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Review

Laser-induced breakdown spectroscopy (LIBS) for food analysis: A review

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ABSTRACT

Background: Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopic technique which uses a focused pulsed laser beam to generate plasma from the material. The plasma contains atoms, ions and free electrons which emit electromagnetic radiation as the plasma cools down. The emitted light is resolved by a spectrometer to form a spectrum. Recently, LIBS has become an emerging analytical technique for characterisation and identification of materials; its multi-elemental analysis, fast response, remote sensing, little to no sample preparation, low running cost and ease of use make LIBS a promising technique for the food sector.
Scope and approach: The present article reviews the feasibility of LIBS for food analysis. It presents recent progress and applications of LIBS as an efficient and reagent-free, at-line tool capable of replacing traditional time-consuming analytical methods for assessing the quality and composition of food products. An overview of LIBS fundamentals, instrumentation and statistical data analysis is also provided.
Key findings and conclusions: Although LIBS technology shows many advantages, challenges remain in terms of sample preparation, matrix effects, spectral pre-processing, model calibration and instrument development.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a relatively new, attractive and promising optical technique for food quality control. A diverse range of at-, on- and in-line applications are feasible mainly for mineral composition analysis, but also for a wide range of qualitative determinations such as authenticity control, sample discrimination, bacteria contamination, depth profiling and elemental surface mapping (Kaiser et al., 2012).

Minerals are an essential part of human nutrition necessary for the healthy body functioning and development. However, heavy metals such as mercury, lead, arsenic and cadmium may cause adverse health effects even in small concentrations. Metal contamination in food may originate from raw materials, reagents and solvents as well as process equipment. The monitoring of salutary and toxic elements in food products is essential in order to help prevent under or over exposure in the food chain (Beldjilali et al., 2010). Methods commonly used for the investigation of mineral composition and inorganic impurities in food are based on atomic, nuclear and mass spectroscopy techniques, such as Atomic Absorption Spectroscopy (AAS), X-ray Fluorescence Spectrometry (XRF), Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma Optical Emission Spectrometry/Mass Spectrometry (ICP-OES/MS). Although most of these techniques are very sensitive and accurate, they produce large amounts of toxic waste, require expensive reagents, gases and fume hoods as well as sample dissolution and consequently laborious sample preparation. As such, they are not suited for rapid screening analysis at the production site.

Other important challenges facing the food industry are authentication of raw materials and detection of adulteration. Lohumi, Lee, Lee, and Cho (2015), in their review on vibrational spectroscopic techniques for food adulteration detection, recall recent food scandals and adulteration events. Methods based on these techniques, such as near infrared (NIR) spectroscopy, mid

infrared (Mid-IR) spectroscopy, Fourier transform infrared (FTIR) and Raman have been employed to analyse food composition and identify bacteria, however, most of these methods are typically not sensitive enough for detection of low mineral concentrations or contaminants at the ppm level. Other techniques like biochemical and immunological methods, as well as chromatographic techniques are widely applied in authentication and detection of adulteration in food. These techniques are very responsive and reliable; however, they are relatively expensive, time consuming and generate waste.

Rapid onsite methods for bacteria, biotoxins and fungi identification are also required in the food sector. Typical biological techniques for microbiological hazard identification are based on expensive, time consuming methods, such as polymerase chain reaction (PCR), isoelectric focusing capillary gel electrophoresis (CIEF), enzyme-linked immunosorbent assay (ELISA), fluorescent in situ hybridisation (FISH) and matrix assisted laser desorption/ionization known as MALDI-TOF-MS.

Recently, LIBS has been investigated by researchers as a rapid, micro-destructive food analysis tool. As an entirely optical technique, it is considered a promising analytical tool for qualitative and quantitative chemical analysis, making it suitable as a PAT (Process Analytical Technology) or portable tool. Milk, bakery products, tea, vegetable oils, water, cereals, flour, potatoes, palm date and different types of meat have been analysed using LIBS (Andersen, Frydenvang, Henckel, & Rinnan, 2016; Bilge, Sezer, Eseller et al., 2016a,b; Bilge, Velioglu, Sezer, Eseller, & Boyaci, 2016d; Bilge, Boyaci, Eseller, Tamer, & Cakir, 2015; Cheri & Tavassoli, 2011; Ferreira et al., 2010; Gondal, Habibullah, Baig, & Oloore, 2016; Mbesse Kongbonga, Ghalila, Onana, & Ben Lakhdar, 2014; Mehder, Habibullah, Gondal, & Baig, 2016; Peruchi et al., 2014).

Qualitative analysis with LIBS is rather a straightforward task, however, difficulties may arise for quantitative analysis (Gomes et al., 2011). Low signal to noise ratios of samples with complex organic composition such as fresh food products is the most common challenge (Andersen et al., 2016). Moreover, because of the relatively small amount of mass ablated, LIBS is very sensitive to any inhomogeneity of the examined material. Variations caused by the chemical or physical properties of the sample are known as matrix effects, which lead to changes in signal intensities of the emission lines. In order to obtain reliable results, careful sample preparation and presentation are important, as well as optimisation of the measurement parameters.

The aim of this work is to review the feasibility of LIBS as a tool for food analysis. Besides comprehensively reviewing its applications in the food sector, our intention is to provide the reader a clear guide to LIBS instrumentation and data analysis rather than an in-depth description of its fundamentals, which have been described in reviews by Radziemski and Cremers (2013), Kaiser et al. (2012) and Hahn and Omenetto (2012).

2. Fundamentals of LIBS

The history of LIBS has been thoroughly reviewed by Radziemski and Cremers (2013). Its beginnings are dated back in 1962–1963 when Q-switched pulsed lasers were invented (Kaiser et al., 2012). The first LIBS instrument was developed at Los Alamos National Laboratory to measure lead in paint, metals in soils and particles on filters. Since then, it has been successfully used in metallurgy, mining, biomedical, pharmacological and environmental sectors.

LIBS is based on optical emission spectroscopy (OES) as a laser pulse is absorbed by the analyte surface and a small amount of material is ablated, atomised and ionised to produce a plasma plume (Fig. 1). The generated plasma contains a mixture of atoms, ions and free electrons present in the examined material. As the plasma cools down, the atoms, ions and electrons lose energy and emit light at a characteristic spectral structure for the elements present in the target material (Andersen et al., 2016; Rakovský, Čermák, Musset, & Veis, 2014). Recent interests in LIBS have been focused on the development of high resolution spectrometers, charge-coupled device (CCD) detectors as well as miniaturization and the development of compact, low power, portable systems (Mohaidat, 2011). This work has been accelerated by groups such as NASA, with the launch of ChemCam to Mars, a LIBS instrument for remote sensing (Cremers, 2007).

2.1. LIBS instrumentation

A typical LIBS setup is presented in Fig. 2; it comprises of a pulsed laser, laser focusing optics, plasma light collection optics, spectrometer and sample chamber.

2.1.1. Laser and laser focusing optics

In the area of food analysis, most LIBS systems utilise a high powered Q-switched (pulse mode) Nd:YAG (neodymium-doped yttrium aluminium garnet) laser. The Q-switched mode allows laser pulses (also referred as pulse width) of 5–1000 ns in duration. For the sake of information, it is possible to produce laser pulses of picoseconds or femtoseconds duration by the phenomenon of mode locking, however these types of setups are outside the scope of the present review.

The primary parameters related to a laser pulse energy are fluence ($J\ cm^{-2}$) and power density/irradiance ($W\ cm^{-2}$) which depend on the laser's focus spot size (Rakovský et al., 2014). Maximum irradiance is obtained with the minimum focal area of the laser spot (Thakur, 2007). In most studies, pulse energies applied on food samples are between 30 and 100 mJ and fluencies range from 25 to 50 $J\ cm^{-2}$ (Table 1).

The majority of the studies presented in this review are based on lasers with a 532 nm visible wavelength or 1064 nm infrared wavelength; however Nd:YAG lasers with an ultraviolet emission wavelength of 256 nm and 355 nm have also been used (Table 1). In general, it was observed that shorter wavelengths result in a lower fluence requirement for ablation and a more reproducible sampling of the material (Russo, Mao, Yoo, & Gonzalez, 2007). Repetition rate is another important parameter which determines the number of pulses generated by the laser per second (Hz). It is usually operated at 10 Hz (Table 1). According to Rakovský et al. (2014) the higher the repetition rate, the higher the number of detected spectra and the shorter the measurement time.

Laser focusing optics have been described in detail elsewhere (Galbács, 2015). In most of the studies discussed in this review, an assembly of fused silica convex lens of an appropriate *f*-number has been used to focus the laser beam onto the sample surface (Table 1). This type of setup is well established for laboratory conditions, however, it may not be convenient for field and industrial measurements; for such applications, lenses can be replaced by optical fibres known as fibre optic LIBS (FO-LIBS), which can send the laser beam to the desired location facilitating remote measurements (Galbács, 2015). Fibre optics are especially employed in portable LIBS devices. These kind of instruments have already been tested and their performance was reviewed by Rakovský et al. (2014), however to the best of our knowledge their application in the food sector has not been reported to date.

