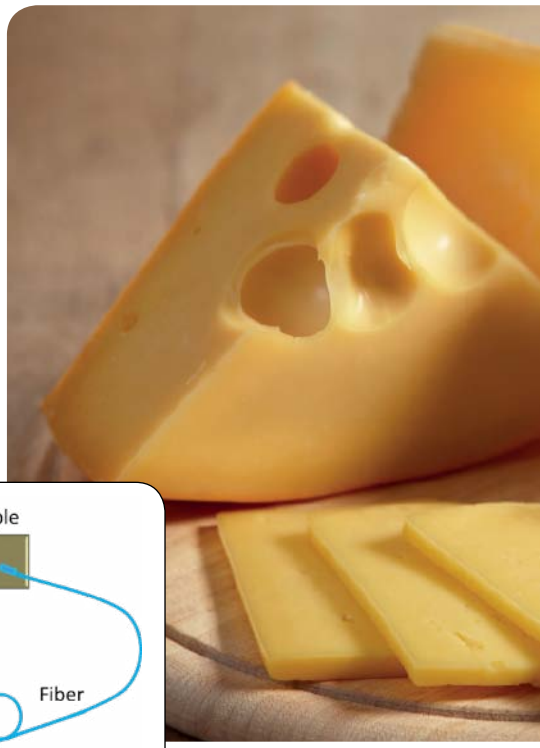
Moisture Measurement Using LIBS

Elemental and Moisture Analysis of Cheese and Other Food Products

Food inspection gathers a large amount of data from elemental (nutrients, pollutants) to molecular and biological analysis, as well as to measure physical properties such as moisture content. In this study, laser-induced breakdown spectroscopy (LIBS), in addition to the traditional elemental analysis, has shown to provide a moisture measurement within the same protocol. This additional feature of LIBS makes it an ideal candidate for an inexpensive, fast and compact on-line food inspection instrument.



Measurement Technique

LIBS is traditionally an atomic emission spectroscopy involving sampling, atomization and excitation of a sample by laser ablation. The radiative cooling of the created plasma is spectrally analyzed to provide the elemental composition of a sample of interest. In 1962, two years after the invention of the laser, Jarrell Ash Co. developed the Laser Microprobe that revolutionized the elemental microanalysis by the concept of laser ablation and cross-excitation by electrodes, which was the precursor of LIBS.

One year later, Debras-Guédon and Liodec [1] demonstrated the independent use of the laser to perform spectral analysis of a large panel of materials. Since then, LIBS still relies on this procedure and instrumentation: a laser pulse from which energy is focused on a sample to create the plasma, and optics to transport the optical emission of the plasma to the spectral analyzer, usually a spectrometer with a detector array (Fig. 1). Such a simple apparatus is attractive to researchers and end-users in many fields where direct access to the sample is difficult, the sample preparation (gas, liquid, solid or aerosols) is not possible or too complicated, or the analysis requires high speed: forensic science, homeland security, geology, on-line material characterization, space exploration, etc..

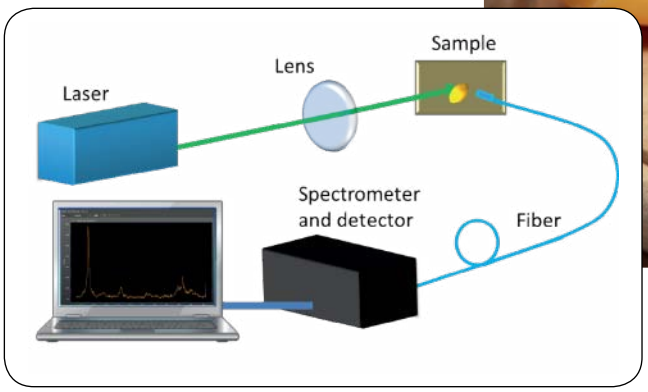


Fig. 1: Typical LIBS apparatus

Food Inspection by LIBS

The advantages of LIBS are attractive to the food industry, because of its potential implementation in the production chain for on-line analysis. Studies have been performed on dried food powders – i.e. flours, milk powder, but more interesting is the demonstration on fresh vegetables [2,3] and the ability to detect elements such as aluminum, titanium, lithium and strontium amongst many others. Nevertheless, such fresh products contain a high water concentration. As a consequence, the laser power is mainly absorbed by the water and not by the food matrix. This has always been considered as a disadvantage of LIBS.

