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Developing Infrared Spectroscopy Methods for Identification of Food Fraud and Authenticity: A Review

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ABSTRACT

In recent years, consumers have become increasingly concerned about the safety and authenticity of their food, as it directly affects their health. Food adulteration is a global issue that poses safety risks and is difficult to detect. Economically motivated adulteration (EMA) frequently results from the diversion of ingredients and unauthorized consumption, making food authenticity an important issue requiring appropriate identification techniques. Advanced detection methods like high-performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS) can identify adulterants but are limited by high costs and complex sample preparation. Therefore, fast, non-destructive, and accurate food adulteration detection techniques are essential. This review focuses on spectroscopic methods, including near-infrared (NIR), mid-infrared (Mid-IR), and Fourier transform infrared (FTIR) spectroscopy, for identifying food authenticity. Studies have shown that these methods, which offer rapid, non-invasive, and cost-effective physicochemical fingerprinting, have largely replaced classical analytical techniques, enhancing productivity and profitability in the food supply chain.

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Intorduction

With the increase in world population, food preparation has become a complex and vital issue in many countries, particularly developing ones. Along with the problem of food shortage, there has been an increase in food fraud, leading to consumption of harmful materials. To determine the appropriate price for their products in the target market,

manufacturers and distributors of unique ingredients must replace them with other products. Lack of regulations and opportunities for higher profit margins in different countries have resulted in fraudulent practices related to food authenticity (Adulteration, 2009). Food authentication is a critical process that involves verifying and matching the

information on a food label with the actual contents of the product. This process is crucial to ensure that the food is safe and of high quality. To achieve this, different approaches are used, most of which rely on identifying and eliminating contaminants. Counterfeiting is a common issue that affects many high-consumption foods such as cereals, dairy products, meat products, spices, honey, tea, and even some canned products like tomato paste (Frenich, Romero-González, and del Mar Aguilera-Luiz, 2014; Spink and Moyer, 2011). Depending on the materials used, some counterfeit products can pose serious health risks to consumers, including muscle cramps, nausea, diarrhea, neurological problems, allergic reactions, and palsy (Spink and Moyer, 2011; Agres 2015). In 2015, there were reports of peanuts and other allergens being added to cumin and paprika powder, similar to the disgraceful addition of melamine to milk powder in China in 2008 (Pei et al. 2011), 30% of Hicks' products in Southern Europe have incorrect labeling, and all exhibit signs of food fraud and inauthenticity (Spink and Moyer, 2011). Food fraud has significant economic and cultural impacts on society. With the rising occurrences of various types of food fraud and the limitations of current analytical methods in detecting them, it is essential to develop more accurate, convenient, and low-cost methods for fraud testing. The coverage of all potential food frauds is impossible, and therefore, the need for more effective methods is crucial (Oliveri and Downey, 2012; Bosque-Sendra et al., 2012). The use of electromagnetic waves, specifically near-infrared spectroscopy technology, can offer a quick, efficient, and non-invasive way to analyze a wide range of samples. Infrared spectroscopy is a commonly used method for detecting food fraud. López-Maestresalas conducted a study which demonstrated that NIR spectroscopy can be used to differentiate and compare minced lamb and beef used in food fraud (López-Maestresalas et al., 2019). This study demonstrates the robustness and reliability of NIR spectroscopy combined with chemical analysis in detecting food fraud. Over the past few years, a significant amount of research has been conducted on the topic of food fraud and authenticity in various food products such as fish, meat, milk, honey, and eggs. The number of published papers has increased from 530 papers between 2010 and 2014 to 1000 papers between 2015 and 2019 (Figure 1).

Methods

Search strategy

This review utilized databases such as Scopus, PubMed, and Google Scholar to locate and obtain abstracts, reports, and research articles on food authentication using spectrometry. Keywords included "food product," "fraud," "adulteration," "infrared," and "spectroscopy," with searches conducted in August 2022.

