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Laser-induced breakdown spectroscopy for food authentication

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With the globalisation of food markets, food authentication has become a significant concern worldwide to ensure food safety and to avoid origin and quality fraud. A multi-elemental fingerprint is a powerful tool for detection of adulterants and geographical origin of foods. Laser-induced breakdown spectroscopy (LIBS) is a promising technique that can provide a mineral fingerprint of food products. LIBS allows a rapid, high-throughput, micro-destructive and multi-elemental analysis of a wide range of samples type. It has already been demonstrated by several authors that LIBS can be successfully used for food authentication. Although LIBS shows excellent potential for at-line or portable applications, improvement in sensitivity of trace elements detection, sample preparation, data analysis and instrument miniaturisation are needed.

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Introduction

Food safety and authenticity are a major concern worldwide. Food adulterations occur globally, and factors such as increased demand for value-added products may provide an opportunity for illegal economic profits [1]. Fraudulent and deceptive practices in the agri-food sector commonly involve the replacement of ingredients with cheaper and lower quality alternatives, use or addition of illegal substances, mislabelling of the products from animal species,

incorrect compositional descriptions or false claims including organic, free-range, wild-caught, and so on [2–4]. Food adulteration is a serious issue as it may cause public health problems. Addition of prohibited substances to the food, substitution of species by a lower quality counterpart, use of prohibited drugs and growth promoters in animal production have resulted in numerous food scares [5,6]. The recent examples of food scandals include 2013 horsemeat scandal in Ireland and UK, 2011 phthalate-tainted food in Taiwan, 2008 baby milk melamine incidence in China and 2008 crisis involving dioxin contamination of food and foodstuff in Ireland [7–11]. Other current issues include contamination of food with allergens and the presence of pesticides residues in fruits, vegetables, spices and herbs [12,13]. Accordingly, food authorities worldwide have developed and enforced many regulations on food safety and authenticity. Furthermore, the detection and prevention of food fraud are a prime concern for the food industry as fraudulent practices affect the quality of their products and consumer confidence [14].

In Europe, these regulations not only focus on protecting human health but also consumers' interests [15]. Consumers are entitled to know what they are purchasing and eating, as well as the provenance of their food [15,16]. Consequently, accurate and reliable labelling is crucial to inform consumers correctly. Foodstuffs under European law must be labelled with a description of the product, a list of ingredients and the country of origin or place of provenance, as well as other information [16]. While not necessarily unsafe, mislabelling, either intentional or unintentional, may deceive consumers as to the nature of the product and consequently affect their eating habits [2].

For all these reasons, food authentication has become a top priority and so has the development of fast and cost-effective analytical techniques capable of verifying the integrity, safety and origin of foods.

Reference methods for food authentication

Current trends in analytical food authentication include fingerprinting techniques, which refer to those methods that display multiple non-targeted parameters providing a characteristic signal/profile of the sample [1,17]. Methods based on mass spectrometry and chromatography typically provide fingerprints of extracted or digested samples [14,17].

Vibrational spectroscopic techniques combined with chemometrics also provide a characteristic spectrum — a fingerprint of each food that allows its identification and differentiation. These techniques allow very a high-speed, high-throughput and non-destructive analysis of a wide range of sample types without laborious sample preparation [18]. Near-infrared spectroscopy (NIR), Fourier transform infrared (FT-IR) and Raman spectroscopy are found to be useful for detection of food adulteration and have been proved to be useful in distinguishing the provenance of certain agricultural products [19–22].

Techniques based on stable isotopes (2H , ^{13}C , ^{15}N , ^{18}O , ^{34}S and ^{87}Sr) such as nuclear magnetic resonance (NMR) and isotope ratios mass spectroscopy (IRMS) are considered as powerful tools for assessing food origin. These analyses allow not only identification of the geographical origin of food but also the feeding regime of animals the food was produced from [23*,24]. The basis for discrimination lies in the fact that the ratios of elements such as $2\text{H}/^{1}\text{H}$, $^{13}\text{C}/^{12}\text{C}$ can vary depending on the geographical origin of soil, water and feed used on a farm [25]. However, in certain situations, the results are difficult to interpret as climate, continent and topography can all influence isotopic fractionation. Taking into consideration all these sources of variations and relativity of the measurements, a well-conceived database is essential for these methods to be useful and accurate [24].

