Non-destructive detection of food adulteration to guarantee human health and safety

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Keywords:

Food
Adulteration
Safety
Quality
Non-Destructive
Authentication

Article history:

Received 15.04.2015
Received in revised form 16.05.2015
Accepted 20.05.2015

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Abstract

Introduction. The primary objective of this review is to critique the basic concepts of non-destructive detection of food adulteration and fraud which collectively represent a tremendous annual financial loss worldwide and a major cause of human disease.

Materials and methods. Literature referenced in this review article was obtained from searches from bibliographic information in CAB abstracts, AGRICOLA, SciFinder, Google Scholar, Modern Language Association (MLA), American Psychological Association (APA), OECD/EEA database on instruments used for environmental policy and natural resources management, and Web of Science.

Results and discussion. Food adulteration indicates the intentional, fraudulent addition of extraneous, improper or cheaper ingredients to products or the dilution or removal of some valuable ingredient in order to increase profits. Under the present conditions, manufacturers try to get as much for their products as possible and frequently this involves compromising product quality by making and selling substandard and frequently adulterated foods. "Non-destructive detection of food adulteration" indicates 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 sample are not altered. Improving the quality and safety of foods by developing scientific methods for the detection of adulteration is a key requisite for maintaining the health of consumers. Precise, objective quality evaluation and adulteration detection in food products is an important goal of the food industry. Due to the increasing sophistication of adulteration, it is essential to stay up to date on the latest, most precise methods of detection and authentication. To this end, the following paper critiques the basic concepts of non-destructive detection of food adulteration that result in economic losses and human disease. It reviews the principles of the devices used for adulteration detection and the use of modern techniques for the non-destructive detection of food adulteration; provides examples of practical applications of these methods for the control of food adulteration; and provides comparative analysis of the advantages and disadvantages of instrumental methods used in food technology. Each of these methods is discussed in relation to products displaying different consistencies – for example products in which the sample analyzed is a gas (headspace gases around a product), free flowing liquids (juices), turbid and viscous liquids (honey and vegetable oils) and intact products (fruits and vegetables).

Conclusions. Non-destructive analytical methods for the detection of adulterants are becoming increasingly important in the control of quality and safety of food products.

Review Methodology

Literature referenced in this review article was obtained from searches from bibliographic information in CAB abstracts, AGRICOLA, SciFinder, Google Scholar, Modern Language Association (MLA), American Psychological Association (APA), OECD/EEA database on instruments used for environmental policy and natural resources management, and Web of Science.

Introduction

The world population exceeded 7.2 billion in 2013 [1] and is expected to reach between 9.6 and 12.3 billion by 2100 [2]. While there is ever greater pressure for increasing the utilization of natural resources, including food, to meet the needs of our growing population, environmental problems such as accumulation of pesticides, mineral and organic fertilizers, petroleum products, and heavy metals in the soil, air and water have become increasingly common. Consequently, modern agriculture can be seen as a source of specific contaminants that are distributed unevenly through the biosphere. Contaminated plant and animal products eaten by consumers too frequently result in foodborne diseases that are a major cause of illness and death.

Food *contamination* is the presence of a minor or unwanted constituent or impurity while food *adulteration* indicates the intentional, fraudulent addition of extraneous, improper or cheaper ingredients to products or the dilution or removal of some valuable ingredient in order to increase profits. While the motivation is economic, the result can too often be a public health problem [3]. Food fraud includes such categories as 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 [4].

Food adulterants and contaminants can act as sources of various kinds of foodborne disease (e.g., liver and vision problems, skin diseases, stomach disorders), some of which are life-threatening. Under the present conditions, manufacturers try to get as much for their products as possible and frequently this involves compromising product quality by making and selling substandard and frequently adulterated foods. Too often the main purchasing criterion used by businesses and consumers is not the quality of the goods but the price. Depending upon the adulterant, this situation can lead to a significant deterioration in the health of consumers.

Contamination can be inadvertent or intentional. The motivation for intentional contamination can range from economics to bioterrorism, the latter being an increasing concern. Food *bioterrorism* is “an act or threat of deliberate contamination of food for human consumption with chemical, biological or radio nuclear agents for the purpose of causing injury or death to civilian populations and/or disrupting social, economic or political stability” [5].

Adulteration varies widely among the thousands of food products and in the level of sophistication, economic and health impact, and difficulty of identification. Examples range from tragic, as in the toxic oil syndrome disaster in Spain where thousands were sickened and an approximately 300 people died [6], to authentication of the varietal (i.e.,

cultivar)[1] purity [7] and geographical origin of a product [8]. Each can represent a significant case of adulteration.

While adulteration would appear to be fairly straight forward, some situations are not always clear. For example, grape juice formulators purchase grapes based largely on fruit sugar content. When there are loads of fruit that have sugar concentrations below an acceptable level, they are routinely blended with sweeter fruit so that the combined juice is above the minimum acceptable level for sweetness. In contrast, peanuts purchased for peanut butter production are tested for aflatoxins, a group of toxic fungal mycotoxins (B_1, B_2, G_1 and G_2) produced by certain moulds in the genus *Aspergillus*. Aflatoxin B_1 is a potent carcinogen and a mutagen in many animals, as a consequence, the United States, European Union and a number of countries set the highest acceptable level of B_1 and total aflatoxins in certain food products. In grape juice where one is dealing with a flavour quality attribute, blending sweet and less sweet juice is seen as a desirable business practice. In peanuts, where the critical parameter is toxic chemicals, is blending also a desirable business practice or adulteration? An additional distinction between contamination and adulteration is that the former is often relatively easy to ascertain while considerable effort is commonly needed from a legal standpoint to establish the intent to adulterate. Intent is a critical part of in determining adulteration. For example, section drying refers to an internal disorder in tangerines, not visible from the exterior, where certain vesicles within a fruit segment either appear dehydrated and/or are collapsed or granulated. Second derivative NIR optical density values at 768 and 960 nm can be used to nondestructively determine the presence or absence of the disorder [9]. If the fruit is not graded for the disorder and is sold with a significant percentage of the fruit defective, it is not adulterated. However, if the fruit are graded with the defective fruit removed and then 1 or 2 defective fruit are added to each bag of good fruit during packing, it constitutes adulteration. In each instance the amount of defective product in the total volume of product may be identical but in the latter case, it was intentionally altered.

With regard to food, the term *"quality"* means the products meet the requirements of an entire complex of criteria, properties and peculiarities, which characterize the product's degree of suitability based on its assessment and consumption. *"Food safety"* is a condition that ensures food will not cause harm to the consumer when prepared and/or eaten according to its intended use. It entails the handling, preparation, and storage of food in ways that prevent foodborne illnesses. Quality and safety remains a major challenge in the production of high-quality foods.

The term *"quality evaluation"* indicates obtaining meaningful information that can be used in making judgements, both positive and negative, about the degree of excellence of a food. "*Nondestructive quality evaluation"* indicates the analysis of a sample and the collection of its essential features in such a way that the physical and chemical properties of the sample are not altered [10-14]. Nondestructive means no alteration or loss of the product, however, in relatively uniform products very small samples are commonly used that are representative of the bulk of the material (e.g., four 1 ml samples of oil from a 10,000 L tank; volume lost = 0.00004% of the total). These samples may or may not be altered during analysis and even when not altered, the material is seldom reintroduced into the bulk material. For practical purposes, the analysis can be considered nondestructive, since the samples typically represent only a minute fraction of the total amount of material (e.g., in liquids such as oils, juices, milk or uniform solids such as ground meals). The number of samples required to accurately assess the presence of an adulterant depends

[1] Cultivar is the correct term in that variety is a taxonomic category.

upon the uniformity of the distribution of the adulterant and/or the percentage of adulterated product units in the bulk sample.

A major distinction between destructive and nondestructive procedures is that destructive analysis is typically used to identify an adulterant that has been added to or removed from a product and to assess the range in concentration. When possible, nondestructive methods are then developed for specific adulterants or a small group of similar adulterants. Nondestructive analyses tend to be less precise than traditional chemical analyses but have the advantage of speed, lower cost and often allow assessing each product unit rather than a sample of an entire volume. Assessing each product unit is important when the adulterant is not uniform, (e.g., when adulterated individual fruit are mixed in with non-adulterated fruit) and each product unit must be individually assessed. This is especially critical when consumer health is imperiled by the adulterant. In such cases, a nondestructive means of monitoring each individual product unit (e.g., near infrared spectroscopy) is required.

