CHAPTER 5

Review of Laser-induced Breakdown Spectroscopy (LIBS) in Food Analysis

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5.1 Introduction

Food fraud, adulteration, quality control and traceability are serious problems in the food industry and hold great importance for customers.[1] Fraud also includes labelling and all sectors are susceptible to suffering from various kinds of fraud and quality failure.[2] The growth of the economy of the world food industry depends on the efforts of scientists, operators and producers to increase quality assurance and authenticity. This is related to the search for new and innovative analytical techniques for the food industry to provide guarantees against potential quality defects, fraud and adulteration. The most important negative effect caused by both food fraud and food alerts is the loss of consumer confidence, which has a negative impact not only on the product concerned but also the entire sector affected. Food fraud and food defence incidents are intentional acts, which result in intentional harm. In addition, fraud is motivated by obtaining economic benefit. In contrast, a food safety incident is an unintentional act with unintended harm.[3]

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However, not only adulteration and fraud have attracted the attention of researchers to apply the laser-induced breakdown spectroscopy (LIBS) technique: heavy metals and carcinogenic elements and contaminants have also been the subject of study. Regarding the latter, it is important to note that complex molecules such as chlorpyrifos can also be detected by LIBS, even though LIBS is an elemental determination technique.

In the last decade, a few reviews have appeared on the application of LIBS to specific issues related to food science. This chapter is intended to give a detailed overview of the latest advances in this technique, not only from the literature, but also from our own experience in the use of LIBS for the control of adulteration and food fraud.

5.2 Brief Introduction to the Principles of Laser-induced Breakdown Spectroscopy

LIBS involves the interaction of a high-energy focused laser pulse with the sample surface that is capable of inducing the rupture of chemical bonds and the excitation of atoms and ions in a process called ablation, which leads to the formation of a plasma.[4–9] These excited atoms and ions produce optical emission from the plasma formed that contains information about the sample, and its spectroscopic study provides useful data for qualitative and quantitative applications.[2,10,11] The LIBS technique has a broad scope due to the possibility of analysing solids, liquids and gases and being able to acquire rapidly a large amount of data. LIBS is able to perform qualitative and quantitative multielemental analyses with little or no sample preparation and no consumables, at low cost and with the possibility of online analysis, making it an important technique in the food industry. In addition, LIBS provides a multielemental spectral fingerprint of the elemental composition of the sample, which allows classification results to be obtained in real time.[1,12] A conceptual scheme of this analytical technique is shown in Figure 5.1.

A conventional LIBS instrument (Figure 5.2) consists of a laser, a spectrometer, lenses, optical fibres, an optical translation stage, an *XYZ* sample positioning stage, a data acquisition system and control between the laser and the spectrometer. The most commonly used laser is the Nd:YAG laser emitting at

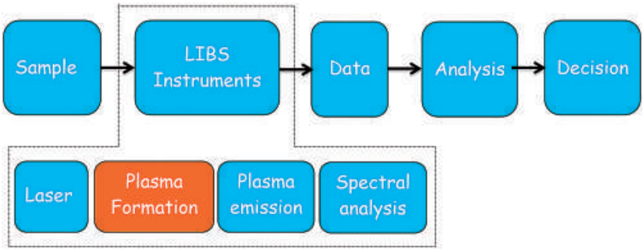

Figure 5.1 Conceptual scheme of laser-induced breakdown spectroscopy (LIBS).

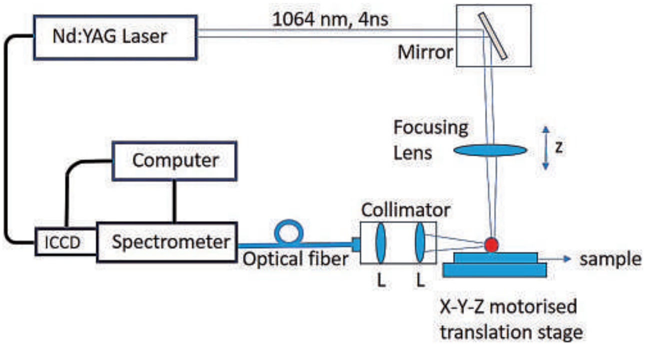

Figure 5.2 Typical configuration of the experimental setup in LIBS experiments.