Another powerful tool for food authentication is based on the multi-elemental fingerprinting of food products. The pattern of macro and micronutrients, trace elements and lanthanides or rare earth elements (REE) in rocks and soils gives insight into their history. Plants growing on these soils take specific elements, and their level in animal products is associated with their concentration in soil and feed [26]. Similarly, as isotopes certain elements are very stable throughout this cycle; thus, they seem to be good candidates to provide a reliable fingerprint. Mineral fingerprints have been proven to provide valuable information for traceability and authenticity of wines, honey, herbs and other types of food and brewages [27,28,29*,30].

Atomic emission spectroscopic techniques such as inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES) and laser-induced breakdown spectroscopy (LIBS) allow elemental fingerprinting of foods which can be used for both origin and adulteration testing [3,29*,31]. Although ICP-MS is frequently the most accurate technique for elemental analysis because of the simple, easily interpreted spectra and the exceptionally low limits of detection, it not only produces large amounts of toxic waste, but also requires expensive reagents, gases and laborious sample preparation. As such, it is not suited for rapid screening analysis at the production or importation site [31].

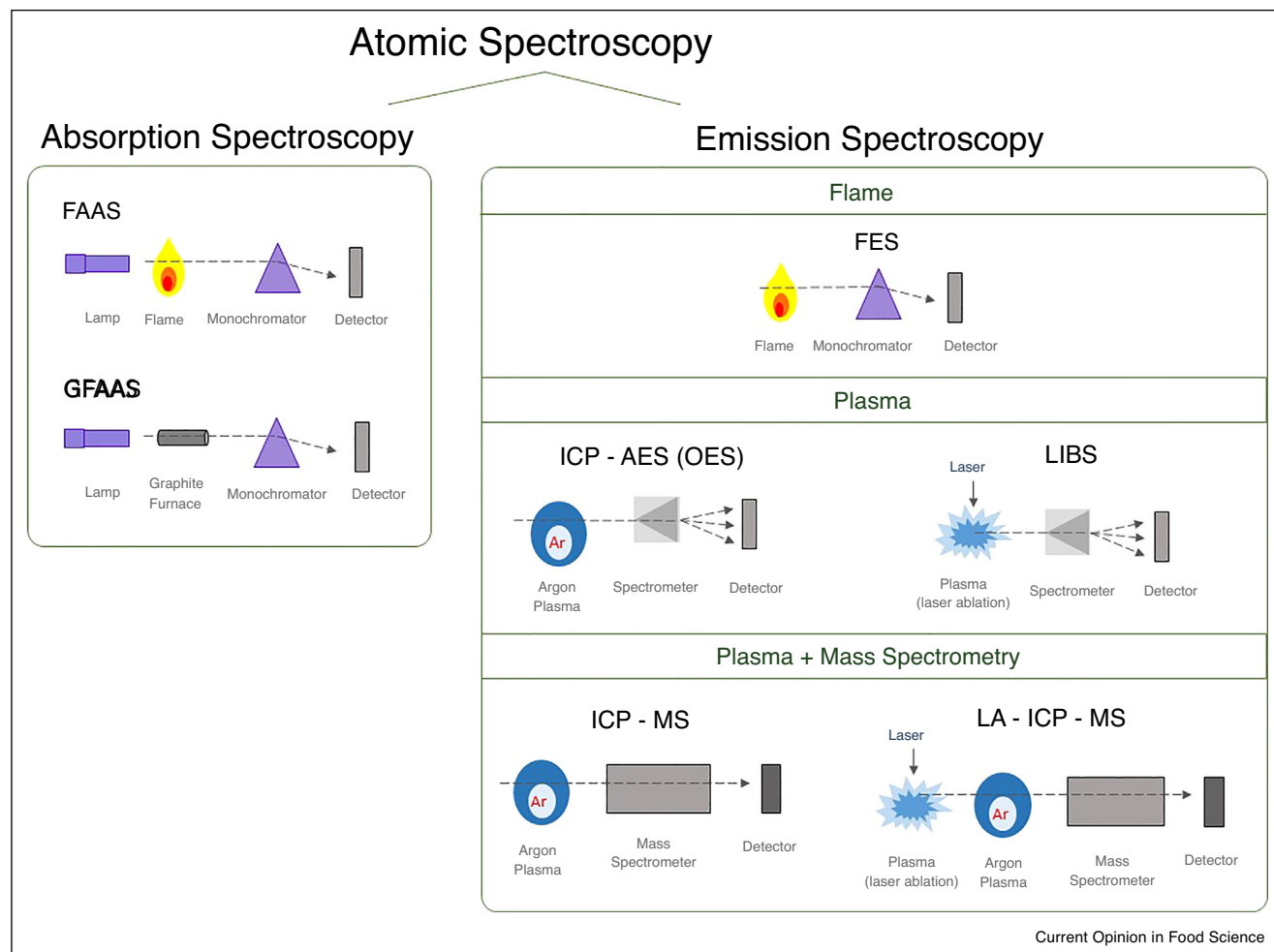
Laser-induced breakdown spectroscopy (LIBS) is a promising fingerprinting technique which uses highly energetic laser pulses as an excitation source and offers rapid analysis, no need for chemical reagents and minimal sample preparation as advantages [32]. These characteristics make LIBS an optimal technology for routine control analysis of foods. This review presents the principals of the technique, the latest applications of LIBS on food authentication together with our opinion on the potential and future trends of the method.