It is possible to classify food adulterants based on their impact on the consumer. *Critical* – adulterants that can cause death or seriously endangerment in the health of consumers. *Major* – adulterants affecting a significant percentage of the individual product units due to the level of adulterant present. Long-term consumption can have an impact on the health of the consumer. *Intermediate* – adulterants that impact the products quality without affecting the health of the consumer. *Minor* – adulterants that typically have only an economic impact e.g., varietal or geographic miss-representation.

Depending upon the type of adulterant and product, the health implications of adulteration, the ability to determine the presence and concentration of the adulterant, the seriousness of the consequences of the presence of the adulterant, the cost of analyzing for the adulterant, the precision of the analytical method and other factors, accurate assessment of an adulterant may require sampling anywhere from a minute quantity of the product to testing every individual product unit (i.e., 100%). The method of sampling is therefore a critical decision that is modulated by many variables. For a tremendous number of food products, it is not possible to assess each product unit for the presence and concentration of an adulterant. This is especially so for liquids, finely ground dried products or products in which the individual product units are extremely small (e.g., individual seeds). As a consequence, a sample – a small amount of the product drawn from a larger volume or population is obtained and data derived from the analysis of the sample is used to estimate the presence and approximate amount of an adulterant in the total volume of product.

Due to the enormous range in types of products and forms of adulteration, sampling is an exceptionally complex process. Critical decisions include: 1) the optimum location in the total volume of product to collect a sample; 2) how should the sample be taken; 3) how often should a sample be collected; and 4) what is the optimum size and number of samples? Data from the analysis of the samples must then be analyzed using an appropriate statistical method [15,16] to determine the level of confidence one can place in the results.

It is important to note that product assessment for adulteration involves a cost that may be quite high, especially if every product unit must be individually assessed in a nondestructive manner. In such an instance, it is essential to first singulate individual product units, then accurately assess and remove unacceptable units, all at a very high rate of speed (i.e., units/second). Therefore, the value of an individual product unit and the cost, speed and precision of the instrument are critical factors in the potential to assess each individual product unit [17]. As the value of each product unit decreases (watermelon → blueberry), assessing 100% of the product becomes progressively less economically viable. In addition, as the detrimental effects of an adulterant on the health of the consumer

increases, it becomes essential to assess each product unit, removing the adulterated product or until the risk or cost is determined to be sufficiently great that all of the product must be destroyed. At the present, rapid, non-destructive, precise, and on-line evaluation for adulterants remains a major challenge in the production of high quality foods [18].

Both contamination and adulteration result in tremendous health and economic losses annually. The U.S. Government Accountability Office [19] reported in May 1996 that up to 81 million cases of foodborne illnesses and as many as 9,100 deaths from these illnesses occur each year in the U.S. alone. According to the U.S. Department of Agriculture, the costs associated with these illnesses and deaths range from $6.6 to $37.1 billion U.S. dollars. It is estimated that these diseases kill approximately 1.8 million people annually (many of whom are children) in less developed countries. For example, since 1990, the prevalence of digestive diseases in the adult population of Ukraine increased by 55%; the mortality rate due to digestive diseases increased 2.5 times between 1990 and 2003 and in children (0-14 years) 57.1% between 1990 and 2004.

Food adulteration alone is believed to cost the world economy around $49 billion annually [20]. It is estimated that about 10 percent of the food we purchase in the U.S. is adulterated [21] and 7 percent contains fraudulent ingredients [22].

According to the State Inspection of Ukraine which is charged with the protection of consumers, about 80% of foods in Ukraine are adulterated with one or more inappropriate components [23]. In each instance human health problems are associated with food safety and quality.

As the economic advantage of adulteration and/or the repercussions of being caught increase, many adulteration techniques became progressively more sophisticated. Over the centuries there has been in effect an “arms race” between progressively more difficult to detect methods of food adulteration and methods of food authentication.

A major early advance in detection was the wide spread availability of microscopes and precise balances and the development of analytical chemistry in the 1800’s. One of the first analytical methods for identifying adulteration, specific gravity, was described by Robert Boyle in the latter part of the 17th century [24]. The increasing presence of analytical chemists greatly enhanced the ability to detect and prosecute cases of adulteration, however at the same time, other chemists used these analytical techniques to developed newer, more subtle methods to evade detection.

Improving the quality and safety of foods by developing scientific methods for the detection of adulteration and/or contamination is a key requisite for maintaining the health of consumers. Precise, objective quality evaluation and adulteration detection in food products is an important goal of the food industry. The most recent detection methods are at the molecular level, for example the use of isotope ratios and chiral analysis. The latter involves determining the amounts and ratios of molecules that are found in two forms, mirror images of each other but otherwise identical. Addition of a racemic compound as an adulterant alters the ratio of the enantiomers. Stereochemistry chiral resolution allows establishing the alteration in product chemistry. Certain racemic compounds vary with the production location of the crop and the cultivar and are increasingly used for authentication of products such as wines.

Due to the increasing sophistication of adulteration, it is essential to stay up to date on the latest, most precise methods of detection and authentication. For many products and adulteration methods, rapid non-destructive authentication techniques are becoming progressively more essential. To this end, the following paper critiques the history of adulteration and the basic concepts of non-destructive detection of food adulteration and fraud that result in economic losses and human disease. It reviews the principles of the

devices used for adulteration detection and the use of modern techniques for the non-destructive detection of food adulteration; provides examples of practical applications of these methods for the control of food adulteration; and provides comparative analysis of the advantages and disadvantages of instrumental methods used in food technology.

Each of these methods is discussed in relation to products displaying different consistencies – products in which the sample analyzed is a gas (headspace gases around a product), free flowing liquids (juices), turbid and viscous liquids (honey a plant-derived product, vegetable oils) and intact products (fruits, vegetables, seeds). A comparative analysis of the advantages and disadvantages of the main methods of food analysis are likewise presented.

History of Food Adulteration. Food adulteration is not a new phenomenon nor does it show any signs of dying out. The English word *adulteration* (the action of adulterating, corrupting or debasement by spurious admixture) was first used in 1506 [25,26]. Adulteration most likely began on a significant scale prehistorically with the onset of agriculture (i.e., ~9,500 BCE). The storage of surpluses allowed the presence of individuals (priests, bureaucrats) that did not directly produce food. Specialization evolved rapidly with the advent of agriculture, paving the way for the development of civilization, class society and the state [27]. Surplus grain, therefore, set the stage for the beginning of commerce and with it, adulteration. Surpluses provided unscrupulous individuals the opportunity to increase their profits by adulterating foods, typically by adding weight or volume with less expensive substitutes.

The history of food adulteration can be dated back to Assyrian tablets from several thousand years BCE and Egyptian scrolls. The Bible contains a number of dietary laws, and Roman civil law covered the use of false weights and measures [28]. Greek and Roman writers (Theophrastus (BCE 370-285) [29], Cato (BCE 234-149) [30], *Apicius de re coquinaria* (~ BCE 27 – CE 476) [31] and Pliny the Elder (CE 23-79) [32]) were each concerned with adulteration. Pliny described altering the flavour and colour of wine and the adulteration of flour, herbs and spices and how it was possible to detect adulteration (smell, colour, weight, taste and the action of fire) [33]. In contrast, *Apicius de re coquinaria*, a collection of Roman cookery recipes from the 4th or 5th century CE, describes methods for covering up decomposition in foods (broth, birds) using seasonings and how to convert bad honey to good honey [31].

Grains and spices initially were not marketed as a ground product which made them not particularly good candidates for adulteration since visual inspection could generally identify irregularities. Foods such as honey, ales, wine and oils offered far better opportunities for hiding adulteration [34].

During the mid-1700s, adulteration was so rampant in England that there were two books published decrying the practice [35,36]. “Death in the Pot” was a Biblical phrase (II Kings 4:40) that began to be used to heighten awareness of the seriousness of the food adulteration problem in the early 1700s [37]. Jasper Arnaud, an English physician, described the adulteration of a number of products including meat – “…an ill Practice exerci*f*ed by *f*ome, of cutting off the Out*f*ide of Meat when it is almo*f*t *f*tinking, and then rubbing the *f*ame with Blood, to make it look fre*f*h, and pa*f*s for good Meat” [35]. During this time period, cruder forms of adulteration began to be replaced by more skillful and novel techniques in an attempt to circumvent detection by inspectors and health officers. It was even possible to find examples of the adulteration of adulterants.