However, since the water content does influence the LIBS signal, the change of LIBS spectra may provide information about the moisture content in the sample if a correlation between the signal and the water concentration can be established. This represents a new feature of a LIBS instrument in parallel with elemental analysis.

Moisture Measurement

Such a correlation between the moisture content of a sample and the LIBS signal was studied on cheese samples. The choice of the sample was mainly due to the importance of cheese in our diet and the critical role of moisture content in the evaluation of the cheese quality and freshness. Moisture can be measured by monitoring the mass difference between the fresh sample and the dried sample. In order to observe a large range of water concentration, the moisture content was determined continuously during drying by the following formula:

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

in which ξ is the moisture in percent at a certain time t, $m(t)$, $m(\infty)$ and $m(0)$ are the mass of the cheese at time t, the mass of the dry cheese (kept in air for more than one day), and the mass of the fresh cheese (after opening the package), respectively. After each instantaneous moisture determination, LIBS analysis was performed.

The LIBS measurements were taken with a traditional apparatus. A frequency doubled nanosecond Nd:YAG laser (Quantel Brilliant) at 532 nm was used to create the LIBS plasma. The plasma emission was collected and transmitted into a Czerny-Turner spectrometer (Princeton Instruments Acton 2300i), and the spectra were recorded on an Intensified CCD (ICCD) camera (Princeton Instruments Pi-max2). Since the plasma emission typically lasts microseconds, the gating capability of

the ICCD camera improves the signal-to-noise ratio of the LIBS spectrum.

Data Analysis

As expected, spectra from hydrogen and oxygen were found to be in relation to water content in

the cheese samples. However, these signals could also come from the organic matrix. In this particular study, emission from oxygen atoms was used as an indicator of water mainly because of their much higher proportion in water (one out of three atoms in the water molecule) than in organic molecules such as protein and fat. Meanwhile, hydrogen atoms are abundant in both water and organic molecules and as a consequence not as representative of the water content.

As mentioned above, the LIBS signal is weaker when the water content is higher, but at the same time, the oxygen emission is larger. During measurements the raw oxygen intensity showed to be randomly fluctuating. In order to compensate for the negative effect of water, the oxygen signal was internally normalized with the CN signal, representative of the carbon-based organic matrix of the sample. Once the spectral signature was found, the amount of laser energy to use for ablation, atomization and excitation was a crucial parameter to optimize.

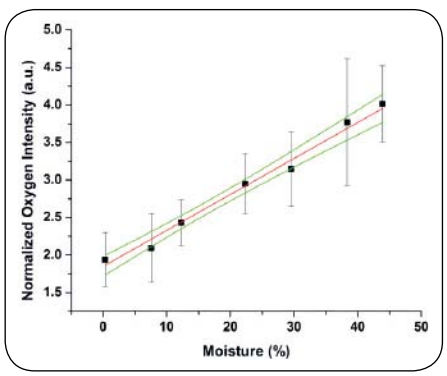


Fig. 2: Calibration curve for the moisture content using the normalized oxygen intensity. The red line is the linear fit of the experimental data (black squares), and the green curves are the confidence interval at 95 %.

If the laser irradiance is too low, the atomization can be incomplete and the signal is uncorrelated to the concentration of oxygen in the sample. On the contrary, if it is too large, the laser pulse can excite or even breakdown the air which is dominated by oxygen and nitrogen. In this situation, the O signal is no longer representative of the original sample. In this study, the optimized LIBS signal was obtained with a laser irradiance of 4 $GW \cdot cm^{-2}$.

The normalized oxygen signal as a function of time showed a similar decay with the moisture decrease in time. Both of them could be characterized by an exponential decay with a time constant of 3.9 ± 0.1 h for moisture and 3.1 ± 0.9 h for the normalized oxygen intensity. Based on this observation, a linear calibration curve was established with a correlation of 0.99 in a range of moisture content extending from 0.5 % to 45 % (Fig. 2).

Conclusion

Laser-induced breakdown spectroscopy was known as a powerful tool for elemental analysis. Additionally, our investigation of cheese samples shows that the water content of a sample can also be determined. Since the described method can be regarded as a general one, it can also be applied to other food products. This exceptional combination of molecular and elemental information is attractive to the food industry. LIBS, in a single laser pulse, can replace multiple sensors and provide information on nutrients, heavy metals and moisture content.

References

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