Review

A review of vibrational spectroscopic techniques for the detection of food authenticity and adulteration

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A B S T R A C T

Background: **Food adulteration**, commonplace throughout human history, remains a concern today, with several notable instances involving the agro-food industry.
Scope and approach: In this review, we introduce four **vibrational spectroscopic techniques** (near-infrared, mid-infrared, Raman spectroscopy, and hyperspectral imaging) for the determination of food authenticity and adulteration. The characteristics and applications of these techniques, along with the major barriers and limitations, are discussed, with an emphasis on the treatment of spectral data using **chemometrics**.
Key findings and conclusions: Vibrational spectroscopic techniques have potential to fulfill the industrial need for food quality and authenticity analysis, however, still requires measurement accessories and dynamic chemomatric analytical methods for modern food inspection. We believe this review will be an **effective guide** for food industry researchers and engineers to aid in the selection of spectroscopic methods to analyze food quality and authenticity.

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1. Introduction

Food may be accidently or deliberately contaminated with chemical or physical substances that should not be present for legal or other reasons (Lakshmi, 2012). The authentication of agro-food products has become a crucial issue over the past decade as several major food adulteration events were discovered. These events include the adulteration of protein in China (2007), where samples of wheat gluten were mixed with melamine to increase the protein content (Lakshmi, 2012), the 2008 milk scandal in China (Editorial, 2009), and the 2012 milk scandal in India, where milk was adulterated with detergent, fat, and even urea (Lakshmi, 2012). Other significant occurrences involve the contamination of chili powder with dye in 2005, and the presence of an adulterated chili powder exported from India to Britain in a Worcestershire sauce (Ramesh, Jha, Lawrence, & Dodd, 2005). Recently, many incidents in China of gelatin-like chemicals used to increase weight in the aquaculture market were reported (Wu, Shi, He, Yu, & Bao, 2013). Several instances of the adulteration of spices with ground material (e.g., artificial colors and husks) have been noted worldwide, commonly in India and in European countries.

The adulteration of food products for economic gain with cheap ground or chemical materials could pose serious health threats to consumers. The Chinese milk scandal is a typical example of this, where at least six children died and several thousand were hospitalized (Branigan, 2008). Another example is the adulteration of paprika with lead oxide for color, which resulted in more than 60 hospitalizations (Everstine, 2013). Another toxic adulterant is red lead (Pb_3O_4), which is used to give a vibrant color to cayenne pepper (Ellis et al., 2012). Lakshmi (2012) reported the use of formalin, which can have several short-term or even carcinogenic effects on human health, to make fish appear fresh. The Irish pork crisis was a major food contamination event that affected both the economy and health. A mass recall of Irish pork was initiated as a result of the contamination of pork with dioxin (Kennedy, Delaney, McGloin, & Wall, 2009). As a result, 1800 jobs have been lost in the Irish pig industry, and the estimated cost of the crisis was 138 million USD (Wikipedia in Irish pork crises, 2008). The adulteration of olive oil with hazelnut oil is reported to cause an economic loss of approximately 4 million euros per year for countries in the European Union (Ozen & Mauer, 2002). Recently (2011), millions of pounds of Asian honey were banned in Europe owing to the presence of illegal antibiotics in the honey; moreover, the honey was

actually made from an artificial sweetener (Schneider, 2011). The use of the phthalate plasticizer di-2-ethylhexyl phthalate to replace palm oil in food and drinks as a clouding agent has recently attracted the attention of regulatory agencies and the general public (Yang, Hauser, & Goldman, 2013; Yen, Lin-Tan, & Lin, 2011). The Taiwan food scandal in 2013 included the contamination of cooking oil, health pills, alcoholic beverages, milk, and rice (Yang et al., 2013).

Over the last decade, adulteration has been found not only in a wide variety of food, but also in feed products. The major agro-food commodities subjected to adulteration are spices (Everstine, 2013; September, 2011), edible oils (Lerma-Garcia, Ramis-Ramos, Herrero-Martínez, and Simó-Alfonso, 2010, and honey (Gallardo-Velazquez, Revilla, Loa, & Espinoza, 2009; Kelly, Downey, & Fouratier, 2004; Sivakesava & Irudayaraj, 2001a,b). In addition, adulteration of a wide variety of food products, including milk and milk products, fruit juice, alcohol, coffee, flour, meat products, and even fruits, is on the rise (Lakshmi, 2012; The Food Journal, 2013).