2.1.2. Plasma light collection and spectrometers

Collection optics consist of lenses and mirrors collecting the light emitted from the micro-plasma and focusing it directly either into the entrance of an optical fibre or the entrance slit of the spectrometer (Santos et al., 2012).
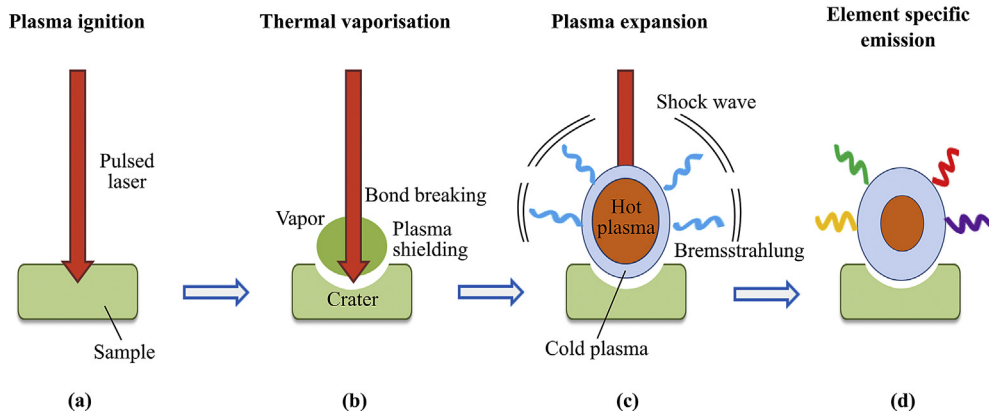
Plasma lifetime schematics

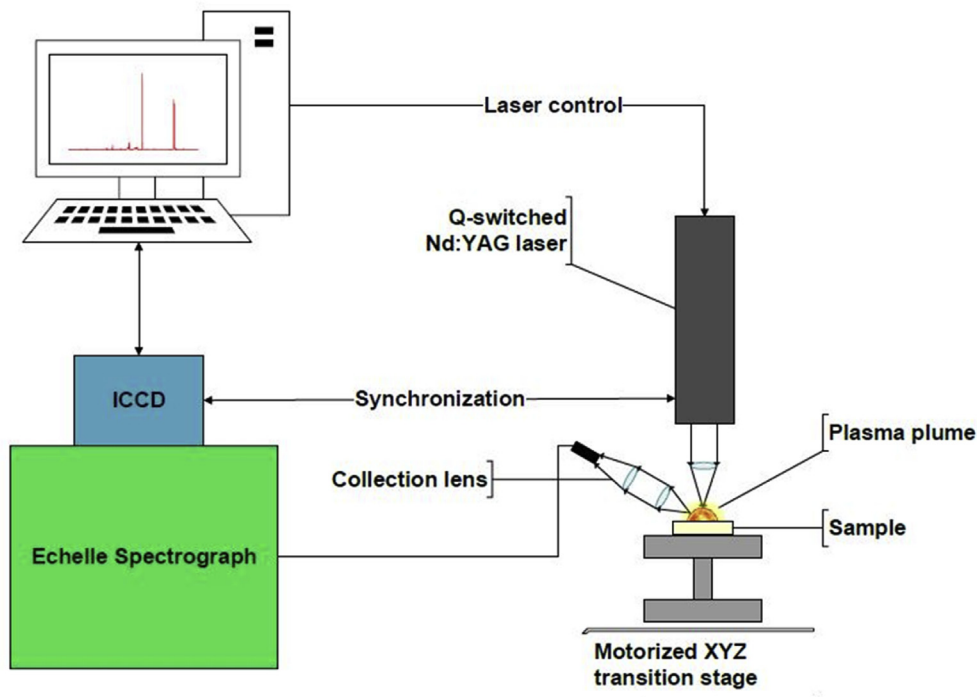**Fig. 1.** Schematic of the laser-induced breakdown process.

Fig. 2. Schematic diagram of the LIBS setup.

A spectrometer is an integral part of the LIBS system and comprises of a spectrograph and a detector. The spectrograph separates the incoming light into a frequency spectrum and the detector measures the intensity of the different frequencies of the electromagnetic radiation. There are three main parameters which determine the performance of the spectrometer: spectral range, resolution, and acquisition time (Rakovský et al., 2014). The spectral range defines the measurement capability of the LIBS setup. In the current market, various LIBS devices are available with different spectral ranges. Atomic emission lines related to important elements analysed by LIBS occur within the range from 190 to 850 nm; wide wavelength coverage allows simultaneous recording of several elements. Spectral resolution determines the ability of the spectrograph to resolve features in the electromagnetic spectrum. It is measured in terms of resolving power (R) which is the ratio of

the wavelength (λ) and the line width ($\Delta\lambda$) at the wavelength λ, i.e. $R = \lambda/\lambda\Delta$. A high resolution (0.003–0.01 nm) avoids interferences between lines and provides a more defined spectrum.

The time needed for the acquisition of the spectral information is comprised of two parameters: delay time and integration time. The delay time or gate delay is the time duration between the plasma formation and the activation of a detector in order to avoid the background continuum (bremsstrahlung and recombination events). The strongest background continuum occurs in an early phase of the plasma lifetime when it is hot. Generally, the background noise might be negligible after a delay time of about 0.1 µs while the intensity of most neutral atom spectral lines is maximum in the 0.1–2.0 µs range. The integration time (referred also as gate width or temporal window) is the time duration when the detector window is opened for signal recording (Rai & Thakur, 2007). Both

Table 1
Overview of LIBS devices and chemometric methods used for food products analysis.

