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FOOD FINGERPRINTING : A NOVEL APPROACH FOR AUTHENTICATION OF FOOD

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ABSTRACT

Authentication is the process of confirming the characteristics listed on a product's label as well as assessing the extent to which food has been tampered. Food adulterations and frauds have skyrocketed in the last few years. A range of methodologies that offer analytical signals about the food's composition in a non-selective manner are officially referred as fingerprinting methods. In the realm of food authentication, there are two primary approaches: targeted and untargeted. These methods include GC-MS, HPLC, NMR spectroscopy, Raman spectroscopy and IR spectroscopy. Significant benefit of IR and other spectroscopic approaches is their ability to provide inexpensive, quick and non-destructive examinations with high throughput. The act of fingerprinting is driven by the desire for quick and easy financial gain. When it comes to food authenticity, the focus is on biomarkers particularly metabolites that can identify different geographic origins, production methods, and molecular evidence of food adulteration or spoilage. Therefore, food fingerprinting has the potential to improve current regulatory frameworks by uncovering important aspects of food safety and authentication.

Key words : Food Fingerprints, Authenticity, Spectroscopy, Adulteration, Biomarkers.

Introduction

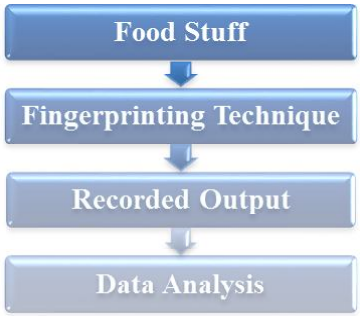
Food fraud is a growing global problem and it poses a threat to both the food industry and consumers' trust. The term "fraud" refers to the deliberate attempt to deceive consumers about the content and quality of food products, usually done to increase the supplier's profits. Adulteration of food can lead to major health problems and weaken public confidence in government and food sector authorities. Adulterating can also disguise counterfeit goods, add volume and weight, and swap genuine ingredients with less expensive ones. Although it is illegal to intentionally tamper with food and beverages for the purpose of deceiving consumers, the lure of making fast and easy money is becoming more prevalent and is affecting a wide range of food and drink products. Effective vigilance must be maintained at all times to ensure food safety in the face of potential adulteration and contamination (Llano *et al*., 2018).

Global interest in food product authenticity has surged with the development of techniques to detect falsification, mislabeling and counterfeiting. Various stakeholders (Macready *et al*., 2020) such as legal authorities, businesses, trade associations, academic institutions, consumers and food producers have expressed serious concerns regarding food authenticity. A variety of laws, both domestic and global, ensure that food labels accurately protect public health. New scientific technology is constantly advancing (Abbas *et al*., 2018) to maintain food authenticity like food fingerprinting.

Food fingerprints are molecular indicators that can determine the condition of food, allowing for better discrimination between products. It's a system of markers that helps to verify the authenticity of food, for instance "Are those organic tomatoes really organic? Is Kashmir

the genuine source of this saffron? Is any adulterant present in the food?" (Cubero-Leon *et al.*, 2018). However, finding these fingerprints is crucial for ensuring the products' safety and quality. The most promising method for food fingerprinting at the moment appears to be a combination of current spectroscopic approaches based on NMR, IR, and sensor technologies, among others, with well-known and established high-resolution analytical techniques, such as mass spectrometry techniques. Establishing the composition of a product and certifying its integrity is crucial in detecting fraud, adulteration, and contamination (Tette *et al.*, 2017). The food fingerprint can be used to ensure that food is genuine, traceable, and free of contaminants and unwanted substances. This provides greater protection for consumers and promotes transparency and knowledge about food (Camara *et al.*, 2022).

Food composition is typically analyzed through non-selective fingerprinting procedures which result in a spectral fingerprint. Food items can be identified by analyzing their unique patterns through mathematical algorithms. The process of analyzing food using fingerprinting techniques is relatively straightforward process, as shown in the diagram below:



The samples can be inspected either right away or after a simple extraction process. The data obtained from analysis is processed using the suitable statistical techniques, which vary depending on the specific problem. In several cases, it is feasible to verify the assertion regarding the origin of a particular food item and also validate the authenticity of a product using specific technological methods (Ahad and Nissar, 2017).