Examples of Adulterated Foods. Properties of foods that were commonly altered included weight, volume, colour, odor, taste, composition, texture, geographical origin, and cultivar designation. Adulteration of fruits and vegetables may occur through the addition of water, substitution of high-quality products with low-quality ones, sale of immature or overripe products, addition of antibiotics, preservatives, nitrates, transgenic vegetables/fruits, and stimulators or inhibitors of product ripening. Products may be adulterated by immersing them in cold water to increase their weight and treatment of vegetables with dyes (e.g., malachite green) which can contain pesticides and other chemical compounds.

Frederick Accum, a German chemist and pharmacist established a laboratory in London dedicated to detecting adulterants in food. In 1820 he published a book listing foods adulterated, adulterants, and the names and addresses of merchants selling them [38]. A quarter of a century later A.H Hassall, a physician in England, published the results of his investigations into the adulteration of foods, listing adulterants found in a large number of products, e.g., coffee – chicory, roasted wheat, corn, acorns or beans, iron oxide, roasted wurzel-mangel, coconut shell; cocoa – coconut shell, coloured earth, cocoa shell, starch; chicory – roasted wheat, corn, bean or carrot, sawdust, Venetian red, sand; green tea – exhausted tea coloured green, mineral pigments, foreign leaves [39].

Hassall found a food adulterated with essentially a criminal disregard for the health of consumers was candy, frequently consumed by children. Colours for candy were often derived from lead, arsenic, copper, mercury and chromium compounds which are highly toxic. For example, lead chromate was used for yellow or orange coloured candy. In 1880, 46% of the candy sampled in Boston contained primarily lead chromate. It became evident that adulteration was widely prevalent and represented a serious public health problem [34].

Fruit juices can be adulterated by the addition of water, sugar, pulp, seeds or peel and alternative cheaper juices. Modern manufacturing technologies involve the addition of organic acids, beet and corn sugars, thickeners, artificial colouring and flavouring agents, preservatives, intensifiers of acidification, flavours, and other less expensive juices. Orange juice can be adulterated with monosodium glutamate, ascorbic acid, potassium sulphate, corn sugar, grapefruit solids; pomegranate juice can be diluted with grape or pear juice, sugar, and high-fructose corn syrup.

Honey is a classic object of adulteration. Sucrose, sugar, glucose, partial invert cane and corn syrups, and beet sugar, dextrin, starch, unripe honey, molasses, honeydew, and artificial sweeteners have been intentionally added to natural honey. Some tested samples of honey did not contain pollen, but can be contaminated with heavy metals, pesticides, and antibiotics.

Adulteration of olive oil usually is through dilution with alternative cheaper oils, such as sunflower, vegetable, hazelnut, corn, peanut, soybean, palm, and walnut. In Spain in 1981-82, adulterated cooking oil resulted in 20,000 cases of illness and 12,000 hospital admission. Some 300 people died from what was called Toxic Oil Syndrome [6]. The cooking oil was illegally refined denatured rapeseed oil. Even 30+ years later the actual toxic agent in the oil has yet to be identified. Pet food from China in 2007 adulterated with melamine, a plasticizer which mimics high quality protein in routine quality control tests, resulted in thousands of dogs and cats dying and raised concerns about the safety of human foods imported from China [40]. An estimated 2.5 to 3 million people in the U.S. had consumed chickens that had been fed feed containing contaminated vegetable protein from China [41].

Laws, Enforcement and Punishment for Adulteration. Food regulations date from the earliest societies and have been found in ancient Chinese, Egyptian, Greek, Hindu and Roman literature [42]. Many early regulations were in the form of religious prohibitions. With time, adulteration became a government responsibility and was dealt within many of the first enactments codified. As societies developed, legislation began to detail acts that were considered food adulteration, appropriate punishments and how they were to be enforced. Hutt and Hutt [43] have published an exceptionally thorough history of government regulation of adulteration and laws that protect the public from food fraud.

Establishing uniform weights and measures were among the earliest English statutes established in the 9th century and subsequently detailed in the Magna Charta in 1215 [44]. Early laws focused on controlling the availability and price of specific staples (e.g., bread, butter, ale, wine). Commonly lacking however, was a means of enforcement.

In the 13th century, guilds began self-regulating their respective commodities to prevent adulteration. The first public food inspectors ("garbleers") in England were charged with detecting and removing impurities and adulterants from spices and similar products [34]. Forms of adulteration (e.g., putrid bread, beef, capons, pig, fish, and pigeons; unsound wine; concealing bad oats with good oats, bread deficient in weight) were detailed and rigorously enforced [43]. Punishment for not obeying the statutes for bread and ale in 13th century England were documented – "….he shall suffer Punishment of the Body, that is to wit, a Baker to the Pillory, and a Brewer to the Tumbrel, or some other Correction" [44].

Punishments for the adulteration of foods have been detailed in many countries. The legal code during the T'ang Dynasty in China (618–907 CE) stipulated that: "When dried or fresh meats cause men to become ill, all the left-over meat portions should be speedily burned. The violator will be flogged 90 strokes. He who deliberately gives or sells it to another will be banished for a year, and if the person to whom it has been given or sold dies, the offender will be hanged" [45]. Fines and the prohibition of selling the product for a given time interval were the most common penalties for adulteration, however, when serious injury or death occurred, punishment was often much more severe.

While the governments in much of Europe developed rules concerning food supply in the Middle Ages and Renaissance, England made considerable strides in controlling adulteration. Many of the laws in the U.S. were derived from English statutory and common laws [43].

The wide spread adoption of laws governing adulteration began in the 1800s, a time when there was a pronounced increase in adulterated foods. Several important technological advances were the development of analytical chemistry, the analytical balance, and the microscope [34]. These advances increased detection skills, however, they also increased the sophistication of individuals adulterating foods. In England the first general food law, the Adulteration of Food and Drink Act was passed in 1860 and was subsequently replaced in 1875 by the Sale of Food and Drugs Act [34].

The first food adulteration law in the United States was passed by the Massachusetts Legislature in 1784; subsequently a number of individual states passed food laws. The first federal law in the U.S. was enacted in 1906 which covered the adulteration of food [46]. It was later replaced by the Federal Food, Drug and Cosmetic Act in 1938 that addressed limitations in legal standards, authority to inspect food establishments and control false or misleading claims on food labels [47]. A number of additional amendments to the act have been subsequently enacted that further strengthen control over food quality and safety.

Analytical Methods for the Detection of Adulteration

Analysis of the Headspace Gaseous Phase of Products

Headspace is the gas space or volume surrounding a sample in a closed but not necessarily sealed container. With respect to fruits and vegetables, the headspace contains volatiles emanating from the sample that diffuse into the surrounding gas phase. Thus, headspace analysis of foods is an effective analytical technique for the quantitative and qualitative analysis of food aromas and the presence of inappropriate volatile compounds. The occurance of certain volatiles can indicate the presence of adulterants and/or the degradation of product quality.

Flavour is comprised of aroma (odor) and taste and is one of the most important quality attributes of foods [48]. The aroma of food products depends on the concentration and combination of volatile organic compounds (VOCs) produced by these products. The term "*volatile*" relates to the tendency of these compounds to vaporize at normal ambient temperatures and pressures due to their low boiling points.

VOCs emanating from fruits and vegetables can be classified according to their metabolic origin [49] [e.g, terpenoids (e.g., mono- and sesquiterpenes and apocarotenoids), phenylpropanoids/benzenoids (e.g., eugenol, benzaldehyde), fatty acid derivatives (e.g., hexenal, hexenol) and amino acid derivatives (e.g., thiazole, 2- and 3-methylbutanal)]. From a chemical point of view, these VOCs can be divided into esters, alcohols, aldehydes, ketones, lactones, terpenoids and a cross-section of miscellaneous compounds [50]. The following number of VOCs have been identified emanating from specific fruits and vegetables: strawberry – 147 [51], pear – 303 [52], tomato – more than 400 [53], orange – 203, banana – 225, mango – 273, apple – 356, and grape – 466 [54].