Ref.	Laser (wavelength, pulse width, repetition rate, pulse energy – used in the experiment)	Spectrometer (spectral range, resolution), gate width, gate delay, detector	Laser focusing optics (LFO); beam size; Plasma collimated optics (PCO)	Additional equipment	Statistical methods
(Lei et al., 2011)	(Quantel Brillant) Q-switched Nd-YAG laser (355 nm, 5 ns, 10 Hz, 50 mJ)	(Mechelle, Andor Technology) Echelle spectrometer (240−820 nm, R ≅ 5000) Gate width 1−4μs ICCD (iStar, Andor Technology)	LFO: quartz lens, f = 5 cm; beam size ~500 μm; PCO: pair of parabolic mirrors and optical fibre of 50 μm core diameter	Pellets were moved using a stepper motor; Laser pointer and a CCD camera were used to control lens-to-sample distance	–
(Liu et al., 2012)	(Quantel Brilliant) Q-switched Nd-YAG laser (532 nm, 5 ns, 10 Hz, 7.5 mJ)	(2300i Acton) Czerny-Turner spectrometer Gate width: 10μs Gate delay: 0.1ns ICCD camera (PIMAX 2, Princeton Instruments)	LFO: lens f = 3.6 cm. beam size~ 240 μm PCO: two lenses f = 3.5 cm (front) and f = 6 cm (back), optical fibre	XYZ automated translation stage (PT3-Z8, Thorlabs)	–
(Abdel-Salam, Al Sharnoubi, & Harith, 2013)	(BRIO Quantel) Q-switched Nd-YAG laser (1064 nm, 5 ns, 1 Hz, 100 mJ)	(Mechelle 750, Multichanell) Machelle spectrometer (200−700 nm) Gate width: 2μs Gate delay:2μs ICCD (PCO, computer optics)	LFO: planoconvex quartz lens f = 10 cm; PCO: optical fibre	X-Y micrometric translation stage	–
(Andersen et al., 2016)	(Quantel, Bozeman, CFR400) frequency doubled Nd:YAG laser (532 nm, 9 ns, 230 mJ)	(Aryelle 200, Lasertechnik) Echelle spectrometer (200−800 nm). Gate delay: 3μs CCD detector (Andor)	LFO: lens f = 15 cm; Beam size~ 0.7 mm; PCO: lens f = 5 cm	Automated XY stage; Mercury lamp used for calibration of wavelength	Baseline correction, Normalization, Bootstrapping, Partial Least Squares Regression, Cross Validation
(Beldjilali et al., 2010)	(Quantel, Brio) Nd:YAG laser (1064 nm, 4 ns, 20 Hz, 10 mJ)	(LTB, Aryelle Butterfly) Echelle spectrometer (R ≅ 1 × 10⁴). Gate width: 5μs Gate delay: 1μs ICCD (Andor, iStar)	LFO: plano-convex lanes f = 15 cm; Beam size~ 120 μm; PCO: two lenses f = 15- and 3.5 cm and optical fibre 600 μm	3D computer controlled translation stage	–
(Ferreira et al., 2010)	(Big Sky Laser Ultra50) Q-switched Nd-YAG laser (1064 nm, 8 ns, 50 mJ)	Seven spectrometers (188−980 nm, R~0.1 nm)	–	Cryogenic mill; Ablation chamber	–
(Kim et al., 2012)	(Surelite II-10, Contunuum) Q-switched Nd-YAG laser (1064 nm, 7 ns, 10 Hz, 80−140 mJ)	(Ocean Optics) LIBS 2000 + Broadband spectrometer (200−980 nm; R = 0.1 nm)	LFO: plano-convex lanes f = 9 cm	Automatically rotated sample holder	Partial Least Squares Discriminant Analysis
(Ma & Dong, 2014)	(Beamtech Optronics Ltd.) Dawa-200 Q-switched Nd:YAG laser (1064 nm, 3~5 ns, 20 Hz, 50 mJ)	(Ocean Optics) Spectrometer HR 2000+ (200−1100 nm; R = 0.2 nm) Gate width: 2000μs Gate delay: 2μs	beam size~ 100 μm; PCO: optical fibre	Self-developed 3D precise motion platform	–
(Peruchi et al., 2014)	(Brilliant, Quantel) Q-switched Nd-YAG laser (1064 nm, 5 ns, 10 Hz, 177 mJ)	(ESA 3000) Eschelle spectrometer Gate width: 5.0μs Gate delay: 2.0μs ICCD (LLA Instruments GmbH)	LFO: convergent lens f = 20 cm; Beam size~ 750 μm; PCO: 2 lenses f = 5- and f = 8 cm and optical fibre 1.5 m, 600 μm core	Cryogenic mill; Manually controlled two-axis translation stage	Least Square Regression, Root Mean Square Error of Prediction
(Bilge et al., 2015)	(Quantel-Big Sky, Bozeman) Q-switched Nd-YAG laser (532 nm, 1 Hz, 14 mJ)	(HR 2000 Ocenoptics Dunedin) Spectograph Gate width: 20μs Gate delay: 0.5μs			Relative accuracy
(Gondal et al., 2016)	Q-switched Nd-YAG laser (266 nm, 8 ns, 20 Hz, 30 mJ)	(Andor SR 500i-A) 500 mm spectrograph (200−900 nm) ICCD camera (iStar 320T)	LFO: UV convex lens f = 3 cm; PCO: optical fibre		–
(Mehder et al., 2016)	(Big sky Laser) Nd-YAG laser (266 nm, 8 ns, 10 Hz, 15−18 mJ)	(Andor SR 500i-A) spectrograph ICCD	PCO: fibre optic	Rotary sample holder	–
(Singh et al., 2016)	(Continuum Surelite III-10) Q-switched frequency doubled Na:YAG laser (532 nm, 4 ns, 2 Hz, 40 mJ)	(Andor Technology) Mechelle ME 5000 spectrometer (200−975 nm) ICCD (iStar 734 Andor),	LFO: convex lens f = 15 cm; PCO: collimator CC52 (Andor Technology) f = 5.2 cm; fused silica optical fibre	–	Analysis of Variance, Duncan's multiple range method, Principal Component Analysis
(Bilge, Sezer, Eseller, et al., 2016b)	(Polaris New Wave) Q-switched Nd-YAG laser (1064 nm, 4 Hz, 38 mJ)	Applied Spectra 5 channel Aurora LIBS spectrometer Gate width: 1050μs Gate delay: 0.3μs	LFO: convex lens f = 50 cm; PCO: plano convex lens f = 10 cm		Orthogonal signal correction, Mean Centring, Baseline correction, Four latent variables
(Moncayo et al., 2016)	(Quantel, Brio model) Q-switched Nd: YAG laser (1064 nm, 4 ns, 1 Hz, 42 mJ)	(Tampa, FL) EPP 2000, StellarNet spectrometer (200−1000 nm, R = 0.5 nm) Gate width: 1000μs Gate delay: 2μs	LFO: focal-distance lens f = 100 mm; beam size 100 μm; PCO: 4-mm aperture, and 7 mm focus fused silica collimator placed; optical fibre (1000 mm core diameter, 0.22 numerical aperture)	X-Y-Z manual micro-metric translation stage	Neural Networks

Table 1 (*continued*)

Ref.	Laser (wavelength, pulse width, repetition rate, pulse energy – used in the experiment)	Spectrometer (spectral range, resolution), gate width, gate delay, detector	Laser focusing optics (LFO); beam size; Plasma collimated optics (PCO)	Additional equipment	Statistical methods
(Casado-Gavalda et al., 2017)	(Quantel laser, 601 Haggerty Lane Bozeman, MT)Q- switched Nd:YAG laser (1064 nm, 5 ns, 1 Hz, 150 mJ)	(AvaSpec Avantes spectrometers) Six fibre-optic compact optical spectrophotometers (185 −904 nm) Gate width: 1100μs Gate delay: 1.27μs	6 plasma light collection optics located in the laser head for the different wavelength regions	CCD camera enabling the monitoring of the analysis from the computer screen; Computer controlled X-Y-Z automated sample chamber (XYZ-750, Applied Photonics Limited)	Standard Normal Variate, Partial Least Square Regression

gate delay and width are controlled by a pulse generator which is synchronised with the laser, typically ranging in the microsecond regime. These parameters need to be carefully investigated during the optimisation of signal to background (S/B) and signal to noise ratios (S/N). For more details on signal and noise in LIBS, the reader is referred to the comprehensive review by Tognoni and Cristoforetti (2016).

The multi-elemental detection capability offered by the LIBS technique demands a spectrograph with a wide spectral coverage. The conventional Czerny-Turner spectrograph provides high resolution but only in a limited spectral range covering 20 nm. Thus, to perform the analysis of several elements many laser measurements need to be applied. An instrument which can better handle this task is an Echelle spectrometer coupled with a CCD detector. This system is very compact and provides maximum resolution in the wavelength range between 200 and 780 nm, allowing for multi elemental analysis.

CCDs are micro-electronic devices that are highly sensitive photoelectron detectors used for digital imaging. They consist of many light-sensitive collecting sites known as pixels. The photoelectrons produced as a result of a laser shot are collected by the pixels and converted into electrons, whose number is directly proportional to the intensity. A recent advancement in terms of detectors used in LIBS is the introduction of ICCD, which is a CCD with a multichannel plate intensifier attached. When light hits the photocathode on the front of the multichannel plate, it is converted into electrons, which are then multiplied and hit a phosphor screen to produce photons, which in turn are detected by the CCD (Thakur & Singh, 2007). Light intensity as a function of wavelength is recorded on a computer and analysed using appropriate software. The end product of the spectrometer output is shown as a spectrum.

2.1.3. Sample chamber

Conventional LIBS systems are usually compatible with modular sample chambers fitted with laser protective windows. Sample chambers are designed to accommodate the test sample and provide additional safety for the operator. As the sample is hit by the laser it may move due to the laser force, thus an adjustable sample holder could significantly improve the quality of work and measurements. In order to avoid a crater effect and defocusing of the laser pulse, it is advised to use a fresh surface of sample for each measurement. To facilitate this task, a rotating sample holder or a sample chamber fitted with a 2-D or a 3-D stage can be used. A computer-controlled 3-axis sample translation stage reduces considerably measurement time and provides accurate measurements when multiple shots in different locations are needed. With sufficient accuracy in movement, this approach allows for LIBS maps or images to be produced.

3. Sample preparation and presentation

LIBS has been used for the qualitative and quantitative analysis of the elemental composition of many different types of samples (Rai, Yueh, & Singh, 2007). A recent review by Jantzi et al. (2016) gives detailed description of biological sample preparation techniques for LIBS analysis. In the present paper, methods for food sample preparation proposed by different authors are reviewed (Table 2). Although LIBS application in food industry is required to give fast response at the production line, it is not always possible to analyse material without any sample preparation. However, the sample preparation for LIBS analysis is minimal when compared to reference methods such as AAS or ICP-MS.

3.1. Powders and solid samples

Most of the experiments presented in this review were conducted on a dried, powdered material pressed into the form of a pellet (Table 2). Fresh food products such as vegetables were usually washed, dried to the constant mass, ground and homogenized (Kim, Kwak, Choi, & Park, 2012; Trevizan et al., 2009). As inhomogeneity of the tested powder can affect the LIBS precision, additional milling to improve particle size distribution and microhomogeneity may be required. Both cryogenic grinding and planetary ball mills are found to be very effective to reduce particle size and homogenise the knife mill ground samples (Gomes et al., 2011; Trevizan et al., 2009). A small particle size of the examined powders improves signal and precision by facilitating the vaporization and atomization in the plasma. This results in more homogenous craters with lower border deformities, more uniform plasma, reduced matrix effects and therefore more reliable measurements (Gomes et al., 2011; Jantzi et al., 2016; Santos et al., 2012).