the fundamental wavelength of 1064 nm, with a pulse ranging from 4 to 8 ns. However, many other lasers can be used, the fundamental requirement being to achieve a power of approximately 10^{10}–10^{12} W cm^{-2} when the laser beam is focused on the sample surface. This energy is sufficient to generate a plasma plume with a temperature of 50 000 K, inducing the dissociation of the sample into ions and excited atoms that produce the emission of continuous radiation that is not useful for sample characterization. Plasma cooling is very fast, less than 1 ms reaching temperatures between 15 000 and 20 000 K. At these temperatures, specific lines of ions and atoms are emitted, generating a unique spectrum that allows unambiguous sample identification and multielement quantification.[8,9,13]

Usually the spectrometer has the well-known Czerny–Turner configuration. The slit, number of lines per centimetre in the grating and fibre optics define the optical windows of the spectrum and its form, where the detector is also part of the optical system and defines the spectral response. The spectral range is between 190 and 900 nm, which allows almost all elements of the Periodic Table to be detected. The full range has low resolution, but it may be adequate in many cases. The solution to obtaining greater resolution is to use more than one spectrometer, as many as needed. Charge-coupled device (CCD) and intensified charge-coupled device (ICCD) detectors are now usually used to detect the light emitted by the plasma. It should be mentioned that the spectrum contains, in addition to the emission lines of the ions and excited atoms, also molecular bands and much other information that give a fingerprint of the sample that provides a lot of information, which makes this technique particularly useful for sample identification,[1,14] quality control, fraud detection and determination of the protected designation of origin (PDO).[12]

Typical LIBS spectra of olive oil, wine and goat milk are shown in Figure 5.3a, b and c, respectively. They feature the presence of several atomic emission lines, the intensity of which is proportional to the concentration of particular elements in the sample. As can be seen, the spectra are more complex than those observed with a pure metal and differ considerably