Food products have long complicated processing and supply chains, which make the products vulnerable to adulteration. Thus, authentication is important, both for official bodies in charge of labeling and for the industries where incoming batches of raw materials and finished products must be tested for compliance with specifications (Baeten & Dardenne, 2002). The authenticity of food must also be confirmed to maintain quality and consumer satisfaction, and possibly to prevent economic fraud. With increasing trends in food adulteration, fast, reliable, and competent analytical methods are needed to tackle authentication challenges and ensure product quality. A range of physical and chemical methods has been used for adulteration and authenticity detection in food and agricultural commodities. Physical methods usually look for physical parameters, such as density, texture, color, and solubility. Chemical techniques, such as chromatography techniques and mass spectroscopy, are based on chemical properties of the samples and have shown good robustness in component identification and adulteration detection in food commodities (Joshi, Pullala, & Khan, 2005). High performance liquid chromatography (HPLC) and mass spectroscopy are powerful analytical techniques, but undesirable when the work flow is relatively fast and the samples are expensive, as the sample is destroyed during the analysis. Currently, a range of vibrational spectroscopic techniques, in conjunction with chemometrics, have shown potential as sensitive and fast techniques for the authentication and quality analysis of a wide variety of agro-food samples. Advantageously, these techniques are non-destructive and are comparatively low cost.

In this review, we present an overview of four vibrational spectroscopic techniques (near-infrared (NIR), mid-infrared (MIR), Raman spectroscopy, and hyperspectral imaging (HSI)) for the determination of food authenticity and adulteration or contamination. The objectives of this review are:

(a) To present the characteristics, applications, potential, and limitations of these four vibrational spectroscopic techniques for food quality and authenticity evaluation.
(b) To demonstrate the importance and robustness of these techniques, both in industry and in the laboratory, for the analysis of food authenticity.
(c) To discuss the principles of spectroscopic chemometric techniques and improve the understanding of spectroscopic data analysis for quality prediction and classification of agro-food commodities.

In the introductory section, we have reviewed major food adulteration events, their consequences, and outlined the use of spectroscopic and other analytical techniques for the detection of food adulteration. The principles and major applications of various vibrational spectroscopic techniques in diverse fields, such as agro-food, pharmaceuticals, and petrochemicals, are discussed in the section on vibrational spectroscopic techniques. The analytical methods section describes the importance and advantages of chemometrics as a procedure to interpret spectral data and extract relevant information. The barriers and limitations of the spectroscopic techniques are summarized in the limitations section.

1.1. Vibrational spectroscopic techniques

Over the past several years, a number of vibrational spectroscopic techniques have been developed that allow complex chemical information to be determined about the samples being scanned. Different spectroscopic techniques operate over different and limited frequency ranges depending on the process being studied and the magnitude of the associated energy change. A schematic of typical vibrational spectroscopic techniques is shown in Fig. 1. A range of vibrational spectroscopic techniques, such as Fourier transform NIR, MIR, Raman spectroscopy, and HSI, have been widely and successfully used as sensitive and fast analytical techniques for the authentication and quality analysis of a variety of agro-food products. These techniques have the advantage of being non-destructive and have a relatively low analysis cost. In addition, these spectroscopic techniques can be adopted for both qualitative and quantitative analysis of agriculture and food products, and provide an alternative to wet-chemical and time-consuming techniques (Lohumi, Mo, Kang, Hong, & Cho, 2013).

The application of spectroscopic techniques is not limited to the agro-food sector, but has also successfully been used by the pharmaceutical and petrochemical sectors to identify suitable materials. New applications of spectroscopic techniques in the fields of chemistry, drugs, life sciences, and environmental analysis are being demonstrated and published daily (Baeten & Dardenne, 2002). An example of the use of spectroscopic techniques in the pharmaceutical industry is the comparison of the spectra of incoming materials with a library of NIR spectra to positively or negatively identify the compound (Luypaert, Massart, & Heyden, 2007); this method has been used to verify the chemical quality of 7-aminocephalosporanic acid (Andre, 2003). In a study on petroleum, Pasquini and Bueno (2007) investigated the potential of spectroscopy to characterize petroleum by predicting the true boiling point curve and estimating the API gravity.

1.2. Near-infrared (NIR) spectroscopy

NIR signals are associated with molecular vibrations, specifically the overtones and combinations of fundamental vibrations. Chemical bonds between light atoms, such as C—H, O—H, and N—H, generally have high vibrational frequencies, which result in overtone and combination bands that are detectable in the NIR region of 780–2500 nm (Osborne, Fearn, & Hindle, 1993). NIR spectroscopy is regularly used for both qualitative and quantitative analysis of agricultural and food commodities. NIR spectroscopy is very useful for studying bulk materials with little or no sample preparation. Originally, NIR spectroscopy was used only as an add-on unit to other optical devices, but in the 1980s, an NIR spectroscopy system was made available for the chemical analysis of products. The success of this technique was promoted by fast developments in the areas of hardware and software. Early NIR spectroscopy instruments were dispersive, in which the measurements at each wavelength were made sequentially, and the grating was moved between each measurement. This procedure is time-consuming, and the detector was assumed to be the main source of noise. Fourier transform near-infrared (FT-NIR) spectroscopy was