Headspace gas chromatography involves the analysis of VOCs in the headspace gas surrounding a product. There are two general sample collection techniques for gas chromatography: static headspace and dynamic headspace. In static headspace chromatography, the product is placed in a sealed glass container for a specific length of time. A sample of the headspace gas containing the VOCs that were given off by the product is withdrawn and transferred to the gas chromatograph for analysis [55]. Static headspace methods require minimal sample preparation.

The main disadvantage of this method is associated with the low concentrations of the compounds in the sample that can make detecting and identifying some potentially critical quality components difficult. Cryofocusing (cold trap) headspace volatiles [56] makes it possible to solve this problem. A larger headspace sample is introduced onto the GC column in which the first few centimeters is refrigerated to a low temperature using liquid CO_2, trapping the VOCs while allowing nitrogen and oxygen to pass on through the column. When sufficient material has been trapped, the temperature programming of the GC oven begins, volatilizing and then separating the compounds on the column. This allows avoiding heating during sample collection which commonly results in artefacts. This method, for example, has been used for quantifying orange juice volatiles [57].

In dynamic headspace analysis which is based on a "purge and trap" technique, the sample is placed in a vessel and purified air or an inert gas is passed through the container and into a trap (e.g., Tenax) which captures the VOCs from the sample that are in the air. The trap is then rapidly heated in such a way that the volatiles are flushed from the trap onto the GC column. Cryofocusing is typically used since it generally takes a few minutes for all of the VOCs to be released from the trap. The volatiles are then moved through the GC column where they are separated before entering into the mass spectrometer. Since the

purging air or inert gas is constantly moving through the chamber containing the product, it does not reach a state of equilibrium; hence the technique is called "dynamic headspace analysis".

The advantages of dynamic headspace analysis include high sensitivity (dynamic headspace is more sensitive than static headspace), a rapid procedure of analysis, and minimal equipment investment. The method also uses little or no solvent.

Plants emit VOCs from their various plant parts (e.g., flowers, fruits, leaves). A number of apparatuses for the collection of volatiles from living plants have been proposed, e.g., [58]. The investigation of VOCs that are emitted by living plants can avoid inadvertent alterations in the quality and quantity of volatile emissions due to physical damage to the plants and fluctuations in environmental parameters. In this case, the apparatus consists of split glass flask that surrounds the plant, a vacuum pump, flow control devices, a reservoir of clean air to replace the sampled headspace, an adsorbent trap for retaining the VOCs, and a means of sealing the apparatus. The main chemicals emanating from live tomato plants were terpenoids (~30) and the rate of total organic emissions varied with plant age.

Headspace-mass spectrometry has been successfully used for the detection an olive oil adulterated with sunflower and/or olive-pomace oil [59]. Samples of olive oil with different proportions of adulterants produced distinctly different patterns of VOCs when identified by headspace–mass spectrometry. The analysis procedure is characterized by simplicity, speed and relatively low cost.

Adulteration of olive oil with hazelnut oil is one of the most difficult to detect due to the similar composition of the two oils. Direct coupling of headspace VOC collection, mass spectrometry and multivariate regression techniques was used to differentiate adulterated from non-adulterated oils and to determine the type of adulterant present [60].

Honey aroma depends on many factors, such as the plants from which the bees obtain nectar, honey production technology and season. VOCs emanating from honey can be grouped into chemical categories such as aldehydes, ketones, acids, alcohols, hydrocarbons, norisoprenoids, terpenes, benzenes, furans and pyran derivatives [61]. Over 600 VOCs representing a number of chemical families have been identified in honey [62].

Instrumental techniques allow quantifying the bouquet of honey aromas, the presence of undesirable odors, the presence of contaminants and the level of adulteration. VOCs emanating from food products therefore play an important role in quality evaluation and adulteration detection.

Gas Chromatography

Chromatography is a method of separation, analysis and identification of complex mixtures. It is based on the distribution of analyte between the two phases – the stationary phase (a sorbent with developed surface area), and mobile phase (a gas or liquid). The principle of operation is based on the interaction of the component with the walls of the column that are covered with a stationary phase.

The components of the sample introduced into the chromatographic column move with different velocities due to their differing affinities for the sorbent column and successively reach the detector at different times. Each component is separated from the mixture at its appropriate retention time (t_R) and exits the column to enter the detector which gives a signal of registration. With adequate separation, each component of the mixture is presented as a peak. A time-based graphic record of the signals produced by all components is called a *chromatogram*.

The detector estimates the concentration of each component through the comparison of parameters (retention time and area of signal) of a sample being analysed and a standard sample of known concentration.

Gas Chromatography (GC) is an analytical technique that is based on the vaporization of the sample and separation of the components by passing the mixture of gases dissolved in a mobile phase through a stationary phase [63]. The typical gas chromatograph consists of a pressurized source of inert carrier gas, sample injector port, oven with capillary column, and detector.

When moving along a fixed mobile phase, each component of the mixture is deposited (absorbed) on a stationary phase (sorbent) which delays and slows its movement. Since different components have different affinities, a spatial separation of the components occurs. Some components are delayed at the beginning while others move forward. The mechanisms establishing the sequence of components on a stationary phase can be due to: the solute being adsorbed (absorbed) by the surface of the stationary phase *(a)*; the solute being dissolved in the liquid phase, which covers the surface of the solid phase (*b)*; the mobile anions are held by van der Wall's forces of cations that are covalently bound to the stationary phase *(c)*; the separation of small from large molecules that penetrate through the pores of particulate matter *(d)*; and differences in the affinity of the molecules in the mixture that are covalently bound to the stationary phase *(e)* (Figure 1).

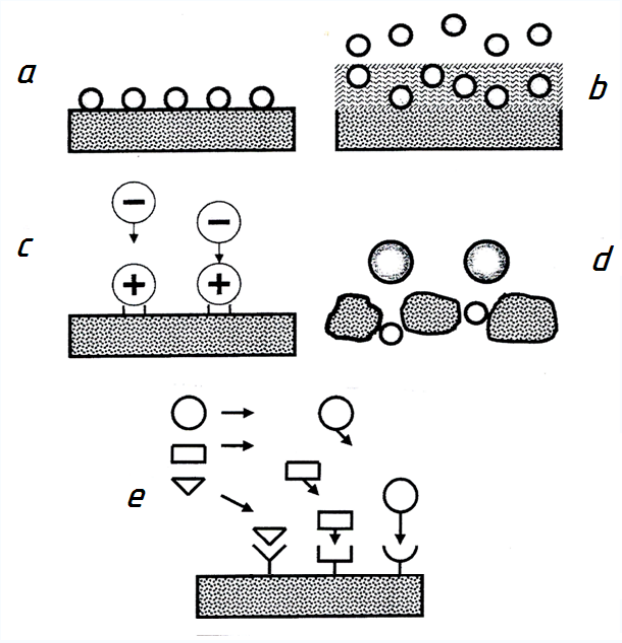

Figure 1. The mechanisms of interaction between the components of the mixture and the stationary phase (explanation in the text)

Gas chromatography involves the use of an inert gas as the mobile phase; nitrogen, helium, argon, and carbon dioxide are commonly used as carrier gases. The sample is introduced into a heated injector by way of a gas -tight syringe or a valve, where the

process of vaporization takes place. The sample is subsequently swept by the carrier gas into the column.

Gas chromatography can be used for the analysis of non-polar, semi-polar, volatile and semi-volatile compounds; it is useful from the point of view of food analysis for identification and quantification of carbohydrates, amino acids, lipids, odorants, flavours, pesticides residues and drugs. However, the analysis of such non-volatile compounds as inorganic salts and large molecular weight organics (e.g., proteins, polysaccharides, complex carbohydrates, nucleic acids) is outside the scope of gas chromatography due to their lack of volatility [64]. In some instances (e.g., simple sugars), the molecules can be derivatized making them volatile and thereby analyzable by gas chromatography.

Gas chromatography is characterized by high sensitivity and the possibility of estimating simultaneously a wide number of VOCs, but suffers from a long response time (from minutes to hours).