Analysis of loose powders is problematic because of the shock wave occurring on the powder's surface. Consequently, it leads to the defocusing of the focal spot and pulse-to-pulse fluctuation in the irradiance level. Moreover, powder is ejected out and varying part of the laser pulse is absorbed in front of the sample resulting in poor reproducibility of the LIBS spectra (Lal, St-Onge, Yueh, & Singh, 2007). To overcome these problems powders are usually pressed into pellets under certain pressure conditions for a period of time (Table 2). Pelletizing provides harder and more uniform sample surface and improves the results. Sometimes, when the powder does not form a cohesive pellet, the use of a binder might be needed. Ideally a binder should contain only hydrogen and carbon to adjust the concentration and bond the powder without influencing the result. Peruchi et al. (2014) investigated the use of cellulose, UltraBind and polyvinyl alcohol to improve the pellets' quality. Their study demonstrated that cellulose and UltraBind provided the most appropriate mechanical strength of the pellets as well as improved crater geometry and emission intensities.

Table 2
Preparation and presentation of food samples for LIBS analysis.

Ref.	Sample material	Sample preparation and presentation	Measurement parameters (no. of shots, spectra, acquisition)	Elements - Emission lines (nm)
(Lei et al., 2011)	Skimmed milk powder, infant formula	Milk powders were pressed into the pellets (10t for 3min).	Each spectrum was recorded by accumulating 60 laser shots; ten spectra were collected per sample.	Ca II 317.9 nm; K I 404.7 nm; Mg I 517.2 nm;
(Liu et al., 2012)	Cheese	2 × 1cm pieces of Yellow American Cheese were placed on the microscope glass slide. With a little pressure the cheese remained on the glass for the duration of the experiment.	Each spectrum was the result of 10 accumulations. Ten spectra, taken at different locations.	Oxygen triplet around 777 nm
(Bilge, Sezer, Eseller et al., 2016a)	Milk, sweet whey, acid whey, demineralized whey	400 mg of powdered sample was pressed into the pellets under 10t.	Samples were measured in triplicate by scanning five different locations and five excitation per location.	–
(Bilge, Velioglu et al., 2016d)	Sirloin, flank, round meat from beef and pork, chest and legs from chicken	Subcutaneous fat was removed, lean meat was grounded with a 3 mm plate grinder. The beef meat samples adulterated with pork and chicken were produced. Meat samples were dried at 105 °C for 2 h and defatted by Soxhlet method. Dried and defatted samples were ground into powder and sieved through 180 mesh screen. Then 400 mg was formed as a pellet under 10t.	Samples were measured in triplicate, scanned in seven different locations and fifteen laser shots per location.	–
(Andersen et al., 2016)	Mechanically separated poultry meat	Before the LIBS measurements, samples were thawed at 5 °C, stirred to mix the meat juice back into the sample and put into quadratic weighing dishes. Then samples were covered with plastic wrap. To obtain even surface samples were pressed upside down to the table. Samples were stored on ice until the time of measurement.	Samples were prepared in 5 replicates. Spectra were collected at 25 points. Each spectrum was recorded by accumulating 15 successive shots.	Ca II 392.10–394.60 nm, 395.41–398.2 nm; Ca I 421.11–424.29 nm; Na I 587.71–590.78 nm; K I 764.81–768.2 nm, 768.5–771.28;
(Beldjilali et al., 2010)	Potatoes	Fresh potatoes were cut into square cuboids of 10 mm^2 surface and 5 mm height.	Spectra were collected at 50 different locations.	Mg I 383.83, 516.73, 517.27, 518.36; Al I 394.40, 396.15; Ca I 431.86; Fe I 300.05, 404.58; Na I 588.99, 589.59; Mn I 403.08; Ti I 498.17; Li I 670.77; Si I 251.43, 251.61, 251.92, 252.41; K I 769.90; Cu I 324.75;
(Kim et al., 2012)	Spinach leaves, unpolished rice; samples were spiked with pesticide (parathion and fosetyl-aluminium).	Samples were washed, dried at 110 °C, ground into powder, filtrated through mesh screens and pressed into pellets (4t for 3 min). Contaminated samples were mixed with 10 ppm of pesticides.	50 spectra per sample.	spinach/rice Mg II 279.6; Ca I 643.9/422.7; Na I 819.5/588.9; K I 766.5;
(Ma & Dong, 2014)	Red Fuji apples	Apples were cut into pieces with diameter of 30 mm and treated with different concentrations of pesticide. Apples were air-dried for 10 h.	10 locations on apple surface were selected and hit by laser.	P I 213.62, 214.91; S II 393.33; S IV 396.89; Cl I 837.5
(Hu et al., 2015)	Orange fruits	In order to contaminate oranges (concentration of 0–200 μg mL^{-1}) they were placed into the vessels with different Cu solutions. After 48 h oranges were taken out and rinsed 3 times in distilled water.	10 spectra of orange peel were collected for each fruit. Every spectrum was the average of 10 different laser spots.	Cu I 324.754, 327.396
(Mehder et al., 2016)	4 different brands of dates	Date samples were deseeded, dried, powdered and made as pellets.		Mg 277.9; Ca 317.9; Cr 520.4;
(Singh et al., 2016)	Seeds of pumpkin, ash gourd, watermelon, musk melon	Seeds were removed from fruits, washed and dried at 50 °C. Next they were ground and sieved through 40 mesh sieve. Then, samples were defatted using Soxhlet method and dried again at 50 °C. 1 g was placed in hydraulic press and pressed into pellet (10t for 5min).	Spectra of averaged 20 laser shots were acquired.	Ca I 422.6, 643.8, 646.2; Ca II 393.2, 396.8; Mg I 285.2, 382.9, 383.2, 383.8, 516.7, 517.2, 518.3; Mg II 279.0, 279.5, 279.7, 280.2; Na I 588.9, 589.5, 818.3, 819.4; K I 766.4, 769.8

Table 2 (*continued*)

Ref.	Sample material	Sample preparation and presentation	Measurement parameters (no. of shots, spectra, acquisition)	Elements - Emission lines (nm)
(Ferreira et al., 2010)	Breakfast cereals of different brands	The samples were firstly submitted to homogenisation with cryogenic mill and then pressed into pellets (12t for 3min).	20 spectra were captured from different regions of the pellet, with each spectrum corresponding to two accumulated laser pulses; 1 conditioning shot.	Ca II 393.3
(Peruchi et al., 2014)	Wheat flour	Samples were mixed with binding agents in a cryogenic mill and 0.5 g of powder was pressed into pellets (8t for 5min).	Each spectrum was obtained after the accumulation of 30 laser pulses per site. 30 accumulated spectra were obtained in the analysis of 30 locations. All experiments were carried out with three replicates.	P I 213.6; K I 404.4; Ca II 315.8; Mg I 285.2; Fe II 259.9; Cu I 324.7; Mn I 257.6; Zn II 202.5
(Bilge et al., 2015)	Bakery products	Bread samples were dried at 105 °C for 2 h, 400 mg of dried powdered bread were pressed into pellets (10t).	5 excitation per location/5 different locations; Samples were measured in triplicate.	Na II 589
(Bilge, Sezer, Eseller et al., 2016b)	Wheat flour with different ash content	Flours were dried at 105 °C for 2 h and pressed into pellets (10t).	Samples were prepared in triplicates. Pellets were scanned with laser at 7 regions and 15shots/region.	–
(Moncayo et al., 2016)	Red wine	50 mL of wine was mixed with 1 g of collagen gel. 2.4 mL of this solution were allowed to form a gel. Then, samples were placed in an oven at 35 °C for 12 h.	100 spectra at different locations were recorded for each sample.	–
(Cama-Moncunill et al., 2017)	Infant formula	Five samples with varying content of calcium were prepared by mixing IF with lactose or calcium carbonate in order to reduce or increase respectively the calcium content. 0.4 g of powder was pressed into pellets (10t in 3min).	Samples were prepared in triplicates. Pellets were scanned with laser at 100 locations.	–
(Casado-Gavalda et al., 2017)	Beef meat, beef liver	Fresh beef striploin steaks and beef liver were minced and dried in oven for 12 h at 105 °C. Dried, samples were further grounded into fine powder using a laboratory blender. A series of mixtures of lean beef powder and liver were prepared. 300 mg of the prepared mixtures was mixed with 100 mg of a binder with the help of a mortar and pestle. The final mixtures were pelleted using a hydraulic press (10t, 3min).	Samples were prepared in triplicates. Pellets were scanned with laser at 100 locations.	Cu I 324.754, 327.396

Another simple approach that can be applied to powders is the use of adhesives. This method involves fixing loose powder onto an adhesive surface (e.g. double sided adhesive tape or thin layer of glue). The excess is shaken off leaving a layer of powder on the tape. This method is simple and according to Jantzi et al. (2016) gives similar results to pellets. The main disadvantage is that some interference may occur from ablating part of the underlying tape, especially when high pulse energy is used; however, collecting the spectra of the tape alone for obtaining the corresponding blank may help to avoid this inconvenience.