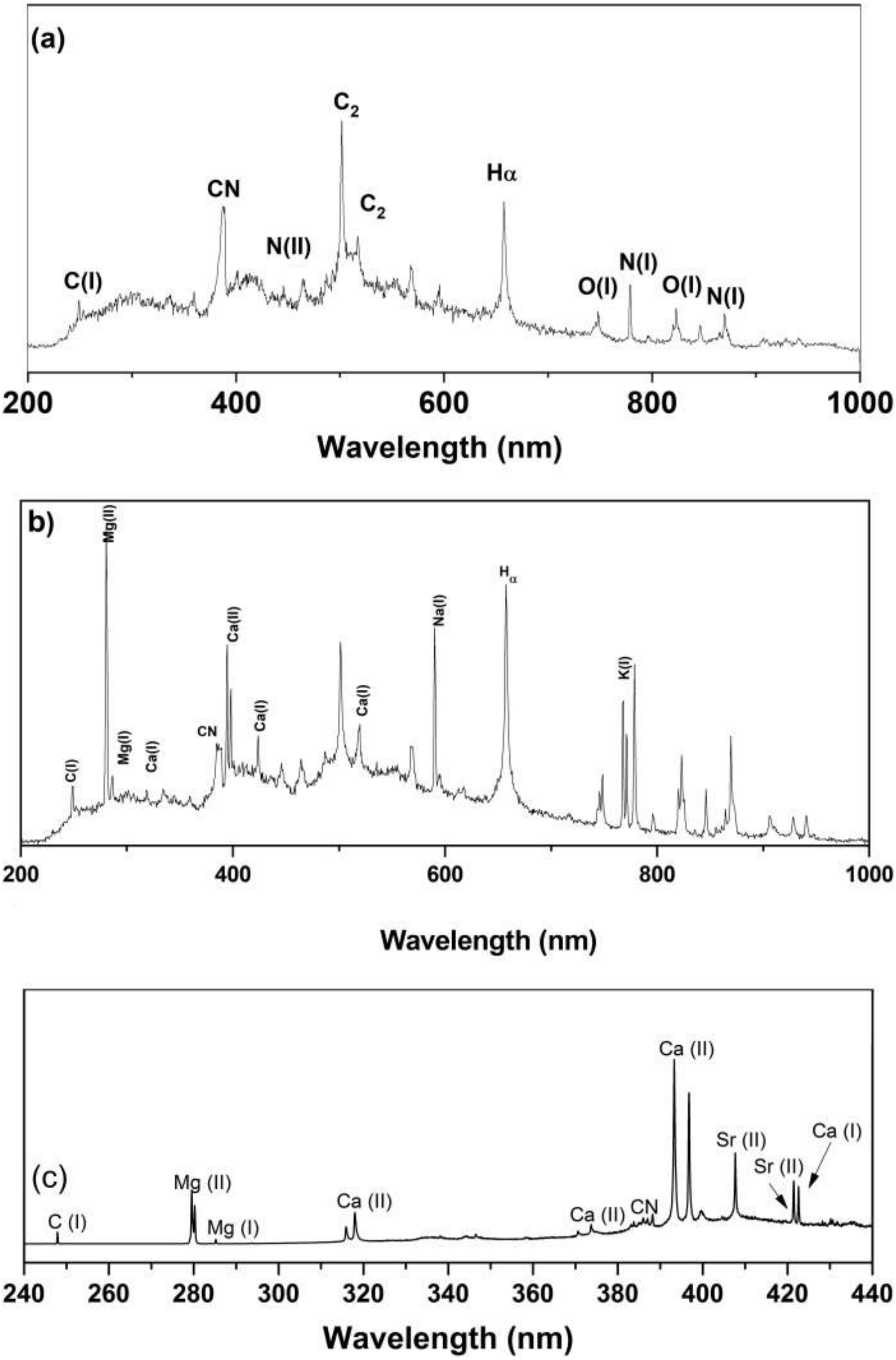

Figure 5.3 (a) Normalized LIBS single-shot spectrum of pure edible olive oil; (b) LIBS spectrum of PDO Rioja wine with the assignment of emission lines; (c) typical LIBS spectrum of a goat milk sample.

from sample to sample. This effect, known as the “matrix effect”, affects the intensity of the emission lines and is related to plasma temperature, chemical composition, hardness, reflectivity, *etc.* Under ideal conditions of local thermodynamic equilibrium (LTE), where no significant variation of temperature is assumed during the experimental measurements, a proportional relationship between intensity and the total species population can be established. However, it is important to note that as a LIBS experiment progresses, although all the experimental parameters (integration time, laser power, *etc.*) remain constant, the plasma temperature could vary owing to factors such as the matrix-dependent ionization potential of the elements. Therefore, the plasma temperature depends on sample composition and species population.[15]

These effects due to the sample matrix have been extensively studied and can now be efficiently minimized. This spectral variation between different types of samples may seem complex and difficult to interpret, but it is one of the cornerstones of the ability of LIBS to perform quality control analysis,[1,16–18] discriminate between very similar samples[12,14,19–24] and determine the geographical origin of different foodstuffs.[1,12,14] The other pillar of the technique is its high capacity to generate a large amount of multiparametric data in a short time, which allows the application of chemometric models such as neural networks for efficient discrimination. Concerning neural networks and chemometric models in general, it should be noted that they are not a “black box” and the models and results are fully interpretable. Some authors do not take into account the need to perform a correct validation of the chemometric model, which results in a lack of real applicability of the model used. It is important to note that in order to apply the outcome of a classification algorithm successfully, the resulting model needs to meet three important criteria: sensitivity, generalization and robustness. The sensitivity (internal validation) evaluates the capacity of the model to classify correctly the spectra of the samples used in calibration, whereas the generalization ability measures the percentage of correctly classified samples that were not used in the training of the model. Moreover, it is also important that the model shows robustness, that is, the ability to identify samples of an unknown class that was not included in the training step as an unknown and not belonging to another class (external validation).[5]

Although limits of detection (LOD) and limits of quantification (LOQ) are often considered to need improvement and are higher than those of other analytical techniques, they have improved appreciably in the last decade.[25,26] However, there is a mistaken notion that it is not possible to achieve LODs as low as with inductively coupled plasma (IPC) methods, and this notion has recently been proved to be wrong. For example, the LOD values for Ti and Fe obtained using LIBS were 3.11×10^{-8} and 2.86×10^{-7} ng m^{-3}, respectively, which are lower than those obtained using inductively coupled plasma optical emission spectroscopy (ICP-OES) (5.25 ng m^{-3} for Ti and 0.06 mg m^{-3} for Fe).[27]