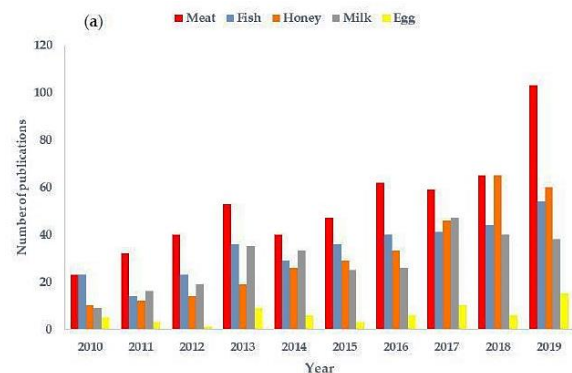


Figure 1. Temporal progress of reported studies on the authenticity of various types of animal origin foods during recent years (Hassoun et al., 2020).

Results and Discussion

Fraud and authenticity of food

food fraud and authenticity violations refer to any act of replacement, addition, or manipulation that violates industry rules and standards. The FDA has defined food fraud as any instance where a "poisonous or deleterious substance" is added to food that may harm health or contain an adverse food additive or coloring agent. Additionally, food can be considered adulterated if it has been irradiated in a manner that does not conform to the relevant irradiation regulations. The FDA has approved the irradiation of certain foods, such as uncooked meat that is refrigerated or frozen, uncooked fresh or frozen poultry, and seeds used for sprouting (Rahman et al., 2020). During the reign of Henry III, more comprehensive regulations were passed to address the issue of food adulteration. Some of the food additives that were commonly used in the 18th and early 19th centuries were found to be poisonous in the UK. One of the most significant subcategories of food fraud is Economically Motivated Adulteration (EMA), which is defined as intentional contamination of food to gain more profit. For instance, bakers used to add alum and chalk to flour to make bread look whiter. Also, to increase the weight of the final products, they would use mashed potatoes, calcium sulfate, pipe clay, and even sawdust (Evershed and Temple, 2017). Frederick Carl Accum was amongst the first to introduce such practices. After the scandal of melamine-contaminated powdered milk in 2008, it caused the death of 6 children and also the illness of 300,000 children. China has been embroiled in several industry scandals that destroyed the reputation of its dairy products. The issue sacrificed 300,000 in China in November 2008. Six babies' died of kidney stones and other kidney injuries, and 860 babies were hospitalized (Pei et al., 2011). The horsemeat scandal exposed vulnerabilities in Europe's food supply chain. (Spink and Moyer, 2011). Food fraud not only leads to consumer distrust but also results in losses to companies and governments, and reduces the market value of

affected brands. For instance, during the dioxin contamination crisis in Ireland, 1,800 individuals lost their jobs, and the estimated cost reached around \$138 million (Kennedy et al., 2009), Fraud on olive oil with filbert oil is estimated to cause losses. € 4 million a year for the European Union (Ozen and Mauer, 2002). Rodríguez et al. (2019) used Fourier transforms Mid-Infrared Spectroscopy (FT-MIR) to distinguish soybean, maize, and wheat flours. (de Santana et al., 2016) used MIR spectrometry and PLS-DA to differentiate between authentic rose oil and counterfeit rose oil, which often contains soybean, corn, and sunflower oils in varying proportions. (Deniz et al., 2018) reported that FTIR

spectroscopy is a worthwhile method to identify chicken or turkey meat in adulterated beef mixtures. (Chen et al., 2017) proposed using NIR spectroscopy and OCPLS classifier to rapidly and on-site screen melamine in milk. (Wang et al., 2018) discovered that near-infrared spectroscopy can detect frozen-thawed cycles in tilapia fillets in a non-destructive manner, with high potential for practical applications. According to (Candoğan et al., 2021), FTIR spectroscopy has been a beneficial method for structural or functional studies of foods as a prompt, nondestructive, inexpensive, and accurate physicochemical fingerprinting method (Table 1).

