Non-Destructive Methods in the Detection of Food Adulteration

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Economically motivated food adulteration or food fraud is currently recognized as a global threat to public health and a major food safety concern. The detection methods of food adulteration are often time consuming and involve high-end mechanisms. Therefore, considerable interest has emerged for non-destructive, rapid techniques so as to achieve highly efficient results with use of minimal analytical technology. Although sophisticated lab techniques are accurate, precise, and reliable, yet they are costly and time consuming. It is essential to develop screenings tests which are reliable and quick. "Non-destructive detection of food adulteration" indicates that the analysis of the sample and the collection of its essential features are made in such a way that the physical and chemical properties of the food are not altered.

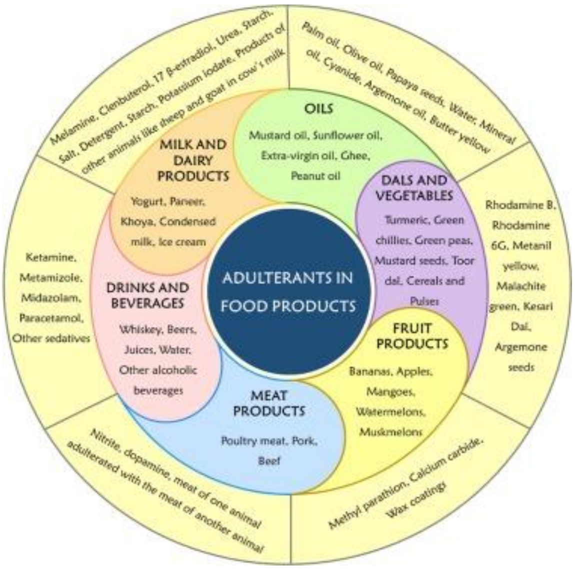

Fig. 1: Common adulterants present in different food products (Source: Ray et al., 2022)

Current Scenario of Food Adulteration

Food Adulteration is performed to achieve more quantity of the food in order to make more profit, following the addition of such chemical substances which should not be present legally or having unwanted status by the recipient. It is astonishing that impostors are at stride ahead of food safety organizations; their escalating technologies protect and allow them to become more refined in their work with each passing moment. Food fraud includes the substitution of an ingredient with a cheaper alternative, miss description of the real nature of the product or one of its ingredients, incorrect quantitative ingredient declaration, and the utilization of non-acceptable processing practices such as irradiation, heating or freezing. There are various packaging techniques to protect food from external damage, but the question remains that, is the food itself safe? Or is it adulterated with contaminants/adulterants which ultimately pose a threat to human health? Hence, to address this issue, such techniques need to be developed through which time and cost-effective rapid analysis of adulteration can be performed.

Type of Methods

The recently developed analytical methods of food adulteration are non-destructive in nature based on experimental researches conducted with different food items. Based on their working principle and techniques, such methods can be divided broadly into:

(i) Non-DNA based and (ii) DNA based techniques.

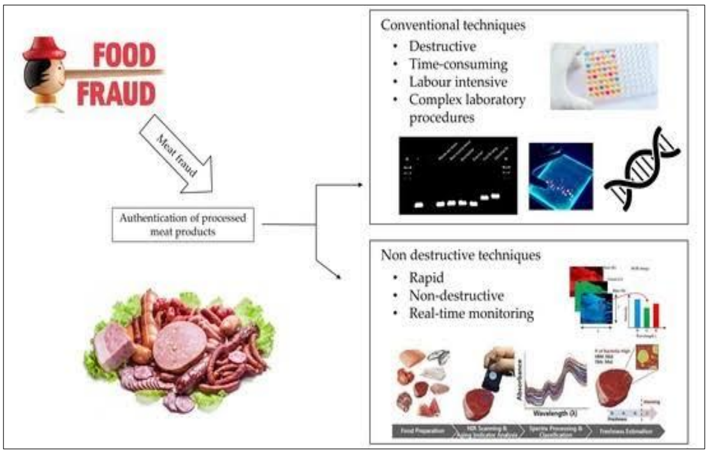

Fig 2. Comprehensive analytical techniques used to detect adulteration in food (Source: Edwards et al., 2021)

Non-DNA based Techniques

Analysis of adulteration by Mass Spectrometry (MS)