5.3 Application of LIBS to Foods

5.3.1 Heavy Metal Detection and Quantification

Traditionally, LIBS has been used for the detection and quantification of metallic elements in metals and alloys, but its usefulness is also evident, for example, in the detection of heavy metals in food. To the best of our knowledge, the first LIBS work on the determination of metals in food dates back to 1991,[28] but reports of its application were scarce until the last decade.[28,29] This highlights the short time that the use of LIBS in food science has been under research and development. Since this earlier work, many other studies on this subject have been published. Juvé *et al.*,[30] Beldjilali *et al.*[31] and Lei *et al.*[32] determined trace elements Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Co and Mo contained in fresh vegetables, mainly root vegetables. Other alkali and alkaline earth metals (Li, Be, Rb, Sr and Ba) were also detected. The results from those studies demonstrate the potential of LIBS as an interesting tool for botanical and agricultural studies and also for food quality/safety evaluation and environmental pollution assessment and control.

In order to mimic the composition of breast milk, trace elements such as Cu, Fe and Zn are usually added. Cama-Moncunill *et al.*[33] successfully determined Cu and Fe in lactose and several infant formula premix samples using LIBS in combination with chemometric techniques including partial least-squares (PLS) regression. Dos Santos Augusto *et al.*[34] applied LIBS to the direct determination of Ca, K and Mg in commercial samples of powdered milk and solid dietary supplements. In order to minimize problems related to sample microheterogeneity and signal fluctuations during data acquisition, 12 types of normalization modes were tested. The proposed method is suitable and rapid and can be implemented for the direct determination of Ca, K and Mg in solid food samples.

The determination of Cr as a contaminant in pork was studied by Huang *et al.*[35] Fresh pork was polluted with Cr solution to create different content levels, then dried and pressed into pellets to eliminate the effect of water and improve the stability and sensitivity of LIBS. Characteristic lines Cr I 425.43 nm, Cr I 427.48 nm and Cr I 428.97 nm were used. The results showed that the model has high predicted precision and accuracy, especially when the Cr I 425.43 line is applied for calibration.

Seafood contamination is important because of its capacity to accumulate heavy metals, and has also been the subject of LIBS studies. Ji *et al.*[36] evaluated the contamination of *Tegillarca granosa* (blood clam) by Cd, Zn and Pb. An interesting mathematical processing method was used for the detection of these heavy metals involving pattern recognition analysis combined with LIBS technology. The performance in discriminating healthy *Tegillarca granosa* samples from toxic samples using three different classifiers was successful and the highest elemental discrimination accuracy of 93.3% was obtained with the random forest classifier. In another study, seven heavy metals, As, Cd, Cr, Cu, Hg, Pb and Zn, were determined in Sargassum fusiforme (*a marine brown alga*) (Figure 5.4).[37] The threshold variables (TV) method was