Few key terms related to food are listed below

- **Authentication** is verifying a product's attributes and determining whether or not it has been tampered. Specific chemical parameters are employed in the authentication processes to distinguish between contaminated and authentic food. When authenticating the products, various factors such as the products' origin, diversity and production methods need to be considered (Bohme *et al.*, 2019).
- **Traceability** is the method by which the relationship between a food product and its material source is confirmed. The pathways of the various stages in a production chain are determined by traceability techniques by analyzing the chemical characteristics. Food samples might be verified as authentic, if they could be traced back to their original ingredients (Saadat *et al.*, 2022).
- **Food fraud** is selling a cheap product at the price of a premium. Food fraud is therefore frequently considered an economic crime, even if it has extremely detrimental effects on customers' health (Guntzburger *et al.*, 2020).
- **Adulteration** is done in food product so as to remove some of its valuable ingredients by introducing fake or inferior items. A product may be given a false strength or additional weight in order to improve its overall look, or it may be added to increase its weight (McVey *et al.*, 2021).

Here are a few instances of food fraud (Saadat *et al.*, 2022):

- Substituting or combining various seafood types; for example, certain varieties of sea trout have been marketed as salmon.
- Switching or merging different kinds or varieties of meat; for instance, mixing sheep meat with donkey or horse meat.
- Combining various fruit juices and/or increasing their sugar content. For instance, orange juice and apple juice have been combined and marketed as orange juice.
- Artificial agents are substituted, mixed, or added to vegetable oils. For instance, pure olive oil is sold after being blended with other vegetable oils, colourant, and/or artificial flavouring.
- Substitution or blending of dairy products of variable quality; for instance, milk has been incorporated with water to elevate its weight.

Food biomarkers

Biomarkers can be used to measure nutritional status of products more accurately. A nutritional biomarker is an objective feature that can be used to quantify biological samples and determine nutritional status based on dietary ingredient consumption or metabolism (Pico *et al.*, 2019). Various substances can be used as biomarkers for food authentication, such as organic acids, phenolic compounds, amino acids, and other volatile organic compounds that belong to different chemical classes. Numerous analytical platforms must be used in order to obtain reliable

methodologies for the detection and quantification of biomarkers that certify the origin, variety, or production system of food items, as well as for the detection of food adulteration or spoilage/freshness indicators.

Highly efficient methods have been created to identify particular metabolites that aid in the differentiation of samples. These metabolites track metabolic alterations in numerous foods and have the potential to be valuable biomarkers of authenticity. Depending on various varieties/cultivars, production systems, geographical origin, adulteration techniques and spoilage/freshness indications, the most significant biomarkers and biological processes involved in food authenticity and safety are listed in Table 1.

1. **Varieties or cultivars :** Nevertheless, it gets increasingly harder to identify between varieties or cultivars as food processing advances, and this fact is frequently exploited to commit food adulterations. Determining and eventually quantifying particular metabolites may provide a solution to this issue. The interpretation of the data should take these interferences into account, as minor differences such as the age of the plant samples might result in a distinct metabolic profile (Medina *et al*., 2018), which plays a vital role in distinguishing different varieties.
2. **Production systems :** Levels of specific phytochemicals may be impacted by the processes used in the manufacture of different foods. The impact of farming, rearing, or feeding practices on the metabolites profile of various foods (food metabolome) has been examined using variable biomarkers in several studies (Cubero-Leon *et al*., 2018). Here, phytochemicals act as important biomarkers.
3. **Geographical origin :** A substantial requests from consumers for more precise labelling of the food's origin have sparked excellent scientific studies employing innovative technologies. Strong statistical approaches were needed to extract the pertinent aspects associated with the product origin and enable an evaluation of the product origin's impact (Klockmann *et al*., 2016) on the food metabolome. It is particularly significant for goods like wines, honeys, cheeses and olive oils, whose uniqueness is determined by their origin and organoleptic qualities (Pattamayutanon *et al*., 2017).
4. **Food adulteration :** Food adulteration is a big problem these days since additives are frequently added to food to make it more substantial, hide spoiling and improve its qualities. The markers retrieved from a chemometric studies are sufficiently dependable to identify these adulterations. Olive oil is more frequently altered with other, less expensive oils from various species because of its higher market worth (Azadmard-Damirchi, 2010).
5. **Spoilage and freshness markers :** The complicated process of food spoiling is influenced by numerous parameters, including temperature, moisture content, pH, and oxygen. When food degrades, it produces hazardous metabolites that can be harmful to humans. Therefore, it's imperative to ensure food safety by identifying the primary indicators of food deterioration (Kuuliala *et al*., 2018). Food freshness also guarantees food safety and aligns with consumer preferences, at least when it comes to the harmful effects of spoiling (Parlapani *et al*., 2015).