Principles of LIBS

LIBS is a relatively new technique that allows a rapid, high-throughput, micro-destructive analysis of a wide range of sample types. The technique is based on optical emission spectroscopy (Figure 1). The laser which is focused on the sample creates a plasma composed of atoms, ions and electrons which emits light as the plasma cools down (Figure 2). The emitted radiation is detected using a spectrometer, and the intensity of light as a function of wavelength creates a spectrum that can provide identification as well as concentration information about the various elements present in the sample [31]. The spectrum covering the range from 190 to 850 nm is typically analysed with LIBS. The spectra contain a large amount of data, including background and spectral peaks that are element-related. The use of chemometrics allows the extraction of useful information and the creation of an elemental fingerprint that can be used to confirm the identity of a sample. A typical LIBS set-up is presented in Figure 3.

The combination of LIBS with chemometrics has shown successful results for samples classification and authentication [33,34,35*,36]. The initial step in the analysis of LIBS data is spectral pre-processing, which includes baseline correction, normalisation, overlapping-peaks identification, outlier removal and noise reduction [37]. Supervised and unsupervised techniques can further classify pre-processed LIBS data. Examples of unsupervised techniques include principal component analysis (PCA) and hierarchical cluster analysis (HCA) [30,38]. These techniques are usually employed to reduce data size and select most relevant LIBS bands as well as to investigate groups/patterns within the data set [39–41]. Supervised techniques are more powerful as they allow the prediction of an output variable based on a model previously developed with a training data set [14]. Supervised techniques for classification include partial least squares-discriminant analysis (PLS-DA), random forest (RF), artificial neural network (ANN), support vector machine (SVM), k-nearest neighbours (k-NN) and linear discriminant analysis (LDA) [36,42,43]; while for quantification, partial least squares regression (PLSR) is the most commonly employed [30]. Unsupervised and supervised methods are complementary and can be superimposed. These methods have been proved to be effective

Figure 1



Schematic of an atomic spectroscopy.

and reliable for studying fingerprints of different food products by numerous authors [14,29*,36,44*].

In order to obtain a homogenous sample, food products analysed by LIBS are usually dried, powdered and pressed into the pellet form before the analysis [31]. Depending on the number of shots and accumulation of pulses per shot, sample collection time may take from few seconds to few minutes. Typically, when the spectra are collected in 100 locations with one pulse (accumulation) per location, the collection time takes around 2 min — 1 to 2 s per shot/location. Although potentially LIBS can analyse liquids, solids and gasses, analysis of liquid samples is challenging as focusing the laser on the liquid surface causes splashing and shockwaves, which affect plasma quality. In order to minimise these effects, new experimental procedures have been proposed. Double-pulse LIBS, LIBS analysis of liquid bulk samples, laminar

flows and jets or droplets and aerosol, can improve the experimental configuration. Modular sample chambers designed for liquid analysis are also currently available, which may be helpful in this type of analysis [31]. However, the transformation of liquid to a solid-state by drying or gel formation is still the most common approach and was applied in studies presented in this review.