Although preparation of powdered samples is the most common technique in laboratory conditions, it is also possible to perform LIBS analysis on solid material. Examples from the reviewed literature include experiments on cheese slices, raw meat and vegetables cut into pieces (Table 2).

3.2. Liquids

The direct analysis of liquids by LIBS can be as problematic as loose powders, because laser pulse causes considerable disturbance to the liquid surface which results in undesirable effects. Undesirable effects include splashing, formation of aerosols above liquid surface and shockwaves on the surface as well as bubbles inside the liquid influence the laser beam and emitted light. LIBS plasmas created in liquids have lower temperature, lower emission intensities, shorter lifetimes, and smaller maximum dimensions than their counterparts generated on solid samples in air (Galbács, 2015). To overcome these problems, a variety of experimental strategies have been proposed. LIBS analysis of bulk liquid samples, use of double-pulse configuration, laminar flows and jets or droplets and aerosol, might improve the experimental configuration. Liquid analysis modular sample chambers are currently available which may be helpful in this type of analysis. They present the liquid to the laser beam as a thin film on a rotating stainless steel wheel in such way that the volume of liquid at the focal lane of the laser beam is continually replenished; by optimising the measurement conditions, it is possible to obtain stable plasma formation without splashing of the liquid. However, to the best of our knowledge, none of the above techniques has been tested on liquid food products.

Transformation of liquids into solid samples is a more common technique. It can be achieved by freezing the liquid or by depositing

small volume of solution onto a porous solid substrate. In the case of the second approach the preparation time is very short which allows this protocol to be applied on-site, however the choice of the substrate is of significant importance since it must be adapted to the type of liquid to avoid any contamination (Jantzi et al., 2016). In 2013, Abdel-Salam, Al Sharnoubi, & Harith used ashless filter papers to examine 0.5 mL droplet of breast milk and liquid infant formula. Choi et al. (2014) examined Ca content in the tap, bottled and ground water samples. The dissolved Ca^{2+} ions were pre-concentrated on the filter papers. The filter paper was placed in the crystallisation dish that was filled with 80 g of water sample and placed in an oven at 105 °C for 1 h to evaporate water.

3.3. Gases and aerosols

LIBS is also feasible for gas and aerosols analysis, indeed rapid detection and identification of various gases and biological aerosols has already been demonstrated mainly in the field of environmental science (Dutouquet et al., 2014; Tjärnhage et al., 2013; Yueh & Singh, 2007). To the best of our knowledge, research on food products has not been conducted so far.

Presented sample preparation techniques may seem limiting for food industry as they are not possible in all industrial situations. However, potential at-line and on-line LIBS applications are feasible for several food sectors. The manufacturers of cereal products, milk powders as well as dried species, herbs and fruits may benefit from this technique as numerous studies has confirmed LIBS suitability for these products (Bilge et al., 2016a,b,c,d; Bilge et al., 2015; Cama-Moncunill et al., 2017; Mehder et al., 2016). Although most of these studies need further enhancement in terms of predictive accuracy or improvement of the sample preparation step, they present the potential of LIBS to be applied as an at-line validation method. Laboratory-scale experiments should be encourage to broaden LIBS applications to fresh foods and liquids, providing more implementations for the food industry.

4. Spectral acquisition

4.1. Sampling environment

LIBS measurements are usually performed under ambient atmospheric conditions. However, the use of a vacuum or a low-pressure inert gas may improve the analytical spectral range in the deep-UV region for elements such as: carbon, phosphorus, sulphur, chlorine, bromine, iodine, oxygen and nitrogen. Different gases such as helium, argon, and carbon dioxide are found to lower the limit of detection (LOD) and have a significant influence on the evolution, morphology and emission characteristics of laser induced plasmas (Hahn & Omenetto, 2012). In a study by Peruchi et al. (2014), a laminar stream of argon (5.0 L min^{-1}) was fed to the sample chamber in order to displace the ambient air atmosphere from the sample surface. Similarly, Trevizan et al. (2009) reported that the use of argon atmosphere significantly enhanced the intensity of the LIBS spectrum during the analysis of B, Cu, Fe, Mn and Zn in plant material.

4.2. Lens-to-sample distance and number of shots

As previously mentioned, a LIBS spectrum is obtained by applying a high laser irradiance (commonly referred in the literature as a shot or pulse) to a sample's surface followed by collecting the light emitted from the plasma. As a result, a few hundred nanograms of sample are vaporized and a small crater is formed. Dimensions of the craters depend not only on the physical properties of the sample and laser focusing ability but also on the lens-

to-sample distance (LTSD); thus, small changes in the LTSD can affect the craters' shape as well as the intensities of atomic emission lines. A constant LTSD during measurements is crucial for the accuracy and precision of the system (Anabitarte, Cobo, & Lopez-Higuera, 2012; Santos et al., 2012).

The number of shots to fire on the sample surface depends on the experimental design. In the case of a homogenous samples one to ten shots may be sufficient, however for heterogeneous samples such as food, usually tens to hundreds of shots at different locations might be needed in order to obtain a representative measurement (Table 2), (Tognoni & Cristoforetti, 2016; Yueh & Singh, 2007).

Conditioning shots and multiple accumulations may be beneficial for improving the reliability of measurements and signal intensity. Conditioning shots are laser pulses fired before the actual analysis in order to clean the surface of the sample from contamination. Multiple accumulations are the sum up of the individual intensities of different spectra at a particular location resulting in a final spectrum with higher intensities. Accumulation shots are of particular interest when determining low concentrations. Both conditioning and accumulation shots can improve LOD for elements with low concentrations; however they must be used with caution as the growing crater modifies the geometry of laser-sample interaction.

4.3. LIBS spectra

A LIBS spectrum can usually contain a large number of spectral lines. Examples of LIBS spectra can be found in Fig. 3. The National Institute of Standards and Technology (NIST), the Institute for Atomic and Molecular Physics of University of Hannover and the Vienna Atomic Line Databases (VALD) provide online databases which are commonly used to identify emission lines. Spectral lines are characterised by three properties: wavelength, intensity and shape, which depend on the atomic structure, temperature, pressure and electron density of the discharged plasma (Thakur, 2007).

In some cases, spectral lines do not reflect the real intensity. This might happen when the spectrograph does not have sufficient resolution and signal saturation occurs, leading to the phenomenon called blooming. Lines observed as a consequence of blooming are called 'ghost lines'. To avoid this, measurements must be performed under the conditions of non-saturation (Rai & Thakur, 2007).

Another common phenomenon is self-absorption, which often occurs when the plasma is not in the local thermodynamic equilibrium (LTE) state and it absorbs its own emission. This mainly happens in the case of resonance lines connected to the ground state, however other lines can also be affected. Self-absorption tends to deform and broaden the profile of the spectral line and in extreme cases, makes spectral lines appear greatly flattened (Rai & Thakur, 2007). If plasma temperature drops in the outer regions of the plasma plume and the light from the central region passes through these colder parts, the line broadens and shows a dip at the centre. This phenomenon is called self-reversal, giving the lines the wrong impression of being doubled (Rai & Thakur, 2007; Russo et al., 2007). There are several approaches based on LIBS plasma parameters for obtaining information about the effect of self-absorption on the emission lines. For example, Lei et al. (2011) used a method proposed by El Sherbini et al. (2005) which is based on the quantification of the line width and is relevant when the plasma electron density is known and Stark broadening parameters are available. It evaluates the ratio between the measured line intensity and the intensity expected in the absence of self-absorption and, if necessary, corrects the effect of self-absorption on the line intensity (El Sherbini et al., 2005).