Acquiring food fingerprints

Food safety, authenticity, and quality can all be determined by obtaining food fingerprints. The sample preparation and analytical platforms' are important parameters for evaluation and should be carefully chosen in order to create an experimental design that is appropriate for sample. Food safety and authenticity are tracked using a variety of analytical methods, including spectroscopy and chromatography. Mass spectrometry techniques are particularly well-liked because they can discern minute variations among materials in intricate matrices. To ensure food authenticity, further analytical techniques are also frequently used.

In particular, a fingerprinting method works well for (Ahad and Nissar, 2017).

- Product authentication in the absence of target analysis based on particular markers.
- The identification of unidentified adulterants.
- Quick and high-throughput sample screening prior to more complex confirmatory analysis.

Method of analysis

Apparently, there are targeted and untargeted approaches for analyzing the realm of food authentication. The untargeted technique's primary intent is to distinguish between patterns of metabolites that may be altered by environmental, genetic, or human modifications, whereas the targeted approach concentrates on an assessment of a particular metabolite or collection of metabolites (Llano *et al*., 2018).

Table 1 : Specific biomarkers in food stuff indicating variable applications and techniques.

Food stuff	Biomarkers	Applications	Techniques	References
Grape juice	Catechin, chlorogenic acid, epicatechin, gallic acid, myricetin, *p*-coumaric acid quercetin	Production systems	HPLC-DAD HPLC-FLD	Granato *et al.* (2015)
Apple	Alanine, citramalic acid, citrate, epicatechin, galactose, isoleucine, myo-inositol, quinic acid	Species, Varieties or cultivars	NMR	Eisenmann *et al.* (2016)
Date	2,3-Butanediol, cinnamaldehyde, hexanal, hexanol	Species/Varieties	GC-MS	Khalil *et al.* (2017)
Tomato	β1-Tomatine, dehydrotomatine, tomatidine	Production systems	HPLC-LTQOrbitrap MS	Caprioli *et al.* (2014)
	2-Methyl-6-methyleneoctan-2-ol, 2,2,6-Trimetylcyclohexanone, 3- octanone, 4-octadecylmorpholine, (*Z*)-methyl-3-hexenoate	Species, Varieties or cultivars	GC-MS	Figueira *et al.* (2014)
	Fructose, glucose, fatty acids, alanine, methanol, acetylglutamic acid, GABA, glutamine, glutamic, aspartic acids. trigonelline, tryptophan, tyrosine	Geographical origin	NMR	Mallamace *et al.* (2014)
	Fructose, citric acid and malic acid	Varieties	NMR	Sanchez Perez *et al.* (2011)
Wheat	Protocatechuic acid	Production systems	LC-HRMS	Weesepoel *et al.* (2016)
Meat	3-Oxohexadecanoic acid glycerides, arabitol, citric acid, oleic acid, creatinine, ethanolamide, glycine, malic acid, PG(36:4), phosphate, myo-inositol, pentadecane, pyroglutamic acid, heptadecane, glucose 6-phosphate, Ncarboxyethyl-gaminobutyric acid, decanoylcholine, TG (16:0/15:0/18:4), xi-2-ethyl-1-hexanol	Adulteration	GC-MS; UHPLC-MS	Trivedi *et al.* (2016)
Saffron	Picrocrocin, glycosyl esters of crocetin	Geographical origin	NMR	Sobolev *et al.* (2014)
	Curcuminoids, fatty acids, picrocrocin, glycosyl esters of crocetin	Adulteration	NMR	Petrakis *et al.* (2015)
Manuka honey	Terpineol	Geographical origin	HPLC	Lin *et al.* (2017)
Olive oil	Terpenes, squalene, linoleic acid, aldehydes, b-sitosterol	Geographical origin	NMR	Sobolev *et al.* (2017)
	Oleic acid, saturated fatty acids, the total content of triacylglycerols	Varieties	NMR	Piccinonna *et al.* (2016)
Carrot	Arabinofuranosyl-[a-L-arabinofuranosyl]-L-arabinose, chlorogenic acid, citric acid, Larginine, sedoheptulose	Production systems	UHPLC-MS	Cubero-Leon *et al.* (2018)
Apple juice	4-*O*-*p*-Coumarylquinic acid, abscisic acid, arbutin, isorhamnetin-3 -*O*-rutinoside	Adulteration	HPLC-PDA; LC-MS/MS; NMR	Willems and Low (2018)
Milk	Linoleic acid, oleic acid, saturated fatty acids, triacylglycerol, cholesterol contents	Adulteration	GC-MS	Kim *et al.* (2015)

Table 1 continued...

Table 1 continued...