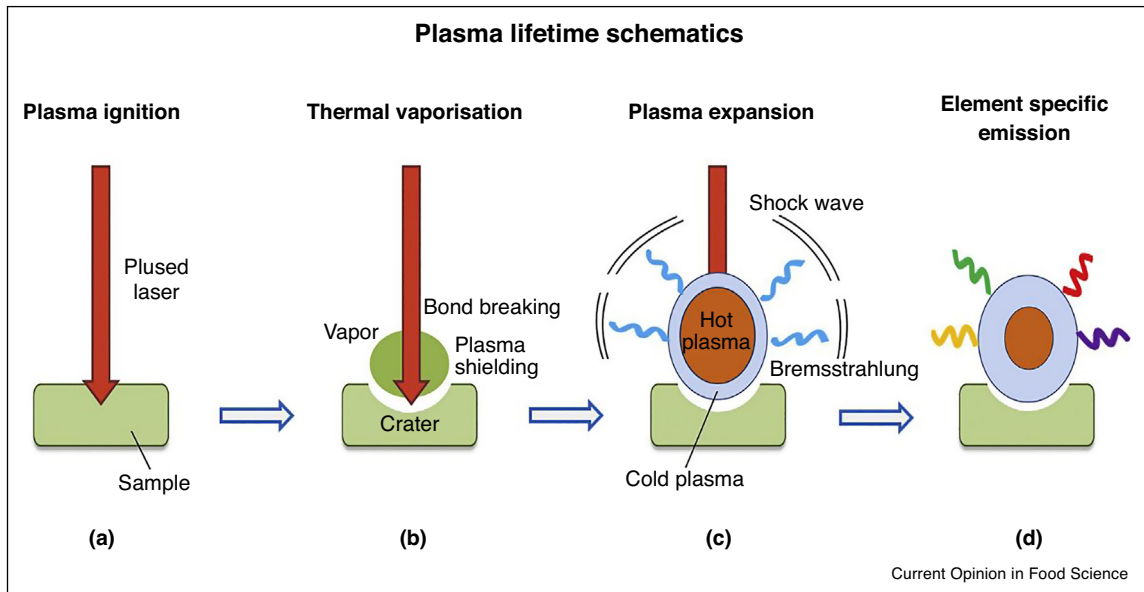
Applications of LIBS for food authentication

The substitution of one species by another and the mislabelling of geographic origin are the most common fraudulent practices in food markets [26].

Detection of adulteration by LIBS

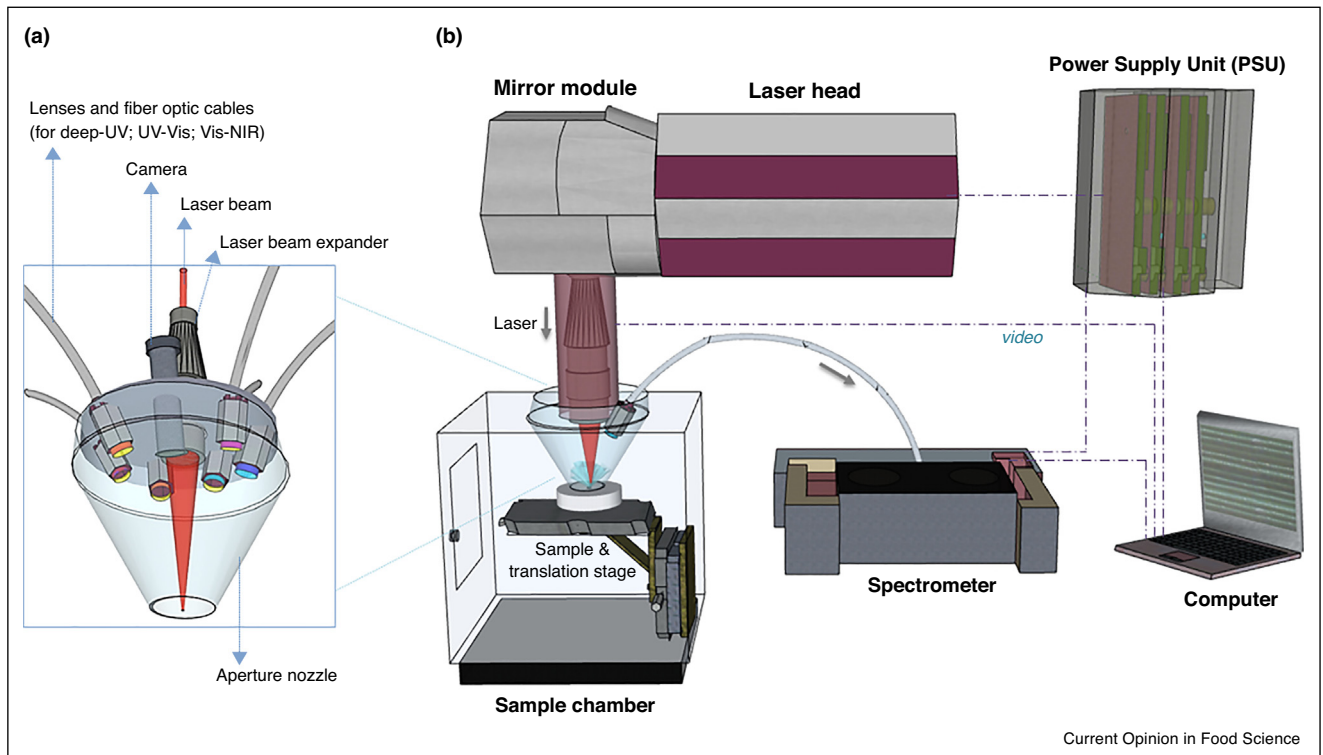
LIBS has been successfully applied to detect adulteration in various foods such as dairy products, meat and coffee. Milk and dairy products adulteration occurs in many