The intensity of lines in a LIBS spectrum is different for different elements. For example, alkali metals and alkali earth metals, such
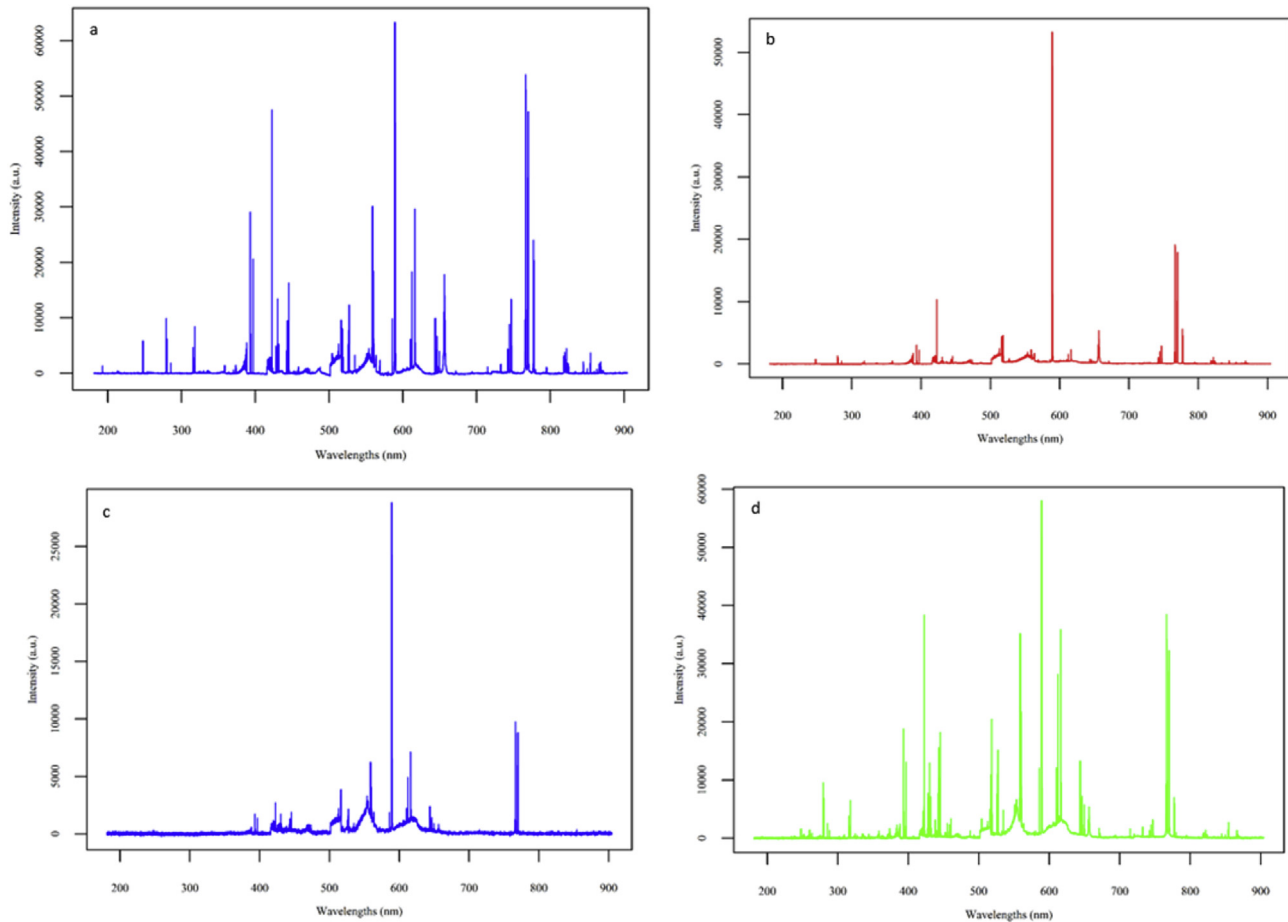
Fig. 3. Examples of LIBS spectra: (a) from whole milk powder, (b) lamb meat, (c) infant formula and (d) oregano.

as Mg, Ca, Na and K are very easily detected. Moreover, elements of interest might be presented by many emission lines with different intensities. Hu et al. (2015) examined two emission lines for copper Cu 324.75 and 327.39 nm. Although the first line was almost 1.5 times more intense than the second one, coefficients of determination were similar for both. It is also common to detect lines of O, N and H if the analysis is carried out in air. Although the LIBS technique is essentially an elemental analysis, it can be used for the detection of organic materials; this is possible by following the presence of molecular emission bands such as CN, C_2 and OH. In 2013, Abdel-Salam et al., assessed the protein concentration in milk using the CN band in the LIBS spectra. The appearance of CN bands originates mainly from the recombination of carbon and nitrogen atoms in the LIBS plasma. Carbon atoms are emitted from the sample, however nitrogen atoms can originate from the sample or from the surrounding air. Eliminating the atmospheric nitrogen would allow to use the information contained in CN bands for protein determination. Liu, Gigant, Baudelet, and Richardson (2012) used LIBS spectra for measuring the moisture content in cheese samples. The oxygen triplet emission line at around 777 nm was considered to be more correlated to water content than the hydrogen emission line at 656 nm.

5. Data analysis

Examinations of samples by LIBS consist of the indirect analysis of multiple spectra. A large amount of data is available from a LIBS spectrum, often containing over 10,000 individual wavelength measurements. To obtain quantitative information, calibration curves using mathematical and statistical models to extract analytical information from the corresponding spectra are often applied.

5.1. Calibration approach

The quantification of an element of interest is usually conducted by constructing a calibration curve. The number of calibration samples depends on the variability of the examined food product; for complex and heterogeneous specimens the number of calibration samples need to be increased to obtain sample representing spectra. A univariate calibration curve consists of the plot of the emission line intensity of a particular element versus its concentration (Bilge, Sezer, Eseller, et al., 2016b,c; Gondal et al., 2016). Calibration curves provide a means to estimate the concentration of a specific element in an unknown-target sample.

There are a few strategies in building a calibration curve. A calibration sample with a matrix containing similar physical and chemical properties to the analysed material is key to ensure its commutability and often difficult to obtain (Da Silva Gomes, De Carvalho, Santos, & Krug, 2013; Lei et al., 2011; Peruchi et al., 2014; Santos et al., 2012). The most common approach is to use either standard reference materials (SRMs) that have the certified concentration of an element of interest or non-certified materials previously analysed by a reference technique (Choi, Lee, & Yoh,

2013). Trevizan et al. (2009) examined the composition of bean leaves; to create a calibration curve they used biological certified reference materials with different elemental composition, such as wheat and rice flour, cabbage, spinach, apples and olives leaves. In order to build the calibration curve, Ferreira et al. (2010) used seven samples of commercial breakfast cereals with different Ca concentrations as calibration standards and other nine samples to evaluate the LIBS method. Kim et al. (2012) exploited certified spinach leaves and certified rice flour to prepare calibration sets for rice and spinach analysis, obtaining a range of mass concentrations of nutrient elements by diluting standard samples with lactose anhydrous. Lei et al. (2011) prepared calibration samples by mixing certified milk with cellulose in order to determine the mineral composition of milk powder. In their experiment, the matrix effect was observed and affected the analytical results. Da Silva Gomes et al. (2013) prepared matrix-matched calibration pellets by using acid extraction of essential elements from target samples (powdered sugar cane leaves) in order to build a calibration curve with an extended range towards lower concentrations. The resulting material was mixed with the original laboratory samples at appropriate ratios, homogenized and pressed into pellets to prepare the calibration standards. With this approach, the matrix effect could be avoided as the standard pellets had similar properties to the target samples. In order to obtain calibration samples of higher concentrations than the analyte, Singh, Kumar, Awasthi, Singh, and Rai (2016) and Mehder et al. (2016) spiked their specimen with different concentration of the analyte elements. This method is known as analyte additive method or standard addition method (Haider & Khan, 2012).

The procedure for calibration assumes that the excitation conditions for the unknown and standard samples are the same. To avoid this drawback, an internal standard method is often used. It emends uncontrolled random fluctuations of the emission intensities by normalizing the LIBS signal of the target element by some common line of another element (Thakur, 2007). It is often applied to minimise shot-to-shot variations and matrix effects, as the intensity of the internal standard line is affected by the same random fluctuations as that of the element under investigation. Two different types of internal standards can be used, however, in both cases the ionization state and intensity of the emission line should be similar for the internal standard and the element of interest. In the first approach, the emission line of the element which is already present in the sample and whose intensity remains constant for all standard samples can be used. In general, the weaker emission lines of major matrix elements, with energy levels similar to those of an analyst emission line, are often selected as reference lines (Choi et al., 2014). The second approach is applied to samples with composition among replicates too variable. In this case, a line of an added element that is not present in the unknown and standard samples can be used (Jantzi et al., 2016; Thakur, 2007). According to Thakur (2007), the internal standard procedure proved to be very effective in reducing error for quantitative analysis.

Kim et al. (2012) normalized their data with C, H, O and N lines and found that internal standardisation with an appropriate selection of normalizing elements can be helpful in improving the linearity of the calibration curve. In 2014, D. Choi et al., reported an analytical approach for improving LIBS precision of Ca measurements in water by adding strontium chloride to examined solutions and using strontium as an internal standard. Their results imply that an ideal internal standard should have a valence electronic structure close to that of the analyte element. For example, Ca and Sr or K and Rb would be the ideal internal standards for each other because of their similar valence electronic structures, leading to close spectroscopic and chemical properties (Choi et al., 2014). Liu

et al. (2012) chose the CN emission line at 774 nm as an internal standard for measuring the intensity of the oxygen line at 777 nm. After baseline correction, the oxygen intensity was divided by the CN emission line intensity to generate the normalized oxygen intensity.