	N-acetylcarbohydrates, ethanolamine, carnitine, citric and amino acids, citrate, lecithin, acetate, creatine D-sucrose	Species	NMR	Li *et al.* (2017)
Oyster	Dimethyl sulfide, trimethylamine	Spoilage and freshness	Bioelectronic nose; GC-MS	Lee *et al.* (2018)
Wine	Catechin, epicatechin, sinapic acid, syringic acid, vanillic acid, epicatechingallate, epigallocatechin, *p*-coumaric acid, *p*-hydroxy benzoic acid, caffeic acid, gallic acid, gentisic acid, chlorogenic acid, epigallocatechin gallate	Geographical origin	HPLC	Sun *et al.* (2015)
Egg	Nitrosotrimethylurea, putrescine,	Spoilage	GCxGC-TOF-MS	Cheng *et al.* (2015)
Citrus fruits	Carotenoids	Freshness	Raman spectroscopy	Nekvapil *et al.* (2018)

The following techniques regarding fingerprinting were explored:

- Nuclear Magnetic Resonance Spectroscopy (NMR)
- Gas Chromatography-Mass Spectrometry (GC-MS)
- High Performance Liquid Chromatography (HPLC)
- Infrared Spectroscopy (IR)
- FT- RAMAN Spectroscopy

Nuclear Magnetic Resonance Spectroscopy (NMR) : In the late 1800s, Zeeman made the initial discovery of the peculiar reactions of specific nuclei to intense magnetic fields. However, the application of this phenomenon, *i.e.* "Zeeman effect," did not occur until the 1950s, when NMR spectrometers were made publicly accessible. Analyzing molecules by observing how radiofrequency electromagnetic radiation interacts with their nuclei while they are in a strong magnetic field is known as nuclear magnetic resonance (NMR) spectroscopy. It is a physicochemical method which determines the structural details of molecules.

A superconducting magnet, a probe and a sophisticated electronic system (console) run by a workstation make up the three primary parts of an NMR spectrometer. Sample preparation is usually minimal or nonexistent, and it allows for the collection of an entire metabolic profile in a single experiment.

NMR works on the key concept that certain nuclei exist in particular nuclear spin states in response to external magnetic fields. Nuclear spin, an inherent characteristic of atomic nuclei, changes as a result of net energy exchange due to radiofrequency electromagnetic radiation interaction with sample (Carreras, 2021). The detector records this energy shift, and the data is shown on the display panel. Numerous compounds present in a sample can have their chemical structures determined and their fingerprints identified using spectroscopy.

High performance liquid chromatography (HPLC) : With the objective of isolating, recognizing, and quantifying the active components, this particular type of column chromatography is typically utilized in biochemistry and analysis. The main components of HPLC are a column that's filled with packing material (stationary phase), a pump that circulates the mobile phase(s) across the column, and a detector that displays the molecules' retention durations. The interactions among the stationary phase, the molecules under study, and the solvent(s) employed determine the retention time. A tiny amount of the material to be analyzed is added to the mobile phase stream, and it is hindered by particular physical or chemical associations with the stationary

phase. The kind of analyte and the chemical nature of the stationary and mobile phases determine the extent to which retardation occurs (Malviya *et al*., 2010). The process of gradient elution involves separating the sample molecules in order to change the composition of the mobile phase during the analysis. Analyte mixtures are separated by the gradient according to the analyte's affinity for the currently existing mobile phase (Sadapha and Dhamak, 2022).

Gas Chromatography-Mass Spectrometry (GC-MS) : A very potent analytical method for identifying various chemicals in a test sample is GC-MS, which combines the capabilities of mass spectrometry and gas chromatography. Although mass spectrometry works well for identification, gas chromatography is the most effective method for separation. Therefore, this device separates mixtures of chemicals and molecularly identifies the components. It is appropriate for metabolite analysis that has a lower boiling point, low degree of polarity, or volatile post-derivatization. Since, it can conduct a 100% specific test that verifies the existence of a certain chemical, GC-MS has earned the reputation of being the "gold standard" for substance identification.

Gas chromatography involves passing the analyte to be examined through a column that has been packed or coated with a stationary phase using a gaseous mobile phase (inert gas such as argon, helium, or nitrogen). The chromatography column is a lengthy tubular column into which the sample is inserted. Certain substances take longer than others to move through the column, therefore the substances in a sample are isolated from one another. The length of time an analyte spends in the stationary phase as opposed to the mobile phase determines its retention time (Pramod *et al*., 2021). Analytes with polarity closer to the stationary phase have longer retention durations. Later on analytes are passed into mass spectrometry where an ion source, a detector, and a mass analyzer are its three elements. A fraction of the material is transformed into ions by the ioniser (Al-Bukhaiti *et al*., 2017). When an ion travels across or collides with a surface, the detector captures the current or charge that is generated. The mass to charge ratio of the ions is indicated by the mass spectrum.