Mass spectrometry is an analytical technique for the separation of ionized atoms and molecules according to their mass-to-charge ratio using electrical and magnetic fields in a vacuum and identifying the composition and structure of the chemicals. There are various methods which uses the principle of MS, such as:

Gas chromatography-mass spectrometry (GC-MS): This combines gas chromatography and mass spectrometry to identify different substances within a sample. This method is effective in separating compounds into their various individual components and the identification of the specific substances. The GC-MS method combines the capabilities and advantages of both GC and MS analytical approaches. GC-MS combines high resolution separation of components, making it possible to achieve a high level of precision in the identification of unknown chemicals that cannot be achieved using GC or MS separately. GC-MS method has been developed for the detection of honey adulteration with high fructose inulin syrups.

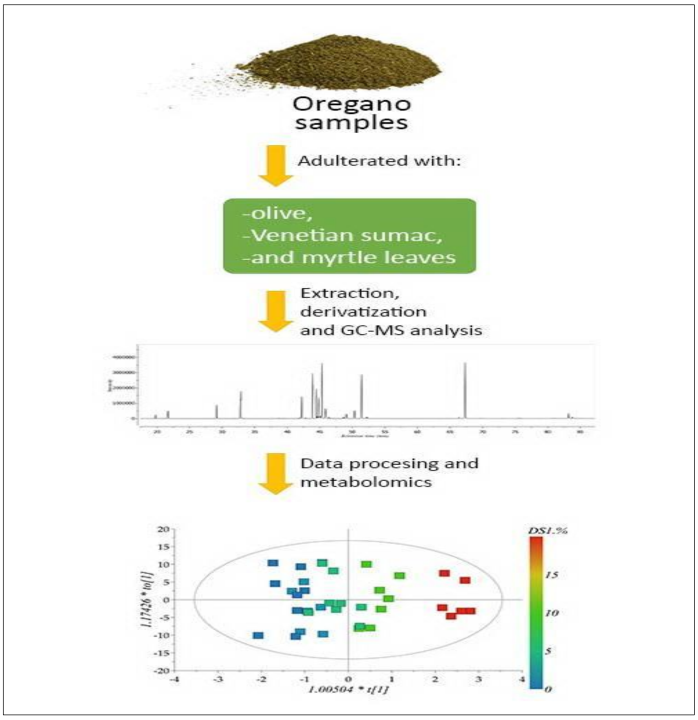

Fig 3. GC–MS-based metabolomics for the detection of adulteration in oregano leaves (Source: Ivanović et al., 2021)

Proton Transfer Reaction Mass: PTR-MS utilizes chemical ionization that is based on proton-transfer reactions; hydroxonium ions H3O+ are used as the reagent ions since the volatile compounds have a higher affinity for these ions. This analytical technique has been used for adulteration detection of individual cultivars of extra virgin olive oil through the analysis of volatile organic compounds, when the fraud involves mixing valuable oil with cheaper oils or by mixing the oil of different cultivars. The instrument has a high sensitivity (i.e., pptv level), fast response time (~1 second) and a compact and robust setup. It is relatively inexpensive and can be fully automated.

Mass Spectrometry with Inductively Coupled Plasma (MS-ICP): This method utilizes inductively coupled plasma as the ion source and a mass spectrometer for separation and detection. It is characterized by high sensitivity and the ability to identify metals and nonmetals, and in some instances at concentrations not exceeding 10– 10 % or one part per 1012 (trillion) parts. The MS-ICP method makes it possible to obtain isotopic information on the elements determined. Determination of the geographical origin of rice is an example of a practical use. This can prevent possible mislabeling and/or adulteration of rice products.

Isotope Ratio Mass Spectrometry: The main elemental constituents (H, C, N, O, and S) of bio-organic material have different stable isotopes (^{2}H, ^{1}H; ^{13}C,^{12}C; ^{15}N,^{14}N; ^{18}O,^{17}O,^{16}O; ^{36}S, ^{34}S, ^{33}S, and ^{32}S). Isotopic ratios can be measured precisely and accurately using Isotope Ratio Mass Spectrometry (IRMS). Analysis of these ratios shows potential for assessing the authenticity of food of animal origin. Researchers have demonstrated that δ^{13}C and δ^{15}N isotope values of fat and defatted fraction have different values between each other depending on if a cheese was produced with raw milk or with pasteurized milk thus allowing differentiation between these 2 kinds of product. Juice adulteration is achieved by either dilution of juice concentrate with water or addition of exogenous sugars. Such products can be detected by measuring 18O, the measurement of the 13C/12C ratio, or the deuterium content D/H of sugars isolated from the juice, thus making it possible to identify adulterated juices.