5.2. Pre-processing of collected data

Pre-processing techniques are applied to spectroscopic data in order to improve subsequent qualitative or quantitative analysis and overcome matrix effects. Techniques such as Standard Normal Variate (SNV) transformation, Multiple Scatter Correction (MSC), Savitzky-Golay and Poisson scaling have been widely used to normalize and correct undesired baseline effects in the LIBS spectra (Table 1). Further reading can be found elsewhere (Rinnan, Berg, & Engelsen, 2009; Zhang et al., 2015).

5.3. Multivariate analysis

Multivariate statistical analysis is a chemometric method employed in qualitative and quantitative assessment of analytical data. It offers several advantages, including simultaneous analysis of multiple variables, data dimensionality reduction and extraction of relevant information (Myakalwar et al., 2011). Because of the complexity of the LIBS spectra and the large sets of data obtained, several chemometric techniques have been employed in LIBS analyses of food products for both qualitative and quantitative studies.

5.3.1. Qualitative analysis

Two chemometric tools widely used in qualitative analysis are Principal Component Analysis (PCA) and Partial Least Squares Discriminant Analysis (PLS-DA). PCA is a technique mainly employed in data dimensionality reduction and pattern recognition (Cremers & Radziemski, 2013). It is an unsupervised technique as it does not require prior information regarding object classes to develop the model. The aim of PCA is to simplify the analysis of data consisting of numerous variables while retaining the variation occurring in the data set. To this end, new variables known as Principal Components (PCs) are calculated from linear combinations of the original variables on the basis of maximum variance (Miller & Miller, 2010). This way, the first set of PCs describes most of the variation in the data set; the second set of PCs the next largest variation and so on. Normally, the first PCs are then displayed as points in maps allowing the identification of similarity patterns between the samples (Abdi & Williams, 2010).

PLS-DA is a PLS-based technique used for classification. Unlike PCA, PLS-DA is a supervised technique and unknown samples are classified according to pre-defined object classes. In order to do so, it searches for the linear combination (latent variables) from the spectral data which can better discriminate samples on the basis of maximum covariance with the object classes (Bassbasi, De Luca, Ioele, Oussama, & Ragno, 2014). Kim et al. (2012) demonstrated the possibility of using LIBS in combination with PLS-DA as a rapid discrimination tool for pesticide-contaminated rice and spinach samples.

5.3.2. Quantitative analysis

Partial Least Squares Regression (PLSR) is a multivariate statistical technique used to predict a set of dependent variables or responses from a set of independent variables or predictors (Lopes, Costa, Alves, & Menezes, 2004). It is particularly useful when the number of independent variables is considerably high, which makes it suitable for spectroscopic data analysis (Table 1). PLSR is based on the calculation of new variables known as latent variables

or factors; these are extracted from the predictors with highest predictive ability and correlation with responses (Miller & Miller, 2010). In order to do so, PLS simultaneously decomposes the original blocks of data X (predictors matrix) and Y (responses matrix) into smaller orthogonal matrices in such a way that the factors explain as much as possible the covariance between X and Y. Ultimately, a linear regression model is developed by using the set of factors exhibiting better performance to estimate the responses (Abdi, 2010).

Artificial Neural Networks (ANN) is a computation method which can be used for both qualitative and quantitative analyses. ANN emulates the performance of neurons in the brain and their high degree of interconnection, hence this method consists of linked layers of artificial neurons by which a set of given inputs and outputs are associated. A training set is used to infer the relationship between inputs and outputs so that it can be utilized to predict unknown input data (Yueh, Zheng, Singh, & Burgess, 2009). The network constantly adjusts and corrects itself until a certain degree of accuracy is reached, which is evaluated by a test set (Miller & Miller, 2010). Moncayo, Rosales, Izquierdo-Hornillos, Anzano, and Caceres (2016) used LIBS in combination with ANN as a screening tool for red wine origin discrimination.

5.4. Calibration-free algorithms

Many authors indicate the calibration approach for complex organic materials can be inefficient. Moreover, the adequacy and lack of standards for the development of calibration models adds difficulty in obtaining robust results (Beldjilali et al., 2010; Lei et al., 2011). The calibration free (CF) method offers an independent analysis from the sample matrix, by measuring the plasma temperature and electron density. It provides quantitative results without a calibration data set (Bilge, Sezer, Eseller et al., 2016a). Recently, the CF-LIBS technique has been used in an increasing number of experiments, showing its suitability in the food sector (Beldjilali et al., 2010; Lei et al., 2009, 2011). Details on the construction of the CF-LIBS algorithm are widely discussed in a review article by Tognoni, Cristoforetti, Legnaioli, and Palleschi (2010), thus in this paper we will focus only on the basic fundamentals.

The CF-LIBS approach relies on several assumptions that must be fulfilled to apply the method. Firstly, laser induced plasma must be optically thin and in the local thermodynamic equilibrium (LTE); in such conditions, plasma composition is considered to be representative of the actual sample composition. Another important factor refers to the line selection; lines should be free from spectral overlapping, saturation and self-absorption (Lei et al., 2011). In order to check if the above mentioned conditions are satisfied, plasma temperature and electron density must be measured. Electron density is usually determined using the Stark broadening of the H?? line at 656.3 nm, and temperature is extracted from the Saha-Boltzmann plot using a set of several visible atomic emission lines from the same element. From the accurate Saha-Boltzmann plot exact elemental concentrations can be determined.

Examples of CF-LIBS technique applied to foods are less common than chemometric methods. This might be related to the fact that conditions necessary to obtain LTE can be difficult to overcome, especially in case of raw food products which spectra are very noisy (Andersen et al., 2016). However, information about LIBS plasma parameters are more and more often provided by authors (Beldjilali et al., 2010; Gondal et al., 2016; Lei et al., 2009, 2011; Mehder et al., 2016). So far, the CF-LIBS has been applied to analyse milk powders and potatoes (Beldjilali et al., 2010; Lei et al., 2009, 2011).

6. Applications of LIBS in food sciences

6.1. Adulterations, nutrient and elemental analysis

6.1.1. Milk and dairy products

In 2011, W. Q. Lei et al., used LIBS for Ca, Mg and K determination in seven different brands of infant formula and two types of milk powders. The performance of the calibration and calibration free technique was compared. Quantitative analytical results were validated with the ICP-AES method. The study demonstrated that the CF-LIBS procedure contributed to the significant reduction of the matrix effect by taking into account the plasma parameters in the calculation of the elemental concentrations. Consequently, it provided more accurate results compering with the standard calibration technique.

Liu et al. (2012) assessed the ability of LIBS to determine moisture content in cheese. Their study revealed that there is a high correlation ($R^2 = 0.99$) between the oxygen emission line and the moisture content at the level between 0.5 and 45% in Yellow American cheese. These results indicate that LIBS may be effectively used for moisture determination in cheese and possibly in other food products.

Abdel-Salam et al. (2013) presented a qualitative study concerning the mineral composition of maternal milk and infant formula. LIBS was able to detect differences in Mg, Ca, Na and Fe content in different types of milk. The authors also introduced a method for protein content estimation based on molecular emission bands for CN and C_2, however, no testing for accuracy was described.

Determination of whey adulteration in milk powder by LIBS was performed by Bilge, Sezer, Eseller et al. (2016a). The proposed method was based on elemental differences between milk and whey powder. Based on LIBS spectra of standard samples and commercial products, the specimen was identified using PCA. The discrimination rate of milk and whey powders was 80.5%. The study also demonstrated that LIBS combined with PLS can be applied to the quantitative determination of the adulteration ratio of skim milk powder with sweet and acid whey powder.

Recently, Cama-Moncunill et al. (2017) employed LIBS to determine calcium content in infant formula samples. The study showed the potential of LIBS as an at-line validation method for quantification of calcium in the infant formula manufacturing industry. Moreover, study presented chemical mapping of calcium distribution, which indicate the suitability of LIBS to provide special information of heterogeneous material.

6.1.2. Meat

In a recent study, Bilge, Velioglu et al. (2016d) used LIBS for the identification and qualitative discrimination of beef samples adulterated with pork and chicken. In the same year, Andersen et al. (2016) evaluated the feasibility of LIBS to detect Ca as a marker of bone residues in fresh mechanically separated poultry meat. The aim of the study was to detect calcium directly in raw meat samples with minimum sample preparation. In spite of the relatively poor quality of the obtained spectra, the study demonstrated that LIBS is able to detect differences between three levels of calcium (>20 mg/100 g; 20–90 mg/100 g and <90 mhg/100 g) in fresh meat and could have the potential to be applied as an at-line tool for Ca measurement in mechanically separated poultry meat.

Casado-Gavalda et al. (2017) demonstrated the ability of LIBS combined with chemometrics to detect and quantify liver adulteration in beef by indirect measurement of copper. Moreover, in this study LIBS was also successfully employed for mineral mapping

of meat samples.