Figure 2



Schematic of the laser-induced breakdown process. The figure has been reproduced from the original paper by Markiewicz-Keszycza *et al.* [31].

Figure 3



Schematic diagram of the typical LIBS setup. The figure has been reproduced from the original paper by Markiewicz-Keszycza *et al.* [57].

countries [45]. Substitution of more expensive milk with a cheaper alternative, adulteration with fillers, melamine and less costly ingredients are the most common forms of milk and dairy products frauds. Temiz *et al.* [41] used LIBS coupled to PCA and PLSR to determine butter adulteration with margarine. The intensity differences in spectral lines of Na, K, Fe, Ca, Mg and Mn made an important contribution to successful discrimination analysis. In this study, limit of detection (LOD) and limit of quantification (LOQ) values were 3.9% and 11.8% respectively, which was found satisfactory to determine this type of adulteration [41].

Another example highlighting the usefulness of LIBS in food fingerprinting and detection of adulteration is a study of Bilge *et al.* [33]. The authors used LIBS combined with PCA and PLSR to detect and quantify adulteration of milk powder with whey powder [33]. Sweet and acid whey powders were used as adulterants. The discrimination rate of milk and whey powders was 80.5%. Limit of detection was 1.55% for sweet whey powder and 0.55% for acid whey powder.

Similarly, in another study carried out in Turkey, LIBS with chemometrics successfully discriminated caprine and ovine milk adulterated with bovine milk. The limit of detection values for caprine and ovine milk were 1.39% and 1.29% respectively [45].

Moncayo *et al.* evaluated LIBS combined with a neural network (NN) to detect the adulteration of ovine and caprine milk with bovine milk. Powdered samples were prepared by mixing the respective pure milk with the percentages ranging from 25 to 75% v/v of adulterating milk [46]. The LIBS-NN combination allowed 100% correct classification of blended and pure samples. In the same study, the authors presented the results of an experiment in which LIBS-NN was used to detect melamine in toddler milk powder. Commercial toddler milk was adulterated with melamine at concentrations between 1% and 6%. A mean prediction error of 5% was obtained for NN quantitative model in this study. In this case, because of the nature and composition of melamine (C₃H₆N₆) its increased concentration was correlated with the CN molecule emission band [46].

Another widely consumed food is meat. Consumers want to be aware of what type of meat they eat, and accurate labelling is essential to inform their choice. The most common meat adulteration occurs by substitution of original meat species, for example, beef with cheaper meat such as pork [47]. Bilge *et al.* [33] used LIBS to detect this type of adulteration. The minced beef meat was adulterated with pork or chicken meat at concentrations between 10% and 50%. The mixtures were analysed with the PLS method. LOD values for chicken adulterated beef and pork adulterated beef were 2% and 4.4% respectively [47].

Velioglu *et al.* used LIBS combined with PCA and PLS to detect offal adulteration in minced beef [34]. Casado-Gavalda *et al.* used LIBS to detect copper as an indicator of the presence of liver in minced beef [48]. These studies reveal that LIBS method combined with chemometrics has the potential to determine the offal adulteration in beef.

Sezer *et al.* [49] demonstrated the ability of LIBS combined with chemometrics to detect and quantify coffee adulteration with chickpeas, maize and wheat. Coffee is the second most traded commodity, and as such, it is prone to adulteration practices, such as the addition of certain substances [49]. Blends of coffee arabica with chickpeas, maize and wheat were prepared at ratios between 2.5% and 60%. LOD values for chickpeas, maize and wheat, were 0.56%, 0.52% and 0.45% respectively.