High-Performance Liquid Chromatography: It involves the application of high pressure (400 bar) and a fine-grained sorbent (a granular material made of solid particles 3-5 micrometers in size) to separate a complex mixture of substances quickly and completely (average analysis time is 3-30 min) with high resolution. HPLC effectively analyzes the presence of synthetic dyes in food and detects the fraudulent addition of bergamot juice to lemon juice by identifying flavanones of bergamot fruit.

Analysis of adulteration by Spectroscopic techniques

These are the most promising methods as they are quick, simple, require small quantities of the food/sample, and are usually non-invasive. Miniaturization of spectrophotometers and the manufacture of portable or hand-held instruments i.e. in-situ measurements have become a reality. There are many portable spectrophotometers on the market today. They can measure reflectance or transmittance of food/samples and can be used for direct measurement without sample pre-treatment. Some important spectroscopic methods include:

Fluorescence Spectroscopy: Fluorescence spectroscopy utilizes fluorescence emission and excitation spectra of electromagnetic radiation for qualitative and quantitative analysis of the structure and properties of a sample. It is an active process, which is why it is characterized by a high sensitivity. In addition, this technique is very rapid, low-cost and provides non-destructive interaction with the sample. Fluorescence spectroscopy has been utilized for the detection of adulteration of extra virgin olive oil with olive-pomace oil at a level of 5%.

Fourier Transform Infrared Spectroscopy (FTIR): This method works on the principle of interaction of electromagnetic radiations with the molecules of specific food with defined energy. The sensitivity of FTIR ranges from very low parts per million (ppm) to high percent (%) levels. FTIR has been successfully applied to detect grape juice in pure pomegranate juice concentrate and determine the presence of industrial grade glycerol in four brands of red wine at a detection limit of 1%.

Nuclear Magnetic Resonance Spectroscopy: NMR spectroscopy is a technique based on the analysis of the magnetic properties of atomic nuclei that possess spin. NMR spectroscopy is able to qualitatively and quantitatively detect very fine structural components. The adulteration of virgin olive oil with a wide range of seed oils was detected at level as low as 5% by means of application of NMR spectroscopy.

Raman Spectroscopy (RS): This provides spectral information on fundamental vibrations of functional groups in a molecule. It is based on the inelastic scattering of incident radiation through its interaction with vibrating molecules. If a sample has Raman active substances, a small amount of radiation is scattered at different wavelengths due to interactions between the incident electromagnetic waves and the vibration levels of the Raman active molecules in the sample. Surface Active Raman Scattering (SERS) has been used to detect melamine in liquid milk with minimal sample preparation which yielded precise results. This is a simple, fast (only requires about 3 min), cost effective and sensitive method.

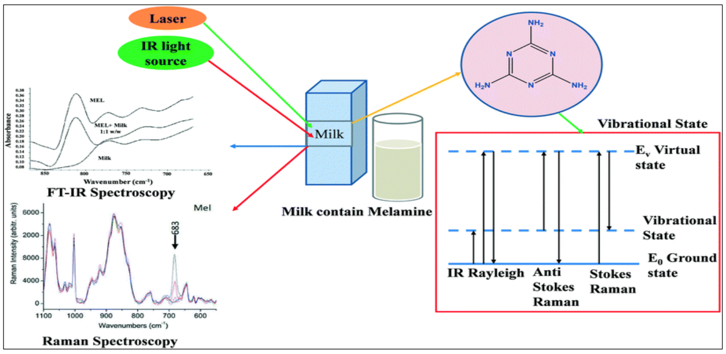

Fig 4. Identification of Melamine in Milk using Raman & FT-IR Spectroscopy (Source: Sen et al., 2022)

Analysis of adulteration by Sensor Technologies

Optic sensors: Electronic noses (e-noses) and electronic tongues (e-tongues) crudely mimic the human smell and taste sensors (gas and liquid sensors) and their communication with the human brain. The e-nose often consists of non-selective sensors that interact with volatile molecules that result in a physical or chemical change that sends a signal to a computer which makes a classification based on a calibration and training process leading to pattern recognition. The e-tongue uses a range of sensors that respond to salts, acids, sugars, bitter compounds, *etc.* and sends signals to a computer for interpretation. Fresh cherry/ tomato juice adulterated with different amounts of the juice from overripe tomatoes has been assessed using e-Nose and e-Tongue measurements, where the simultaneous utilization of both instruments indicated a better performance than when used individually.

