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Capabilities and limitations of LIBS in food analysis

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ABSTRACT

Food is the main source of different elements which are essential, trace and fundamental for human diet and health. The type and level of elements in foods indicates whether it's toxic or not. Therefore, determination of elements and their amounts is crucial for food safety and quality. In order to fulfill the increasing demand on multi-elemental information for product monitoring, rapid and sensitive analytical techniques which are capable of detecting major and trace elements with good precision and accuracy are required. In this review, the most recent literature about the use of LIBS for the analysis of food and capabilities and limitations of LIBS on foods have been reported. This review provides comprehensive overview of the applications on food quality and fraud monitoring of several foods, sampling techniques and some limitations of LIBS. Furthermore, it provides a critical outlook on the developments to analyze food matrices with proper sample preparations.

1. Introduction

Today, many consumers are concerned about what they eat. The choice of one food product over another can reflect individuals' life styles, religious beliefs, diets and health concerns. Therefore, accurate labeling is crucial to help consumers make conscious choices. Elemental composition of food is a very important indicator to understand food quality, nutritional value and authenticity of food. Besides, it is fundamental to assess the presence of nutrients presented in Table 1 [1]. Therefore, determining the elemental composition of a food product is vital especially for certain consumer groups such as children, pregnant women and people with allergies to specific elements. Conventional analytical techniques for determining elemental compositions can be listed as atomic absorption spectroscopy, inductively coupled optical emission spectroscopy/mass spectroscopy, and X-ray fluorescence spectroscopy. Although they are quite sensitive and reliable, they require usage of chemicals, sample preparation procedures and long processes. Nevertheless, these are elemental analysis techniques, and information on elemental composition can also be used for determination of food frauds. Conventional analysis techniques for food adulterations can be listed as chromatographic, biochemical and immunological methods, all of which are time consuming and expensive. Recently, some spectroscopic methods have been used for food quality monitoring. Among them, NIR, FTIR and Raman spectroscopy are frequently used despite their insufficiency at low concentration levels. In order to enforce regulations and obtain comprehensive knowledge of food adulteration and nutritional content of food products, rapid and efficient analytical methods are required.

In the past decade, laser induced breakdown spectroscopy (LIBS) has been applied in numerous fields ranging from space exploration to environmental analysis and has now become a valuable tool in the study of a wide variety of structural and compositional aspects of food analysis. LIBS is an atomic emission based multi-elemental analysis method, and several factors have contributed to increase in the use of LIBS for food science. Common techniques used in food analysis require long time and in some of them, certain hazardous chemicals that may cause environmental pollution are needed to be used. LIBS, on the other hand, is an in-situ method which can analyze solids, liquids and gases and provides versatile detection options with minimum sample preparation processes [2]. Given these advantages, it can be concluded that LIBS has potential to become an ideal analytical tool for food analysis. Many different food matrixes such as bread [3], milk [4], meat [5], vegetables [6] and tea samples [7] can be analyzed using LIBS However, further evaluations are needed to fully understand the interaction with food matrices, plasma formation, radiation emission, and signal analysis. Also, experimental parameters are needed to be optimized in order to improve detection sensitivity.

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Table 1
Classification of foods elemental composition.

Major essential	Trace essential	Ultra trace essential	Nonessential trace	Potentially toxic trace
Ca	F	Cr	B	Al
Cl	I	Co	Ti	As
C	Fe	Cu	Sb	Sb
H	Si	Mn	As	Cd
Mg	Zn	Mo	Ba	Cr
N		Ni	Ce	Cu
O		Se	Ge	Pb
P		V	Rb	Hg
K			Sr	Th
Na				Sn
S				U

In the light of all this information and the increasing interest in LIBS based food analysis, it can be said that LIBS is an important monitoring tool in food science. In this context, the emphasis of the present review will be on applications of LIBS in food analysis, including common challenges accompanied by possible solutions. A brief review of laser induced plasma mechanism, as well as current LIBS instrumentations, is also included.