Adulteration of products such as fruit juices, honey and maple syrup often means the addition of carbohydrates. The principal carbohydrates present are glucose, fructose and sucrose, whose content can reach 98 % of the total soluble solid substances present in the products. Consider, for example, apple juice. It is composed of fructose (F) and glucose (G), typically in a ratio of F/G = 2.0. The essence of adulteration of apple juice is based on the addition of a cheaper sugar source such as inverted beet or cane sugars (F/G = 1.0), corn syrup (F/G = 1.6) and inulin syrup (F/G = 3.0-8.0). To determine the difference in the chemical composition of real and adulterated juice using traditional chemical analysis is a difficult procedure, however, the application of capillary gas chromatography makes it possible to determine the presence of artificially added substances [65]. Comparison of chromatograms of pure and adulterated apple juice indicates significant differences in profiles which can be used for detecting the presence of adulterants.

Solid-phase Microextraction

SPME is a modified method of sample collection that can be used for the detection of VOCs in foods. This method is based on the application of a fused fiber coated with a polymer that traps volatile analytes (VOCs) emanating from a sample. An equilibrium between the sample, headspace above the sample, and the fiber is established. The analyte is deposited on the fiber which is then transferred to the injection port of a gas chromatograph equipped with mass spectrometer detector for analysis. When the fiber is inserted into the injection port, the trapped volatiles are thermally released and subsequently separated on the GC column.

Solid-phase microextraction is fast, simple, fairly sensitive and can be used without solvents, eliminating the need for environmental hazards. The disadvantages of SPME fibers include the high selectivity of the fibers for specific chemicals, lack of robustness, and low reproducibility of results due to ageing of the fiber.

A combination of SPME, gas chromatography and chemometric data analysis allowed differentiating among pure strawberry samples (*Fragraria* × *ananassa* Duchesne) and strawberry samples adulterated with 10, 40, and 70% (v/v) apple purée [66]. Another example of detecting adulteration of honey with thyme oil demonstrated the effectiveness of the SPME-GC/MS procedure which is based on the analysis of specific volatiles such as thymol and carvacrol [67]. The authors demonstrated that adulterated honey had an intense thyme aroma without the characteristic honey flavour; they proposed using the presence of the volatile 3,4,5-trimethoxybenzaldehyde as a possible marker of honey adulteration.

Solid phase microextraction and multidimensional gas chromatography was used to detect the adulteration of olive oil. The presence of filbertone, the principal flavour compound of hazelnuts, indicated the adulteration of olive oil with less expensive hazelnut oil. The sensitivity of method was enough to detect filbertone and to establish the adulteration of olive oil of different cultivars with virgin hazelnut oils in percentages of up to 7% [68].

Mass Spectrometry

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.

A typical mass-spectrometer contains an ion source that transforms neutral molecules of a sample into ions, a mass analyser that separates ions by their mass and charge in applied electric and magnetic fields, and a detector that provides a qualitative and quantitative estimation of sample compounds. There are two principal types of mass-spectrometers: a *sector field mass analyser* that measures the mass-to-charge ratio of charged particles that are accelerated by an electric field and are separated based on their mass and charge in a magnetic field, and a *quadrupole mass analyser* that separates the ions according to their mass-to-charge ratio, which is determined by the trajectories of the ions under the influence of an electric field.

Mass spectrometers are characterized by high sensitivity and accuracy; at the same time, it should be noted the need for a trained operator and the relatively high cost of the equipment. Very often, mass spectrometry is used in combination with other methods, extending the analytical possibilities.

Combination of Gas Chromatography and Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) 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. The gas mixture is separated into components by gas chromatograph according to the retention time of each component whereby forming the chromatogram. After entering the mass spectrometer, these components are captured, ionized and detected. Thus, each peak in the chromatogram is resolved into the mass spectrum components according to their mass to charge ratio (Figure 2).

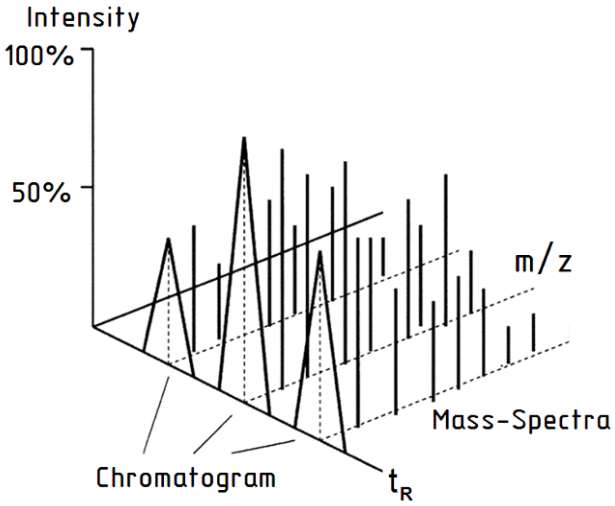

Figure 2. GC/MS spectra: three-dimensional plot of scan number (time) versus mass/charge *(m/z)* versus relative intensity (%)

GC-MS combines high resolution separation of components with very selective and sensitive detection, making it possible to achieve a high level of precision in the identification of unknown chemicals that cannot be achieved using gas chromatography or mass spectrometry separately. GC-MS system with a capillary column is a powerful tool for investigating volatile organic compounds responsible for the aroma of food.

GC-MS is characterized by high sensitivity and a relatively rapid identification of the components in a sample. Nevertheless, it has a high instrumental cost and requires a skilled operator. GC-MS method has been developed for the detection of honey adulteration with high fructose inulin syrups [69].

Proton Transfer Reaction Mass Spectrometry

Proton transfer reaction mass spectrometry **(**PTR-MS) utilizes chemical ionization that is based on proton-transfer reactions; hydroxonium ions H_3O^+ are used as the reagent ions since the volatile compounds have a higher affinity for these ions. A scheme for a PTR-MS system is shown in Fig. 3.

Water vapor pressure of 150 Pa is applied to the input (1) of the system (2) for ion formation. About 98% of the H_2O vapour is converted into ions (H_3O^+). The air with volatile compounds (V) that are to be analyzed is fed through the input (3) into the drift chamber (4) where ions (N_3O^+) are injected by way of an applied electric field. A proton transfer reaction is accompanied by the formation of ions ($V{\cdot}H^+$) in the drift chamber. These ions drift to the entrance of the mass spectrometer (5) where they are analyzed. A camera system is connected to a pump (6). Sensitivity of this PTR-MS system is about 1 nl/l.

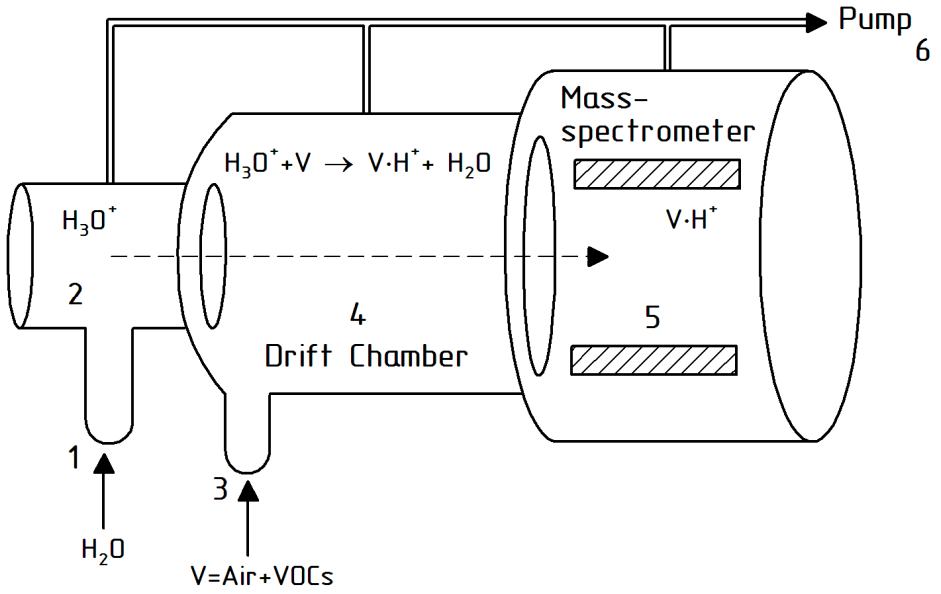

Figure 3. Proton Transfer Reaction Mass Spectrometer (explanation in the text)

Volatile organic compounds containing a polar functional group or unsaturated bonds have proton affinities greater than that of H_2O and therefore will react with H_3O^+ in a proton transfer reaction where a proton is transfered between H_3O^+ and the VOC. The reaction can be described by the following formula:

$$H_3O^+ + V \rightarrow V{\cdot}H^+ + H_2O \qquad (1)$$

where *V* is an individual molecule of a VOC in the analyte.