Geographical origin

Because of the globalisation of food markets and increased variability and availability of food products on store shelves, consumers are increasingly interested in the provenance of the foods they consume. The reasons include patriotism, specific culinary quality and decreased confidence in the quality and safety of products of unknown origin or produced outside their region, country or even blocks such as the EU [50]. Moreover, consumers are more and more concerned about the impact of the food they eat on climate [51]. The local food movements encourage people to choose organic, locally grown products which are considered to place less stress on the environment than the conventional food that has travelled a long distance from production to consumer [52]. In the European Union, the originality of certain agricultural products such as wines, tea, honey, rice or olive oils are protected by legislation on the Protected Designation of Origin (PDO) and the Protected Geographical Indications (PGI) [53,54]. These products are often more expensive as they are considered to have unique and exceptional quality; as such, they are among the most likely foods to be the target of food fraud.

Moncayo *et al.* [35^{*}] used LIBS for the discrimination and the determination of the geographical origin of red wines. Their work aimed to evaluate the feasibility of LIBS combined with NN as a tool for detection the protected designation of origin (PDO) of wines. Thirty-eight red wine samples from different PDOs were analysed to detect fake wines [35^{*}]. Wine samples were transformed into gels using a commercial collagen. In this study, LIBS demonstrated robustness of 98.6%, high sensitivity of 100% and generalisation for the determination –99.2% of the PDO of red wines.

Tian *et al.* [44^{*}] used LIBS to perform a classification of French wines from different regions. The authors used the surface-assisted (or surface-enhanced) sample

preparation method, which enabled detection of 22 metal and non-metal elements. Wine samples were transferred onto a pure aluminium target and dried by evaporation. The residue from a liquid wine in the form of a uniform and semi-transparent thin layer on the aluminium target was analysed by LIBS [44*]. Fifteen elements were selected as fingerprint elements, and a supervised classification model based on a random forest algorithm was developed. Robust classification results were achieved with a classification accuracy of 100% [44*].

Pérez-Rodríguez *et al.* [36] investigated spark discharged LIBS (SD-LIBS) to discriminate rice samples according to their PDO. Brown rice samples from two main rice-producing regions in Argentina were analysed by LIBS coupled to a spark discharge. The selection of the spectral data was accomplished by extreme gradient boosting (XGBoost), and the best performance of classification was obtained using k-nearest neighbour (k-NN) algorithm [36]. The authors presented a method that provided 84% of accuracy, 100% of sensitivity and 78% of specificity in the classification of the test samples [36].

Conclusions

Elemental fingerprinting offers a powerful tool for food authentication and traceability. LIBS technology shows many advantages such as multi-elemental analysis, fast response, low running cost and ease of use. There are many successful examples of the use of this technique for detection of adulterants and geographical origin; however, there is still room for improvement to fully exploit LIBS possibilities not only in the R&D sector but also in industry and regulatory environments. Development of an agile, robust and cost-efficient tool that is able to detect frauds and geographic origin of food is a considerable challenge needed not only in large enterprises but also in small-scale companies.

However, before establishing LIBS as a validated, an at-line or in-field method for food authentication, major improvements are needed. Increase in the sensitivity for trace and rare earth elements detection is a major goal. Most of the studies presented in this review report a spectral signal for 4–7 mineral elements, 4 organic elements and emission bands from diatomic species such as CN or C₂. Higher sensitivity for minor and trace minerals with very low concentrations in a complex organic matrix would increase the usefulness of this method for authentication purposes. Recent advances in the detection of trace and rare earth elements by LIBS [44*,55*] and the continuous development of the technique are expected to give a boost, in the near future, to this detection method. Miniaturisation and the development of a compact, portable LIBS device would provide the possibility for *in-situ* classification, facilitating the adulteration detection coupled with progress in the quality control of agro-alimentary products. Moreover, improvements

need to be made in terms of liquid samples analysis. Transformation of liquids to solids, although very effective, requires additional long sample preparation steps, which impede real-time analysis. Further innovation in LIBS and other optic based technologies, sensor platforms and predictive computation will likely contribute to the development of holistic solutions for food authentication and fraud detection [56].

Conflict of interest statement

None of the authors of this paper has a financial or personal relationship with other people or organisations that could inappropriately influence or bias the content of the paper.

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