity from air. Hence, laser energy

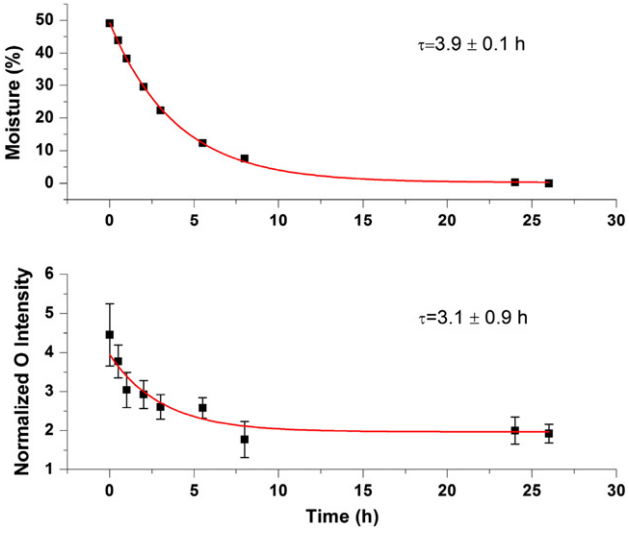

Fig. 4. Decay of humidity and the normalized oxygen intensity of cheese samples. The error bars represent 1 standard deviation over 10 measurements.

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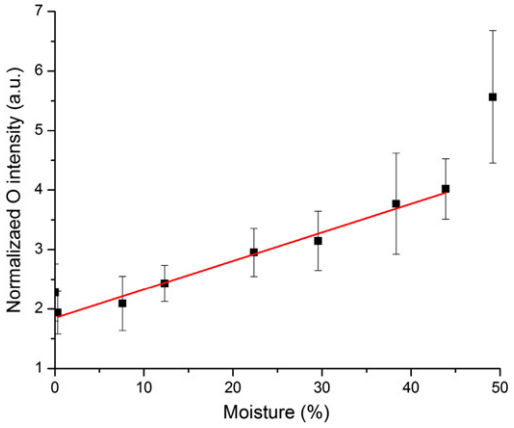

Fig. 5. Normalized LIBS signal of oxygen as a function of the moisture of the cheese sample. The error bars represent 1 standard deviation. The straight line is a linear fit of the data in the range of moisture content [0.5%–45%].

of 7.5 mJ was considered to give representative results for moisture measurements.

3.3. Correlation between moisture and LIBS signal

The experiment was conducted in a laboratory temperature of 23 °C ± 0.5 °C with 49% ± 1% air humidity. Fig. 4 shows the normalized oxygen intensity plotted as a function of time, and compared with the moisture content calculated following Eq. (1). The results were modeled by an exponential decay in the form of $y = A\exp(-t/\tau) + y_0$ and fitted as shown in Fig. 4. The normalized oxygen intensity decays accordingly with the moisture content with comparable decay times of respectively 3.9 ± 0.1 h and 3.1 ± 0.9 h.

This similarity offers the potential to retrieve the moisture information from the LIBS signal as it is shown in Fig. 5. The correlation between the normalized LIBS signal from oxygen and the moisture in the sample was $R^2 = 0.89$ (R^2 being the adjusted coefficient of determination of the linear model) for values of moisture content between 0 and 50%. The extreme values show a deviation from the linear fit, indicating some possible limitations at these values. If the domain of validity of the technique is restricted to 0.5% to 45%, the linear fit (straight line in Fig. 5) shows a correlation $R^2 = 0.99$.

Although the LIBS signal and the moisture content are highly correlated, the error bars show that the data was dispersed. This could be due to different factors. First, the drying of the sample was spatially inhomogeneous. The areas closer to the edges dried more rapidly, thus, the analysis on the full sample area took into account different moisture levels. Furthermore, the evaporation of water can also be inhomogeneous on the scale of the laser spot (240 μm diameter). Another factor was the contribution of oxygen in the sample that was not in the form of water. Since it was an intrinsic part of the sample, it was impossible to remove its influence without extensive sample preparation. However, such influence is relatively low due to the low oxygen percentage in other types of molecules in the sample. Finally, although the laser energy was optimized to lower the influence of the air and still obtain a large signal-to-noise ratio, it was impossible to completely remove the contribution from the surrounding air.

4. Conclusion

Laser-induced breakdown spectroscopy (LIBS) has been demonstrated as a new potential technique for monitoring moisture of fresh food samples at the surface of a sample in air. This study focused on cheese and showed a correlation of $R^2 = 0.99$ between moisture content and normalized oxygen signal in the range of 0.5%–45% moisture. This new method can provide rapid and in-situ information on the moisture content of the sample, providing a solution to representative sampling in the monitoring stage of the process. Moisture measurement by LIBS shows potential for integration of laser spectroscopy techniques in the food industry, as well as in agricultural, forestry and geological applications, where information of water content is needed.

Acknowledgments

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