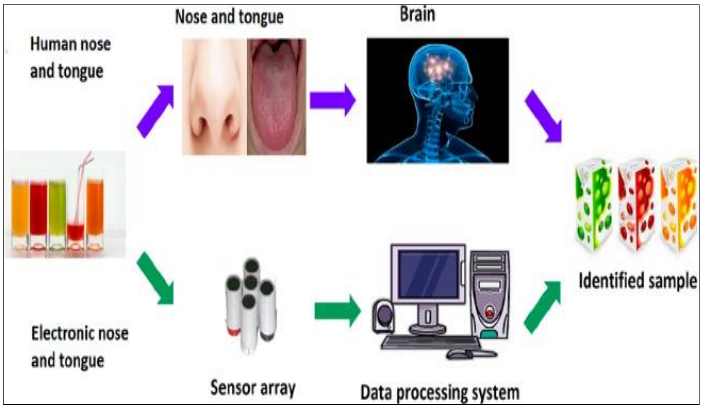

Fig 5. Application of Electronic Nose & Tongue (Source: Sliwinska et al., 2014)

Nanobiosensors: Nanomaterials based biosensing holds great potential in designing highly sensitive and selective detection strategies necessary for food safety analysis. Several metal ions can be specifically identified by amino acid because of the functional side chain (such as cysteine).

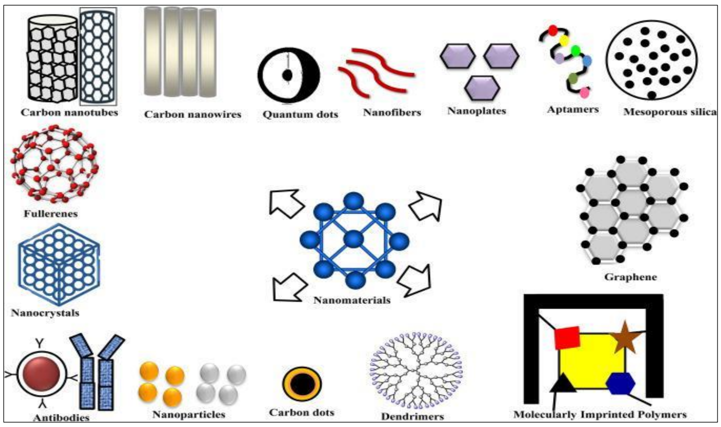

Fig 6. Nanomaterials applied in sensing of adulterants in food samples (Source: Singh, 2023)

DNA based Techniques

Utilization of DNA can be done as an effective tool to detect the adulteration and GMO content in various food products like oil, honey, beverages, baked products, animal feed, fried products, adulteration of milk and milk products. DNA based detection either complement the existing physical, sensory, or biochemical analytical methods or as a stand-alone tool due to its cost effectiveness, high sensitivity and reliability. Two commonly used methods are:

DNA Barcoding: DNA barcoding is a relatively simple technique that is based on the sequence variation in short nucleotide regions called barcodes that enables species identification and commodity authentication. Efficiency of DNA barcoding in seafood traceability has resulted in its adoption as a method for authentication of fish based commercial products by the US Food and Drug Administration.

DNA Extraction: Extracted DNA can be used as a biomaterial for detecting adulterants. An investigation on adulteration of goat's milk with cow's milk in Taiwan, targeting the specific bovine mitochondrial DNA showed a 25% of adulteration in goat's milk and 50% of debasement in goat's milk powder.

Conclusion

Non-destructive methods play a crucial role in quality control and ensuring the authenticity of food products without compromising the product's physical integrity. Real-Time monitoring during different stages of food production and distribution helps prevent adulterated products from reaching consumers, enhancing overall food safety. The character and nature of the product and the adulterant are critical in selecting the most appropriate and effective analytical method. While the spectroscopic methods have proved to achieve robust results time and again, the emerging biosensing and DNA based technologies offer highly sensitive, accurate and precise identification of adulterants in a vast range of food items.

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