6.1.3. Food of plant origin

In 2010 Beldjilali et al., evaluated the concentrations of different minerals in potato skin and flesh by studying the properties of the plasma (Table 2). The presented quantification results of CF-LIBS were in good agreement with the values reported in the literature. Moreover, significant differences were observed between the mineral composition of potato flesh and skin.

In the same year Ferreira et al., published a study demonstrating the ability of LIBS for quantifying Ca in different brands of breakfast cereals. LIBS results showed a high correlation with that obtained by ICP-OES, and the LOD was found to be adequate for the Ca concentration range in commercial cereals.

Kim et al. (2012) performed a study on pesticide detection. The experiment demonstrated that LIBS technique could be a useful tool to discriminate pesticide-contaminated samples (10 ppm of fosetyl-aluminium) in a rapid manner. After applying PLS-DA model to their data, misclassification rates of 0 and 2% for clean and pesticide-contaminated spinach was found. Moreover, the feasibility of LIBS for the quantitative analysis of elements, such as Mg, Ca, Na and K in spinach and brown rice samples was presented.

Ma and Dong (2014) employed LIBS for a pesticide detection (chlorpyrifos) on apple surface. For this purpose, elements such as phosphorus, sulphur and chlorine were used as pesticide's indicators. In this study, differences between clean fruits and those sprayed with undiluted and diluted pesticide were distinguished, however, apples treated with pesticide diluted by 1000 times were not recognized as different from the clean ones. Nevertheless, the study demonstrated that LIBS can allow semi-quantitative detection of chlorpyrifos on fruit surfaces.

Peruchi et al. (2014) investigated LIBS for the determination of Ca, Mg, P, Fe, Mn and Zn in wheat flour. The study revealed that LIBS gave results within the appropriate limits of detection for routine analysis of mineral composition of flour.

Hu et al. (2015) applied LIBS to analyse oranges, especially their peel, artificially contaminated with Cu. A quantitative model based on LIBS spectra intensity and AAS outcomes was created and results showed that the relative error between the predicted and real concentration was less than 6.5%.

In 2015, Bilge et al. found LIBS as an adequate technique for Na and NaCl determination in different types of breads, biscuits and crackers. In 2016, they determined calcium in fortified and adulterated wheat flour by using LIBS. The Ca/K ratio that was used for discrimination of natural and Ca-added flours was also evaluated. This study showed that the LIBS method has potential for the detection of Ca addition in wheat flour (Bilge, Sezer, Eseller et al., 2016c). In their subsequent paper, the same research team used LIBS for ash content measurement in wheat flour (Bilge, Sezer, Eseller et al., 2016b). Data obtained indicate that LIBS is feasible tool to determine ash content in routine analysis of wheat flour.

Gondal et al. (2016) used LIBS for the determination of Fe, Cr, K, Br, Cu, Si and Ca in tea samples. The same research group used LIBS for the spectral analysis of Mg, Ca and Cr in four varieties of date fruits (Mehder et al., 2016). In both experiments, the LTE condition of the LIBS plasma was confirmed prior to the elemental analysis. The quantification was based on the LIBS signal intensity plotted as a function of standard samples with known concentration. In order to validate the LIBS results, ICP-MS was employed as a reference method.

In 2016, Singh et al., used LIBS for determination of Ca, Mg, K and Na in defatted seeds of cucurbits. Their results showed that LIBS technique coupled with a calibration curve method was in good agreement with AAS results which combined with PCA analysis showed potential for rapid discrimination of different species of cucurbit seeds.

6.2. Identification of geographical origins of food

LIBS can be also used as a tool for traceability of food products and raw materials. Traceability has been recognized by European Food Safety Authority regulations as a key factor ensuring food safety, thus fast and reliable analytical approaches for the determination of geographical origin are needed. In recent study by Moncayo et al. (2016) LIBS combined with chemometrics has been employed for a rapid and reliable discrimination and classification of red wines based on their protected designation of origin. This experiment indicated that LIBS can be successfully employed for the identification of geographical origins of food.

6.3. Microbiological assessment

Over the past few years the potential of LIBS for bacterial detection has been investigated. Rapid, positive identification of bacteria in real-time is a challenging task not only for food industry but also for biomedical applications. LIBS has the potential to identify microorganisms based on their unique atomic composition (Mohaidat, 2011). Every microorganism is composed of different elements, thus LIBS signatures have been found to correlate with bacterial membrane composition. A reference library of atomic emission fingerprints for a wide variety of clinically important species has been already created (Mohaidat, 2011). Many researchers showed that rapid discrimination of live bacteria based on LIBS signature alone is possible, as well as discrimination from other biotypes (Baudelet et al., 2006; Diedrich, Rehse, & Palchaudhuri, 2007; Kaiser et al., 2012; Morel, Leone, Adam, & Amouroux, 2003). Multari, Cremers, Dupre, and Gustafson (2013) used LIBS for the detection of bacteria on food products. They could distinguish contaminated and uncontaminated samples and types and metabolic status of bacteria. However, most of the studies have focused on identification and discrimination between bacteria grown and cultivated on nutrient media. For more detailed information on this subject the reader is encouraged to read a comprehensive review from Kaiser et al. (2012).

7. Conclusions and future outlook

Laser-based techniques have developed rapidly in the recent years with commercial instruments increasingly present in the food industry. The replacement of paper stickers pasted onto fruits by laser etching has already been approved for Oceania, Asia, South and Central America, Canada and European Union as the safe way of labelling. LIBS has all the features to become a valuable on-line PAT tool for process control and quality management. Since it allows measurements with relatively little or no sample preparation, in- and on-line applications are feasible.

However, LIBS on-line measurements in the food industry remain challenging and, as far as we know, have not been reported. The major limitation of LIBS for practical applications results from its reduced sensitivity for minor mineral elements and heavy metals with very low concentrations in a complex organic matrix. Furthermore, sample presentation is a crucial issue for food products due to their inhomogeneity. Nevertheless, the additional ability of LIBS to provide spatial elemental distribution with the help of a motorized translational stage has already been successful in different biological tissues, providing great potential to explore this ability in food products (Cama-Moncunill et al., 2017; Casado-Gavalda et al., 2017). Kaiser et al., (2012) used LIBS for mapping the accumulation of Pb, Mg and Cu in plant material. Recently, Gimenez et al. (2016) and Sancey et al. (2014) demonstrated a novel
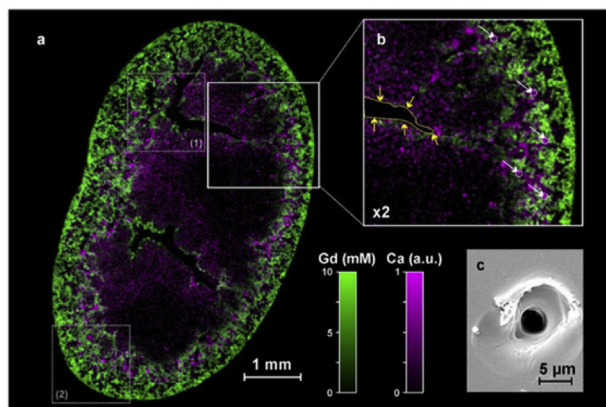
Fig. 4. (a) High-definition 2D elemental image of quantitative Gd (green) and relative Ca (violet) biodistributions in murine kidney; (b) 2 x magnification of the square region presented in (a); (c) example of a single-shot crater observed in scanning electron microscopy. The figure has been reproduced from the original paper by Gimenez et al. (2016). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

approach based on LIBS with an all-optical design and multi-elemental scanning imaging, allowing direct detection and quantification of elements in murine kidney tissues (Fig. 4). These results show the further potential of LIBS as fast tool for elemental mapping, which would be very suitable for food manufacturers.

Moreover, improvements need to be made in terms of the stability of systems, self-absorption, line broadening, and high intensity of the background continuum along with the strong matrix effect. However, the advancement of LIBS instrumentation progresses very fast, so it seems certain that most of the aforementioned drawbacks will be overcame with these improvements. Further progress in chemometrics and data evaluation will also increase reliability of the results. Nevertheless, before LIBS become an established and validated analytical technique for food analysis, further studies both in the research field and at the production lines are needed.

A total of 23 studies on LIBS application for food sector has been presented in this review. These studies cover different aspect of LIBS analysis. Early LIBS publications on food focused mostly on analysis of spectra and plasma physics and created the foundation for further research (Abdel-Salam et al., 2013; Beldjilali et al., 2010; Lei et al., 2011; Liu et al., 2012). Recently, LIBS combined with chemometrics seems to be a common approach for quantification analysis (Andersen et al., 2016; Bilge et al., 2016a,b,c,d; Cama-Moncunill et al., 2017; Casado-Gavalda et al., 2017). Even though LIBS is still in its infancy in the field of food analysis, presented reports show its potential for the food industry. The number of papers on LIBS as a potential tool for food analysis is increasing each year. This indicates that the LIBS food community is growing which will definitely improve and accelerate suitable method development.

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