Table 1. Studies by infrared spectroscopy for detecting food adulteration

Food Products	Adulterated substance	Detect technique	Spectral range/Feature	Data processing	Reference
Pork	Liver and chicken	NIR	12500_3800 cm ⁻¹	PCA, PLS	(Rodríguez, Rolandelli, and Buera, 2019)
Lotus seed powder	Sweet potato powder, corn flour and wheat flour	NIR	10000_4000 cm ⁻¹	SVM, LS-SVM, PLS-DA	(Cai-li et al., 2018)
Rosehip oil	Soybean, corn, and sunflower oil	MIR	4000_600 cm ⁻¹	PLS-DA	(de Santana et al., 2016)
Neem and flaxseed oil	Edible vegetable oil or EVOO	FTIR	4000_600 cm ⁻¹	PLS	(Elzey, Pollard, and Fakayode, 2016)
Peanut oil	Vegetables, canola, and almond oil	FTIR	4000_600 cm ⁻¹	PLS	(Smithson et al., 2018)
Honey	HFCS	Vis-NIRS	400_600 nm; 1500_2000 nm	HCA; PCA; LDA; PLS	(Ferreiro-González et al., 2018)
Ground beef meat	Six types of beef and pork offal	FTIR	4000_550 cm ⁻¹	PCA, LDA, PLS-DA, KNN, SIMCA	(Hu et al., 2017)
Beef	Chicken or turkey meat	FTIR	4000_850 cm ⁻¹	PCA, HCA	(Deniz et al., 2018)
Milk	Melamine	NIR	10000_4000 cm ⁻¹	OCPLS	(Chen et al., 2017)
Milk	Melamine	2D hetero-spectral IR	4000_700 cm ⁻¹	NPLS-DA	(Yang et al., 2016)
Grape nectars	Apple or cashew juice	ATR-FTIR	4000_937 cm ⁻¹	SIMCA, PLS-DA, PLS-DM	(Miaw et al., 2018)
Coffee	Spent coffee grounds, roasted coffee husks, roasted corn, and roasted barley	ATR-FTIR/DR-FTIR	4000_700 cm ⁻¹	PLS-DA, HM, DF	(Reis et al., 2017)
Hazelnut paste	Almond paste and chickpea flour	FT-Raman and NIR	12000_3650 and 3200_290 cm ⁻¹	SIMCA	(Márquez et al., 2016)
Saffron	Sativus stamens, calendula, safflower, turmeric, buddleja, and gardenia	DRIFTS	4000_600 cm ⁻¹	PLS-DA	(Petrakis and Polissiou, 2017)
Black pepper	Sorghum or Sichuan pepper	DRIFTS	4000_400 cm ⁻¹	PCA, GA-SVM, PLS-D	(Hu et al., 2018)
Milk powder	HLP	NIR	11100_5880 cm ⁻¹	PCA, SIMCA, PLS, SVR	(Liu and Zhou, 2017)
Bovine meat	Detection of non-meat ingredients	FT-IR	4000–525 cm ⁻¹	PLS-DA, data fusion	(Nunes et al., 2016)
Pig	Identification of feeding regime	Portable NIR	900–1700 nm	LDA, QDA, and non-parametric Bayes	(Piotrowski et al., 2019)
Beef, lamb, pork	Species identification	FT-NIR	1100–1938 nm	(OC-PLS), SIMCA	(Pieszczyk, Czarnik-Matusewicz, and Daszykowski, 2018)
Pig lard	Origin identification	FT-NIR	750–2500 nm	PLS-DA	(Chiesa et al., 2016)
Tan mutton	Detection of thawed meat	NIR HSI	900–1700 nm	PLS-DA	(Li, Peng, and Zhang, 2019)
Pacific white shrimp	Origin authentication	NIR HIS	874–1734 nm	PLS-DA, LS-SVM, ELM	(Sun et al., 2019)
Norwegian salmon	Species identification	FT-IR	4000–450 cm ⁻¹	PLS-DA	(Wu, Zhong, and Yang, 2018)