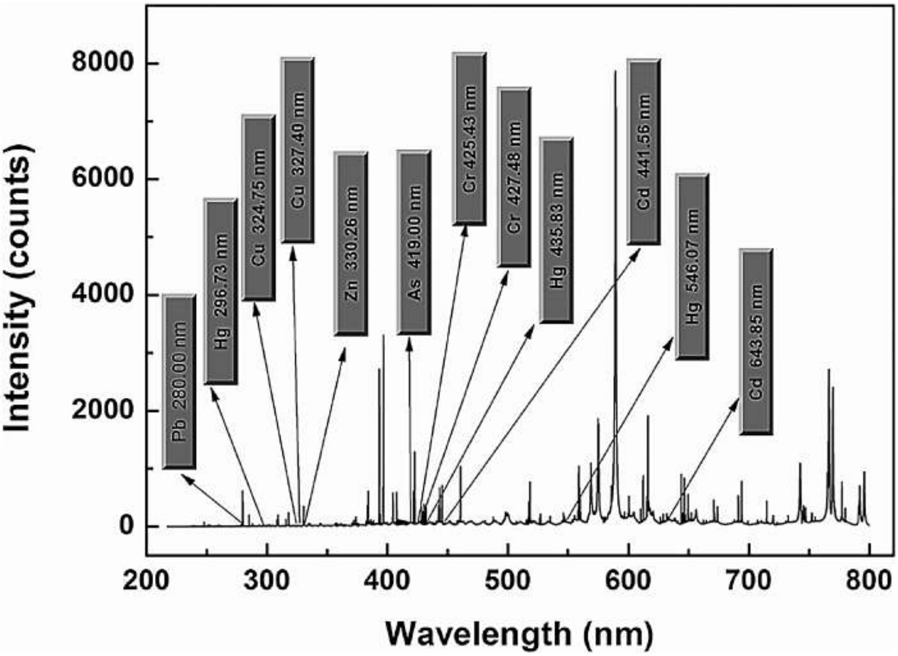

Figure 5.4 Average LIBS spectral profile of *Sargassum fusiforme*. Reproduced from ref. 37 with permission from Elsevier, Copyright 2020.

proposed to eliminate the redundant variables and establish a quantitative detection model. The principle is to set a threshold value by observing the LIBS curve in order to eliminate the variables of which the intensity is less than the set threshold value. Therefore, the purpose of TV is to search for the optimum threshold value for each analyte element.[37] The excellent results obtained demonstrated the capacity of LIBS combined with mathematical models for the measurement of heavy metals.

The determination of Ca in breakfast cereal samples was reported.[38] Inorganic nutrients such as P, K, Ca, Mg, S, Fe, Cu, Mn and Zn in wheat flour in pressed pellets were determined by Peruchi *et al.*[39] using LIBS and energy-dispersive X-ray fluorescence (EDXRF) spectrometry.

Many other studies have used LIBS to detect and determine metals in foods, such as Pb in tea,[40] mineral elements in milk,[41–44] qualitative evaluation of maternal milk,[45] Na in bakery products,[46] Ca addition to wheat flour,[47] Cu residue in orange peel,[48] minerals in cucurbit seeds,[49] Sr in wines,[50] high-sensitivity determination of Cd and Pb in rice,[51] elemental analysis of fish feed[52] and heavy metal detection in mulberry.[53] This extensive work makes it obvious that LIBS has potential for detecting residues of heavy metals in foods for food safety monitoring, and its ability to determine many nutritional elements is also very important.

5.3.2 Food Contamination

Many studies have been carried out on the determination of contaminants in food in general, supported by mathematical models that allow their detection and identification, and some involving the use of LIBS are summarized in this section.

Kim *et al.*[54] proposed the use of LIBS to discriminate pesticide-contaminated products. The concentration of the major elements Mg, Ca, Na and K and the emission spectra of pesticide-contaminated spinach were measured. Standard spinach powder or rice flour was mixed with parathion ($C_{10}H_{14}NO_5PS$), a common organophosphate pesticide which has been used in agriculture on fruits, wheat and vegetables, but is now banned or severely restricted in many countries. In this study, the great potential of LIBS to detect contaminated samples was demonstrated.

The detection of biological contaminants in foods and on food surfaces was studied by Multari *et al.*[55] Different kinds of food (egg shells, milk, bologna, ground beef, chicken and lettuce) and bacteria (*Escherichia coli* O157:H7 and *Salmonella enterica*) were used. This work demonstrated that mathematical analysis can be used to create prediction models to differentiate spectra or groups of spectra collected from samples to show that (1) contaminated samples can be differentiated from uncontaminated samples, (2) the type of contaminants can be identified and (3) the metabolic state of the contaminant can be determined. The same group also investigated the detection of pesticides and dioxins in tissue fats and rendering oils.[56] Progress in LIBS spectral data analysis led to the ability to detect organic chemicals in complex matrices such as foods. In this study, the use of LIBS to differentiate samples contaminated with aldrin, 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin, chlorpyrifos and dieldrin in complex food matrices was studied with successful results.