2. LIBS

LIBS is an optical emission technique that analyze spectral emissions from laser-induced plasma. Due to its advantages over conventional techniques, LIBS applications have been widely used since its invention in the 1960s. In 1963, Q-switched pulse lasers were invented, which can be considered as the birth of LIBS. During the 1980s, Nd:YAG laser became the most common laser used in LIBS applications as it produces well-focused high energy single pulses. Portable LIBS for field measurements began to be used during the 1990s. Since then, researchers have become more interested in LIBS as a promising technology to be used in different areas. As a multi-elemental analytical method, LIBS has been successfully applied in many fields such as space exploration, geology, metallurgy, forensic, and pharmaceutical analysis [8]. Basic LIBS systems contain small number of component which can variably configured for scientific research or made compact and rugged for field measurements. A simple LIBS system consists of four components. These can be listed as (i) solid state, short pulse, Q-switched laser, (ii) optics, (iii) detector and spectrometer and (iv) computer system. This system can be configured close in analysis or stand of distance. Different LIBS techniques were presented in Fig. 1. In LIBS, high power pulsed laser source is focused onto a sample surface (1), which causes molecules of the samples to breakdown into atoms. Rapid energy deposition on the sample makes a minute amount of sample turn into vapor (2) and lead to formation of high temperature micro-plasma with characteristic sound of the ultrasonic shockwave (3) [9]. After that, plasma expands into space (4) and loses its energy and starts to atomize. In relaxing stage, ions and atoms emit light which is detected by a spectrometer (4–8). Temporal evolution of laser induced plasma (LIP) is presented in Fig. 2 [10].

In LIBS system, emitted plasma light is collected with an optical arrangement and then focused in the entrance of slit on the spectrometer with or without fiber optic cable. The spectrometer can accomplish multi elemental analysis, and the choice is based on the aimed spectral selectivity and sensitivity. LIBS has numerous advantages such as minimum sample preparation, the use of small volume of test material, high spatial resolution on the target, relatively simple implementation, and real time response. The analytical performance of LIBS depends on certain experimental parameters such as laser properties (wavelength, energy, pulse duration, repetition rate and shot-to-shot energy fluctuation), optical design, ambient atmosphere, measurement parameters (delay time and integration time) and sample properties (homogeneity, particle size and porosity) [11,12].

3. Capability and limitations of LIBS on food analysis

In this part of the review, applicability of LIBS on foods was evaluated according to sample form and sample matrix.

3.1. Sample form

Foods have complex and nonhomogeneous matrixes (carbohydrates, lipids, proteins, enzymes, *etc.*) and may also contain additives that are used to obtain prolonged shelf life or better color, odor, taste *etc*. Also, even when the foodstuffs are in solid state, they contain certain amounts of liquids such as water and oil. Because of their complex structure, every food item gives a different response to laser interaction.

In a point analysis method like LIBS, this compositional and distributional differences may cause problems in reproducibility of the signal because of the small size of the focused beam and small sample mass vaporized. Most of these problems can be solved by means of choosing the most appropriate LIBS technique, experimental conditions and sample preparations. For example, in powdered materials (*e.g.* flour), large differences in particle size distribution and composition may cause difference in laser-sample interaction, which affect the quality of signal [12]. The most common approach in powdered material is giving the sample a pellet shape with pellet press. In non-homogenous powdered form food items, basic mixing generally solves or minimize the problem. Also, non-uniformities may be averaged out using a number of shots from different areas of a sample which are combined to produce an average measurement. Some binders can be used to keep the pellet form of the powdered sample, but they should be carefully selected since some of them may not be suitable for food items due to their composition. Another sampling method is giving a dry sheet (*e.g.* a small wafer) form to certain food products (*e.g.* cereals). It is a simple procedure that makes use of water, heat and dough formation ability of the sample. However, in this approach, sample composition should not be affected by the applied temperature.

High moisture or fat content can also be problematic in obtaining good quality signal especially for detection of trace elements. In this situation, drying or defatting the sample can be a good solution. However, these preparation steps require longer times or certain chemicals and in some cases, they may not be adequately efficient, which also eliminates the major advantages of LIBS system. For these kinds of foods, using high energy levels or different system designs such as double pulse or plasma spatial confinement may be an alternative to obtain good quality signal. One of the most appealing approaches to increase LIBS sensitivity is