PTR-MS provides real-time, online quantification of VOCs. 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. The shortcoming of the PTR-MS technique is that it characterises VOCs by way of their masses only which is not sufficiently adequate to identify most volatile compounds.

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 a valuable oil with cheaper oils or by mixing the oil of different cultivars [70].

Electronic Nose and Electronic Tongue

A device that can be used to detect odors that are often significant components in the overall flavour of food products is called an *electronic nose (eNose).* It consists of a large array of chemical sensors, a detection system and a computing system. Sensors can be fabricated using different types of polymers, metal oxide semiconductors, metal oxide semiconductor field effect transistors, piezoelectric crystals, quartz crystal microbalance, and surface acoustic wave transducers.

The principle of operation of an eNose is based on the exposure of the sensor surface to an odor (flavour) which is composed of molecules of different sizes and shapes. When a certain polymer film receives a specific molecule, the film begins to swell. The process of film swelling causes a corresponding change in the electrical conductivity of the film that is assessed by the detector. The interaction of flavour components with the sensor array allows detecting a pattern using software recognition.

An eNose system, which was based on the application of 10 metal oxide semiconductor sensors, was used to generate a pattern of the volatile compounds present in samples of sesame oil. Excellent results were obtained in the prediction of the percentage of adulteration in the oil using back propagation neural networks and general neural network regression [71].

The detection of adulteration of virgin coconut oil based on a surface acoustic wave sensor made it possible to generate a pattern of the volatile compounds present in the samples at a level of adulteration between 1 to 20% (wt/wt). Principal component analysis provided good differentiation of samples, accounting for 74% of the variation [72].

The electronic tongue (eTongue) is an instrument that detects dissolved organic and inorganic compounds, some of which are responsible for taste. It contains several sensors (electrodes) that are characterized by differing spectra of reactions and the response is based on the chemical modification of these voltammetric electrodes. The combination of all responses produces a specific fingerprint similar to the human taste reception. Several approaches for the qualitative determination of adulteration levels have been performed using this instrument. For example, it has been used successfully for the detection of fraudulent red wines created through the addition of a range of adulterants [73]. In this case, the sensor array that was used consisted in two families of electrodes, i.e., phthalocyanine-based carbon paste electrodes (CPEs) and electrodes covered with a conducting polypyrrole treated with a range of counter ions.

An e-tongue with 36 cross-sensibility sensors was used for the identification of goat milk adulteration with bovine milk [74]. It was possible to recognize 5 basic taste standards. The proposed e-tongue device exhibited a high sensibility to acid, salty and umami tasting substances but had a lower performance for bitter and sweet sensations. The combination of different signal profiles recorded by the e-Tongue device together with linear discriminantion analysis made it possible to implement a model that could distinguish between raw skim milk groups (goat, cow and goat/cow) with an overall sensibility and specificity of 97% and 93%, respectively.

The combined e-Nose and e-Tongue technologies can also be successfully applied to the detection of adulteration of food products. For example, fresh cherry tomato juice adulterated with different amounts of the juice from overripe tomatoes was assessed using e-Nose and e-Tongue measurements. The study indicated that simultaneous utilization of both instruments would guarantee a better performance than when used individually [75].

A detection method for the adulteration of argan oil with sunflower oil was developed using the combination of a voltammetric e-Tongue and an e-Nose instruments. Metal oxide semiconductor sensors were used in conjunction with pattern recognition techniques which gave excellent results in differentiating between unadulterated argan oil and that adulterated with sunflower oil [76].

Optical Emission Spectroscopy with Inductively Coupled Plasma (OES-ICP)

Optical Emission Spectroscopy with Inductively Coupled Plasma (OES-ICP) is based on the excitation of liquid and gas samples using radiofrequency discharge and the corresponding spontaneous emission of photons from the excited atoms and ions.

Inductively coupled plasma (ICP) is a type of gas discharge, excited by energy that is supplied by an electric current produced by electromagnetic induction during the application of a radio-frequency (1-100 MHz) magnetic field. This method is used to assess trace quantity samples. The excitation of the plasma is accompanied by radiation at certain wavelengths that characterize the elements of interest. The intensity of the radiation is proportional to the concentration of these elements [77].

The OES-ICP-system consists of a plasma source containing three concentric quartz tubes and coils, to which a radio-frequency field is applied. Argon gas flows through the coils and the gas produces a torch due to the powerful radio-frequency. The ionizing process is induced by a discharge arc. A stable, high-temperature plasma (~7000 K) is created due to collisions between the neutral atoms of argon and excited particles (Figure 4).

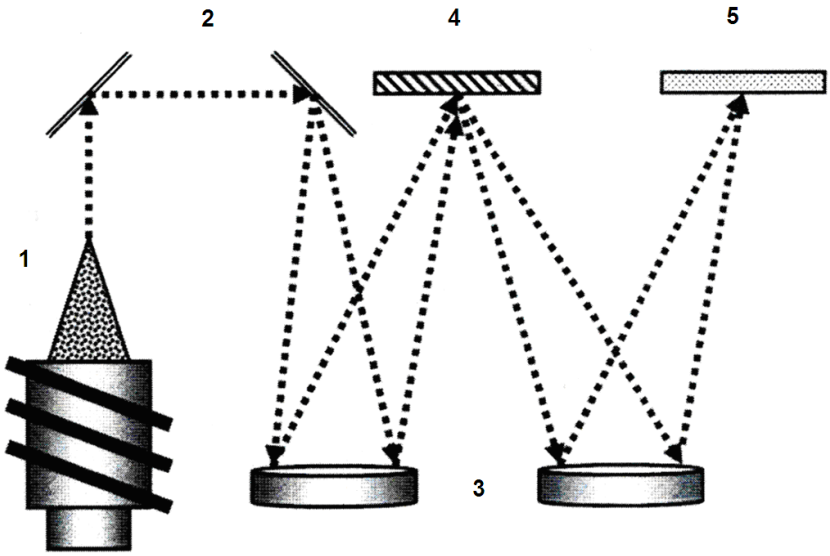

Figure 4. Principle of Optical Emission Spectroscopy with Inductively Coupled Plasma (OES-ICP):
1 – source of plasma; 2 and 3 – mirrors; 4 – diffraction grating; 5 –detector.

The sample is directly introduced into the plasma flame where it collides with charged particles and is broken down into charged ions. The process of losing electrons and their recombination with molecules in the plasma is accompanied by the emission of wavelengths characteristic of the element being studied. The wavelengths and intensity of the spectral lines are measured using diffraction gratings and a photoelectronic multiplier combined with a means of recording the response and analyzing the data.

The advantages of OES-ICP include the need for only a relatively small sample < 10 mL, the potential for automated analysis, low cost, ease of operation and the flexibility of wavelengths and elements. It is necessary to choose wavelengths for each element and to analyse multiple elements at once using standards prepared for each element.

The ICP-OES method in combination with different chemometric approaches has been used for the analysis of the trace element profile of argan oil (e.g., Na, Mg, Al, K, Ca, Ti, Fe, Co, Ni, Cu, Zn, Cd, Pr, Sm, Er and Bi at the μg/g level). Multivariate analysis methods, such as discriminant analysis have been successfully applied to the analysis adulterated argan oil with cheaper vegetable oils [78].

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 [79]. Unlike OES-ICP, measurement of the wavelengths and intensities of the spectral lines is determined using a mass spectrometer. The sample is introduced into the central channel in the form of an aerosol that is obtained by spraying a liquid sample. When the aerosol enters the central channel, it evaporates and breaks up into atoms. A significant part of the atoms are ionized due to the high temperature and pass into the mass spectrometer. Here the ions are separated according to their weight against the charge and the detector receives a signal proportional to the relative concentration of the particles (Fig.5).