Tilapia	Detection of thawed fish	NIR	1000–2500 nm	PCA	(Wang et al., 2018)
Goat milk	Detection of adulterants	FT-NIR	10000–4000 cm ⁻¹	PCA, Q-control, k-NN, SIMCA, and PLS-DA	(da Paixao Teixeira et al., 2020)
Milk powder	Detection of adulterants	NIR	850–2499.5 nm	PLSR	(Ejeahalaka and On, 2020)
Milk	Species identification	NIR	700–2500 nm	PLS-DA	(Mabood et al., 2017)
Milk	Species identification	FT-IR	1700–600 cm ⁻¹	PCA and HCA	(Cirak, Icyer, and Durak, 2018)
Duck, beef, pork	Species identification	NIR	12500–5400 cm ⁻¹	DA, PLSR	(Leng et al., 2020)
Raw chicken	Species identification	FT-IR	4000–500 cm ⁻¹	HCA, ANN	(Candoğan, Altuntas, and İğci, 2021)

Introduction to infrared vibrational spectroscopy

Infrared spectroscopy, also known as FTIR spectroscopy, is a comprehensive method for detecting food fraud (Ellis et al., 2012) In the 9th century, Herschel discovered infrared energy, but it wasn't until the 1950s that it was first applied in industry. Initially, near-infrared spectrometers were only used as supplementary instruments for other optical devices that utilized wavelengths like visible ultraviolet. In the 1980s, mid-infrared spectrometers were developed, but they were mainly used for chemical analysis. However, with the advent of fiber optics in the mid-1980s and monochrome instruments in the early 1990s, infrared spectroscopy became a valuable technique for scientific research. Today, near-infrared spectrometers are widely used to quickly and non-destructively measure biological material compositions for various products. Identifying functional groups in organic molecules is a valuable qualitative technique that defines their composition and structure (Agres, 2015). Each bond has a unique natural vibration frequency, and a bond in two different molecules is in a distinct environment. Therefore, two molecules with different structures will never absorb the same infrared or the same infrared spectrum. Although the absorbed frequencies in the two molecules are similar, two different molecules will never have identical infrared spectra. Hence, the infrared spectrum can be used as a unique identifier, like a fingerprint, to identify molecules in human (Sicherer, Eigenmann, and Sampson, 1998).

In addition, fraud detection in juices, drinks, beer, and alcoholic beverages has been reported. Combination studies using NMR-H LC-MS have been performed to analyze aromatic compounds and directly detect fraud in various drinks (Gil et al., 2003). A recent study examined the impact of changes in water levels on oranges and strawberries. The findings indicated that the spoilage of fruits is significantly related to a decrease in water content. Furthermore, the study revealed that we can use supervised and unsupervised chemical methods to classify a wide range of foods based on NIR spectral information.

Conclusions

This study explored the potential of non-destructive analytical techniques for distinguishing food adulterations. Infrared spectroscopy, particularly NIR and FTIR, proved to be the most promising methods due to their cost-effectiveness and applicability to large-scale operations. Integrating spectrophotometric data further enhances the analysis, offering a comprehensive solution to the complexities of food fraud detection.

Declarations

Conflict of interest

The authors declare no conflict of interest.

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Consent for publications

The authors approved the manuscript for publication.

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Authors' contributions

MP led the overall conceptualization of the review and was responsible for the initial drafting and structure of the manuscript. NS conducted a comprehensive literature search and contributed to the synthesis and analysis of the reviewed studies. SP, as the corresponding author, managed the coordination of the review process, ensured the accuracy of the data synthesis, and provided critical revisions to the manuscript. SMK assisted with the extraction and analysis of data from the literature and contributed to writing sections of the review. YM supported the manuscript with critical insights and revisions, and ensured the clarity and coherence of the final text. All authors reviewed and approved the final version of the manuscript.

Ethical considerations

All ethical issues, including plagiarism, misconduct, data fabrication, falsification, double publication, or submission redundancy, have been fully observed.

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