An interesting study to detect chlorpyrifos from elemental emission lines was reported by Ma and Dong.[57] The emission lines P I 213.62 nm, P I 214.91 nm S II 393.33 nm, S IV 396.89 nm and Cl I 837.5 nm were used. The peaks and peak intensities showed significant differences that could be used to detect chlorpyrifos on the surface of apples. Similar work was reported by Du *et al.*[58]

The detection and quantification of a toxic salt substitute (LiCl) was also studied by LIBS using the Li emission lines at 610 and 670 nm for univariate calibration.[59] The use of Li salts in foods has been prohibited owing to their negative effects on the central nervous system. However, they might still be used especially in meat products as Na substitutes.

A significant contribution was the determination of carcinogenic bromine in bread by Mehder *et al.*[60] A pulsed laser with wavelength 266 nm and the Br I emission line at 827.2 nm were used. Other plasma feature such as LTE, electronic density and plasma temperature were also studied.

5.3.3 Food Adulteration

Food adulteration is an important aspect of LIBS applications, and LIBS has been demonstrated to be able to detect extremely small changes in the matrix and thus to detect small adulterations and be very useful for food quality control. The great ability of LIBS to provide a large amount of multiparametric data (spectra) in a very short time allows the application of chemometric models such as neural networks for efficient discrimination. Probably the main disadvantage of using LIBS for fraud detection in the food industry is that each food requires a specific analytical protocol, which makes it difficult to develop a commercial instrument for general use. In addition, concerning the experimental conditions, the energy can vary depending on the experiment and the equipment used. Different geometries are utilized for plasma emission collection and also different atmospheres (air, He, Ar). Further, there is no standard protocol for food sample preparation. This situation is understandable given that existing results are relatively recent. However, the industry is reacting to this demand and new LIBS-based analytical tools are appearing on the market. In any case, the research efforts made so far represent a considerable improvement over other analytical techniques and the main studies are summarized below.

Another important issue is that authors often overlook the need for a real application method and do not perform all the necessary tests on the chemometric models to determine if they can actually be applied in the real world. Moncayo *et al.*[5] demonstrated that not all chemometric methods are able to provide practical results and fail in classification. They showed the need to meet three important criteria: sensitivity, generalization and robustness. The sensitivity (internal validation) evaluates the capacity of the model to classify correctly the spectra of the samples used in calibration, whereas the generalization ability measures the correctly classified samples that were not used in the training of the model. Moreover, it is also important that the model shows robustness, that is, the ability to identify a sample of an unknown class that was not included in the training step as an unknown and not belonging to another class (external validation). These tests are applicable to both supervised and unsupervised models.

A pioneering study on fraud detection in food using the LIBS technique was carried out by Caceres *et al.*[1] Here a novel spectral treatment based on neural networks was successfully applied to discriminate adulterations of virgin olive oil with different types of cheaper oils. The results demonstrated that the LIBS methodology used combined with neural networks is able to identify adulterations as low as 1%.

The Swan band of C_2 emitted by different vegetable oils in the liquid phase was used by Mbesse Kongbonga *et al.*[61] to classify vegetable oils according to their saturated fatty acid content. They also demonstrated the relation of C_2 compared with C_1 in oils containing more saturated fatty acids, but there was no correlation with the number of double bonds.

Moncayo *et al.*[62] also used Swan band emission intensities for the quantification of melamine in adulterated toddler milk powder. They also studied the adulteration of different milk blends, including binary/ternary blends of milk from different animal species, demonstrating the useful applicability of LIBS combined with chemometric methods to the quality control, traceability and detection of adulteration in milk. Sezer *et al.*[21] also used LIBS to detect milk fraud.

When samples are not extremely similar, analysis by unsupervised methods such as principal component analysis (PCA) and partial least-squares (PLS) calibration models is sufficient to solve the problem of adulteration detection and food quality issues. Bilge *et al.*[63] applied a rapid and *in situ* unsupervised method to detect and quantify adulterated milk powder through adding whey powder, and used PCA and PLS calibration models. The results show that the application of PCA is sufficient to discriminate pure samples from adulterated samples. Butter adulteration,[20] offal adulteration in beef,[64] arabica coffee adulteration,[65] rice geographic origin classification,[66] identification of genetically modified maize,[22] tea geographical origin identification[24] and discrimination of honey samples[67] have also been studied using the same chemometric analysis. Thus LIBS in combination with appropriate multivariate methods can be successfully applied to discriminate different types of samples.