Infrared Spectroscopy (IR) : The measurement of the absorption, emission, or reflection of infrared radiation by matter is known as infrared spectroscopy, also referred to as vibrational spectroscopy or IR spectroscopy. It is employed to investigate and distinguish between solid, liquid, and gaseous forms of chemical compounds or functional groups (Karthika *et al*., 2022).

An infrared light beam is directed through the sample by the source. The unabsorbed beam is now reflected to travel through a detector after passing through a grating, which is a more sophisticated monochromator. Once the processor has processed the data that went through the detector, the necessary reading is finally printed out.

FT-RAMAN Spectroscopy : The electron remains in the system's true electrical level as this transitory virtual state decays, and the photon leaves the system. The scattering is said to be elastic (also known as Rayleigh scattering) if the energy of the scattered photon is equals to that of the entering one and the involved electron heads back to its initial state with the same energy. Inelastic scattering occurs when these conditions are not met. An electron's energy gain or loss during inelastic scattering is equal to the difference among the initial and final electronic energy states. A stokes scattering occurs when the energy of the departing photon is less than that of the entering one, an anti-stoke scattering occurs when the two have the opposite energy. Raman shift refers to the energy disparities between the entering and exiting photons (Orlando *et al*., 2021). Only one out of every 108 dispersed photons will experience Raman scattering, making it a notably weak phenomenon in comparison to Rayleigh. The Rayleigh component is removed from Raman spectrometers using a device of some sort, typically a notch filter.

Usually, a near-infrared laser is selected (Ahlawat, 2014). A laser is employed to excite the sample in an FT Raman instrument. The scattered rays emitted by the sample are gathered by a lens and travel via a filter that efficiently blocks Rayleigh scattering. A high-sensitivity detector then identifies only those rays coming from the raman scattering and executes a fast Fourier transform on an acquired interferogram.

Data analysis

A significant amount of data is produced by fingerprinting procedures. The majority of the data could not be helpful in resolving issues with identity, verification or authentication. For the purpose of solving the issues under investigation, mathematical techniques need to be implemented to this data. Using the fingerprint of a sample, these technologies create a model that can answer any query, like "Are the contents of the product truly what the label claims it is?".

A mathematical equation can be used to transform measurements obtained from a fingerprinting technique, possibly hundreds or even thousands, into a single indicator, or number. This is known as a mathematical model. In food authentication applications, the value of this number

can be used to determine if the product under examination complies with labelling claims regarding its origin or manufacturing process. This can be accomplished using a variety of mathematical techniques, including:

- PLS-DA (Partial Least Squares – Discriminant Analysis)
- SIMCA (Soft Independent Modeling of Class Analogy)
- ANN (Artificial Neural Networks)
- NOPLS (Non-Orthogonalised Partial Least Squares)
- SVM (Support Vector Machines)

Conclusions and Future Perspectives

Foods undergo biochemical alterations brought on by human activity, genetic diversity, or the environment that produce distinct variances, which can be employed as indicators of those items. Owing to the diverse physicochemical characteristics of these compounds, multiple analytical platforms need to be utilized to derive dependable methods for identifying and measuring biomarkers that can affirm the origin, variety, or production system of food items, as well as identify food adulteration or indicators of spoilage or freshness. The capacity to distinguish between authentic and counterfeit meals and beverages is enhanced by the use of untargeted methods. The verification of the genuine nutritional profile of distinct food items is crucial for ensuring their market worth and integrity.

Although, numerous encouraging biomarkers for culinary authenticity have been described in this review, lots of them still need more comprehensive confirmation steps. More routine analysis-enabling technology should become available soon to enable fast monitoring of food authentication, which should speed up this procedure.

When paired with chemometrics, product fingerprinting is an effective tool for controlling and detecting fraud concerning food goods and other biomaterials. Effective analytical results intend to make it possible to precisely measure a specific biomarker in addition to validating its existence, a characteristic that will be crucial for determining spoiling markers. Furthermore, nondestructive analytical techniques for on-site and real-time food verification will undoubtedly be drawn from NMR. For these methods to be effective, "user-friendly" chemometrics methodologies along with authentication biomarker must be established. Customers in the future certainly will be even more knowledgeable and demanding when it comes to food integrity, expecting that food be produced using environmentally friendly and animal welfare-compliant sustainable practices in addition to being safer and healthier. The widespread adoption of chemometrics techniques and improvements in analytical tools are capable of producing massive amounts of data simultaneously, which have led to an increase in the use of fingerprinting techniques in recent years.

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