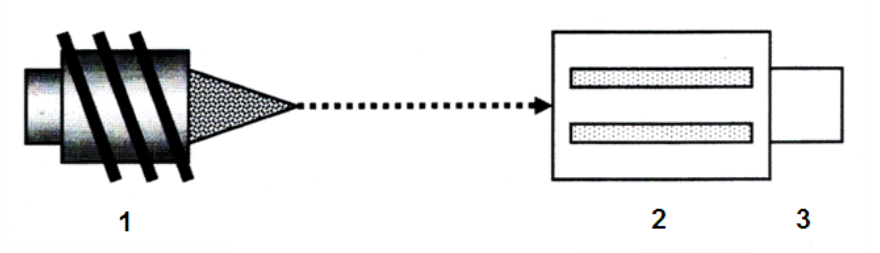

Figure 5. Principle of Mass Spectrometry with Inductively Coupled Plasma (MS-ICP): 1 – source of plasma; 2 – mass-spectrometer; 3 – detector.

Mass spectrometry with inductively coupled plasma is one type of mass spectrometry. It is characterized by high sensitivity and the ability to identify metals, and some non-metals, and in some instances at concentrations not exceeding 10^{-10} % or one part per 10^{12} (trillion) parts. The MS-ICP method makes it possible to obtain isotopic information on the elements determined. A disadvantage of the ICP-MS system is isobaric interferences that are produced by polyatomic species arising from the plasma and the atmosphere.

Determination of the geographical origin of rice is an example of a practical use. This can prevent possible mislabelling and/or adulteration of rice products. High resolution ICF-MS and discriminant analysis was applied to 31 Thai jasmine and 5 foreign (France, India, Italy, Japan and Pakistan) rice samples [80]. The method has also been used to ascertain rice (*Oryza sativa* L.) genotype for determining authenticity and adulteration of food products [81].

Analysis of Free Flowing and Viscous Liquids

High-Performance Liquid Chromatography

The distinguishing feature of *high-performance liquid chromatography* (HPLC) is the application of high pressure (400 bar) and a fine-grained sorbent (a granular material made of solid particles 3-5 micrometers in size). It allows separating a complex mixture of substances quickly and completely (average analysis time is 3 - 30 min) with high resolution.

HPLC is preferred for analysis of liquid samples; and it can be useful for separation of organic compounds independent of their polarity and volatility [64]. The literature highlights the possible applications of HPLC for the quality evaluation of fruits and vegetables and detection of their possible adulteration. In general, this method can be used for analysis of pesticide residues, flavours, organic acids, mycotoxins, antibiotics, additives, food colours, carbohydrates, proteins, pigments, dyes and different adulterants in foods [82].

HPLC analysis of flavanones such as naringin, neohesperidin and neoeriocitrin that are present in bergamot fruit (*Citrus bergamia* Risso and Poit.) juice and essentially absent in lemon juice can be used for detecting the fraudulent addition of bergamot juice to lemon juice [83].

Artificial food dyes are added to a number of food products such as fruit snacks and juices; however some of these dyes can cause cancer, allergic reactions and hyperactivity [84]. HPLC is an effective method of identifying synthetic dyes, determining if synthetic dyes are present in a food and whether they are permitted [85].

Argan oil obtained from the argan fruit (*Argania spinosa* (L.) Skeels) is very popular due to its beneficial dietary properties and its apparent reduction in the risk of cardiovascular disease and cancer. Triacylglycerols were used as indicators of argan oil adulteration with vegetable oils such as sunflower, soybean and olive. These compounds can be readily separated by high-performance liquid chromatography and measured using evaporative light scattering detection [86].

Infrared Spectroscopy

Infrared spectroscopy analyzes the absorbance of infrared radiation in the near (0.75→2.5 μm), mid (2.5→14.9 μm) and far (14.9→1000 μm) infrared regions of the electromagnetic spectrum. The absorption of infrared radiation is related to the transitions in the vibrational levels of the molecules contained in the sample. A set of such transitions determines the infrared spectrum and provides qualitative information about the nature of the functional groups present in a food sample (for example, O–H in water and carbohydrates; C=O and N–H in proteins etc.)

Near-infrared (NIR) spectroscopy has been used for the detection of orange juice adulteration with orange pulp wash, grapefruit juice and synthetic sugar/acid mixtures. The detection level was 50 g/kg [87]. León et al. [88] demonstrated that NIR spectroscopy can be used to identify the adulteration of apple juice with sugar. The detection limit was 9.5% for samples adulterated with high fructose corn syrup (HFCS), 18.5% for samples adulterated with a sugar solution (60% fructose, 25% glucose, and 15% sucrose) and 17% for the combined (HFCS + sugars) adulterants. Discriminant partial least squares (PLS) regression could detect authentic apple juice with an accuracy of 86–100% and adulterant apple juice with an accuracy of 91–100% depending on the type and amount of adulterant.

The detection and quantification of the adulteration of strawberry or raspberry juice with apple juice using visible and near-infrared transmittance spectroscopy was accomplished with a detection level of >10% [89]; and mid-infrared spectroscopy was used to detect the adulteration of maple syrup with cane or beet sugars [90].

A non-destructive method of near infrared spectroscopy was employed to detect the adulterations of cow milk with water and whey. NIR spectra in the region of 1100–2500 nm were used for quantitative estimation of adulterants in milk samples [91].

Santos et al. [92] compared NIR and MIR spectroscopy methods for detection of milk adulterated with tap water, whey, hydrogen peroxide, synthetic urine, urea, and synthetic milk in different concentrations. Classification and quantification models indicated that the tested MIR systems were superior to NIR systems in monitoring adulterants in milk.

Extra virgin olive oil is an expensive product that can cost 4–5 times more than other edible vegetable oils. Therefore, guarantees of genuineness, safety, typicity and absence of adulteration must be provided to justify its higher cost. In particular, as far as extra virgin olive oils are concerned, quality characteristics and taste are largely related to their origin, both geographical and cultivar, as well as to the agronomic techniques and the extraction and mixing procedures used. Bevilacqua et al. [93] developed an NIR spectrometric method for correctly classifying extra virgin olive oil produced in the Protected Designation of Origin of Sabina, Lazio, Italy from those produced from other regions.

Deep-fat frying where foods are cooked rapidly in oil at high temperature is a popular method of food preparation. The quality of fried foods is closely connected to the quality of the frying oil. Upon heating in the presence of moisture and oxygen, frying oil is subject to a series of degradation reactions, such as hydrolysis, oxidation, and polymerization. The compounds generated from these reactions not only have negative effects on the flavour of fried products but also have antinutritional properties and form potential carcinogenic compounds.Thus, frying oil quality control is important for preparing food safely. NIR spectroscopic methods have been successfully developed for determining the degradation products including total polar materials (TPM) and free fatty acids (FFAS) in soy-based frying oil used for frying various foods. TPMs and FFAs in frying oils can be quantitatively measured by NIR in <3 min. The NIR method is fast, simple, accurate, and nondestructive and more applicable for at-line or online quality assessment than conventional methods [94].

Bee honey is a unique sweetening agent that can be used by humans without processing and has significant nutritional and medicinal benefits. It is a rich source of readily available sugars, organic acids, and various amino acids and in addition to a source of many biologically active compounds. Because of its nutritional value and unique flavour, the price of natural bee honey is much higher than that of the other sweeteners, such as refined cane and beet sugar, and corn syrup. Therefore, honey is susceptible to be adulterated with these cheaper sweeteners. NIR spectroscopy can be used successfully to identify authentic honey from honey adulterated with high fructose corn syrup or added fructose + glucose solutions [95, 96].

Fluorescence Spectroscopy

Fluorescence F indicates a radiational transition between ground vibrational state of singlet excited electronic state S_1 and the various vibrational states of the ground electronic state S_0:

$$S_1 \rightarrow S_0 + h\nu. \qquad (2)$$

Fluorescence emission spectrum is the dependence of the fluorescence intensity on wavelength or frequency of emission radiation at a constant intensity and the wavelength of the exciting radiation. The fluorescence spectrum is shifted relative to the absorption spectrum toward longer wavelengths.

Fluorescence excitation spectrum is the dependence of the fluorescence intensity on wavelength or frequency of the excitation radiation at a constant intensity and wavelength of the fluorescence emission.