A rapid classification procedure for the quality control of red wines with protected designation of origin (PDO) and determination of their geographical origin was reported by Moncayo *et al.*[12] Thirty-eight red wine samples from different PDOs were analysed to detect fake wine. A new and interesting sample treatment with dry collagen pellets was used to convert the wine samples into gels. The results showed a robustness of 98.6%, a high sensitivity of 100% and generalization for the determination of 99.2% of the PDO of red wines.

An interesting method for both classification of wine according to trace element content and sample preparation using a pure aluminium plate was developed by Tian *et al.*[68] This method allowed the detection and identification of at least 22 metallic and non-metallic elements in a typical wine sample including major, minor and trace components. An unsupervised classification model based on PCA was first developed for the classification. The results showed a limited separation power of the model, but it allowed, in a step-by-step approach, the physical reasons behind each step of sample separation to be understood and especially the influence of the matrix effect on the sample classification to be observed. Finally, a supervised model based on random forest algorithms was used to reach 100% classification accuracy.

5.3.4 Other Food–LIBS Correlations

The possibility of using LIBS for measuring the moisture content of fresh food samples was studied by Liu *et al.*[69] The normalized line emission of oxygen is highly correlated with the moisture content of the sample, cheese in the case studied, and can be used as a moisture marker in situations where oxygen interference from the matrix is not a critical issue (Figure 5.5). The

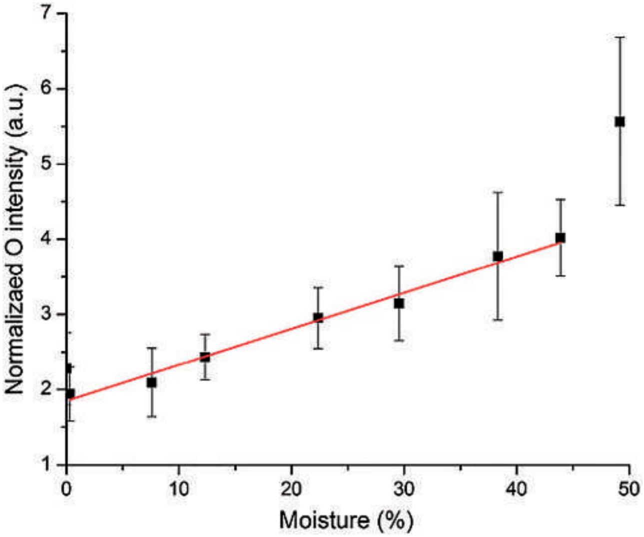

Figure 5.5 Normalized LIBS signal of oxygen as a function of the moisture content of a cheese sample. The error bars represent one standard deviation. The straight line is a linear fit of the data in the range of moisture content (0.5–45%). Reproduced from ref. 69 with permission from Elsevier, Copyright 2012.

linear correlation between the oxygen signal and the moisture content of the sample shows great potential for using LIBS as an alternative spectroscopic method for moisture monitoring.

Protein content was studied by Sezer *et al.*[70] The elemental composition of cereal samples was related to an organic component such as protein, in which the nitrogen content was correlated with the protein content. The results were successfully compared with those given by the standard Dumas method with the aid of chemometric methods.

5.4 Conclusion

In this chapter, the great usefulness of LIBS in food analysis has been highlighted. In addition, and more relevant, it has been demonstrated that despite being an elemental analysis technique, it can be used for the determination of complex organic molecules such as chlorpyrifos and the emission of some lines such as oxygen and nitrogen can be used in the determination of moisture and protein content, which was unthinkable just a few years ago. It has also been shown that the spectra obtained by the LIBS technique contain considerable relevant information that make it possible to classify very or extremely similar samples. Although obtaining LIBS spectra is an easy task, extracting relevant information from them is very difficult. It is evident that the latter cannot be achieved with LIBS alone, and the help of different chemometric methods is necessary. Rapid progress in both instrumentation and the study of chemometric methods has led to optimized spectra that promise a prominent position for LIBS in food analysis.

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