Fluorescence spectroscopy utilizes fluorescence emission and excitation spectra of electromagnetic radiation for qualitative and quantitative analysis of the structure and properties of a sample. Fluorescence spectroscopy 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% [97]. The reason for adulteration is that extra virgin olive oil is the highest-quality and the most expensive oil. As a consequence, manufacturers may be tempted to replace part of this oil with cheaper oils, such as olive–pomace oil.

Application of Fisher's linear discriminant analysis (LDA) and discriminant multi-way partial least squares (M-PLS) regression allowed discriminating non-adulterated and adulterated samples of olive oil. The lowest detection limits of adulteration were at a level as low as 8.4% [98].

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is an analytical system that is used to convert raw data into the actual infrared spectrum of a sample through such mathematical process as Fourier transform that converts an amplitude-time spectrum to an amplitude-frequency spectrum or vice versa. This analytical technique is based on the measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other types of radiation.

One of the main devices for measuring the temporal coherence of light is the Michelson or Fourier transform spectrometer which consists of a light source, beam splitter, movable and fixed mirrors, and detector (Figure 6*a*).

If the source is monochromatic and the movable mirror is moved at a constant rate, the detector signal oscillates with a single frequency. The radiant power can be recorded as a function of time as the cosine oscillation (time domain) or as a function of frequency as the spectral line (frequency domain). The plot of the output power from the detector versus the mirror displacement is called an *interferogram*. If the source is polychromatic, each input frequency can be considered to produce a separate cosine oscillation; the resulting interferogram is a summation of all cosine oscillations caused by all frequencies in the source (Figure 6*b*). The recorded signal is mathematically manipulated using a Fourier transform technique to produce a spectrum that can be used to identify specific contaminants and their concentrations (Figure 6*c*).

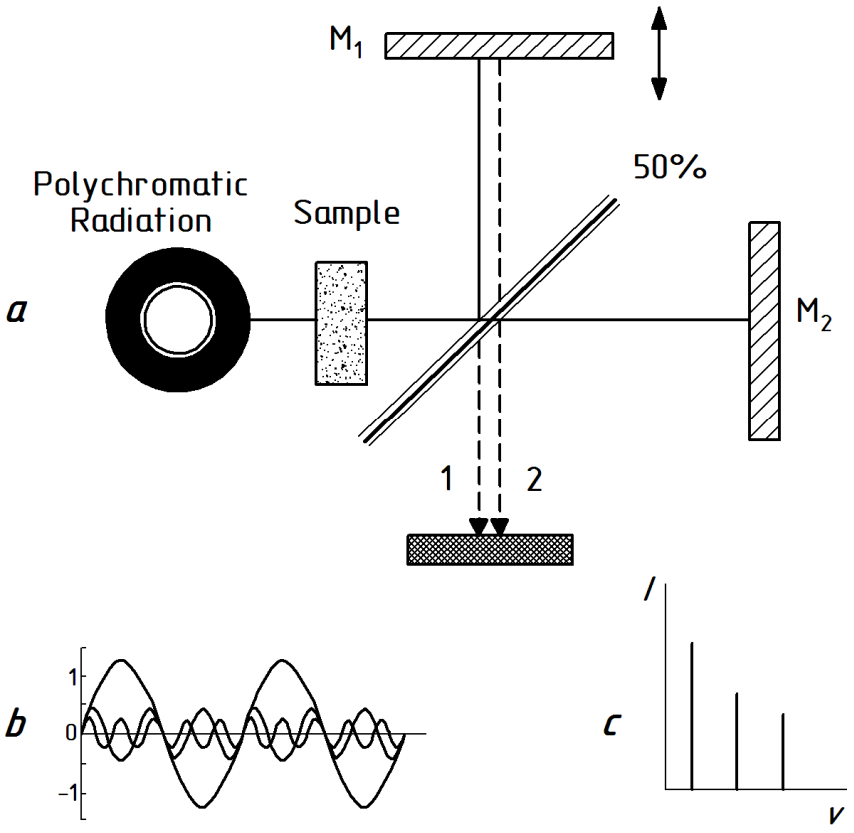

Figure 6. Principle of operation of Fourier transform spectrometer (the explanations in the text)

Fourier transform infrared spectrometer consists of a source of infrared radiation, an interferometer, an enclosed sample cell of known absorption wavelength, an infrared detector and a computer system. The sensitivity of FTIR ranges from very low parts per million (ppm) to high percent (%) levels. This technique is characterized by a non-destructive interaction with the sample. It provides a measurement of up to 30 or more compounds simultaneously and the measurements are very fast [99, 100].

FTIR spectroscopy was successfully applied for adulteration detection in pure pomegranate juice concentrate in which grape juice was added [101]. Three types of fruit purees namely strawberry, raspberry, and apple were successfully classified with 100% success using FTIR in combination with discriminant analysis [102]. It was also possible to classify the source if the purees were made from fresh or freeze-thawed with 98.3% success for strawberry and 75% for raspberry. FTIR spectroscopy was also used to develop a model that predicts the percent composition of Concord grape juice [104]. The model predicted Concord concentrations in samples ranging from 50% to 100% concord juice with a standard error of prediction of 5.6%. This results suggesting that the feasibility of using FT-IR coupled with chemometrics as a production-scale tool for authentication claims of

Concord in grape juice blends, protecting consumers and businesses against deceptive labeling.

Adulterated strawberry purees prepared by the admixture of apple and plum, and glucose and sucrose solutions, grape juice and rhubarb compote, and raspberry purees adulterated with sucrose as well as apple and plum puree were tested using FTIR. These adulterants could clearly be detected down to levels to be expected for adulterated purees on the market, with estimated detection limits of 20% (w/w) for apple and plum and 4% (w/w) for sucrose [105].

Kemsley et al., [105] showed that FTIR spectroscopy with attenuated total reflection (ATR) sampling could be used to detect adulteration of raspberry purees. Pure raspberries puree was detected with 95% success while adulteration with apple and plum could be detected at minimum levels of ~20% w/w, with sucrose at ~4% w/w.

Detection of the adulteration of wine by industrial grade glycerol is a very important quality control measure. Fourier transform infrared spectroscopy with a single bounce ATR accessory was found to be a useful tool in determining the presence of industrial grade glycerol in four brands of red wine at a detection limit of 1% [106].

Adulteration of some olive, peanut, corn germ and pumpkin oils with sunflower oil was identified using FTIR spectroscopy. It was shown that there were subtle spectral differences in the spectra of various types of vegetable oils [107]. FTIR spectroscopy was also used for analysis of extra virgin olive oil adulterated with palm oil at varying concentrations (1.0–50.0% wt./wt.) and with other vegetable oils (corn, canola, and sunflower) [108]. A procedure for the detection of vegetable oils such as canola, hazelnut, pomace and high linoleic/oleic sunflower as adulterants in commercial samples of extra virgin olive oil has been developed with FTIR and partial least squares (PLS) regression [109]. The presence of sunflower oil as an adulterant in extra virgin olive oil can be detected through FTIR spectroscopy using the ATR sampling method. Pure vs. adulterated olive oil samples successfully classified down to an adulteration level of 20mL of sunflower oil in 1 L of extra virgin olive oil [110].

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR spectroscopy) is a spectroscopic technique that is based on the analysis of the magnetic properties of atomic nuclei that possess spin. Certain nuclei have quantum number $I \neq 0$ (for example, nuclei of organic molecules, such as ^{1}H, ^{13}C, ^{19}F and ^{31}P have spin of $I = 1/2$. A spinning charge generates a magnetic field, known as a magnetic moment (μ) which is proportional to the spin. When a nucleus is located in a static magnetic field B_0, two spin states occur, $I = +1/2$ and $I = -1/2$.

The magnetic moments of both states are aligned with the external field ($I = +1/2$) and opposed to the external field ($I = -1/2$) (Figure 7*a*). The difference in energy between the two spin states is dependent on the external magnetic field strength and magnetic moment (Figure 7*b*):

$$\Delta E = \gamma \hbar B_0 = \hbar \omega, \qquad (3)$$

where $\hbar$ is a Planck's constant ($\hbar = 1.054571726 \times 10^{-34}$ Js); γ is the geomagnetic ratio, that is a precise characteristic of each nucleus; ω is the Larmor frequency. For example, the magnetic moments of organic molecules are: μ (^{1}H) = 2.7927; μ (^{19}F) = 2.6273; μ (^{31}P) = 1.1305; μ (^{13}C) = 0.7022.

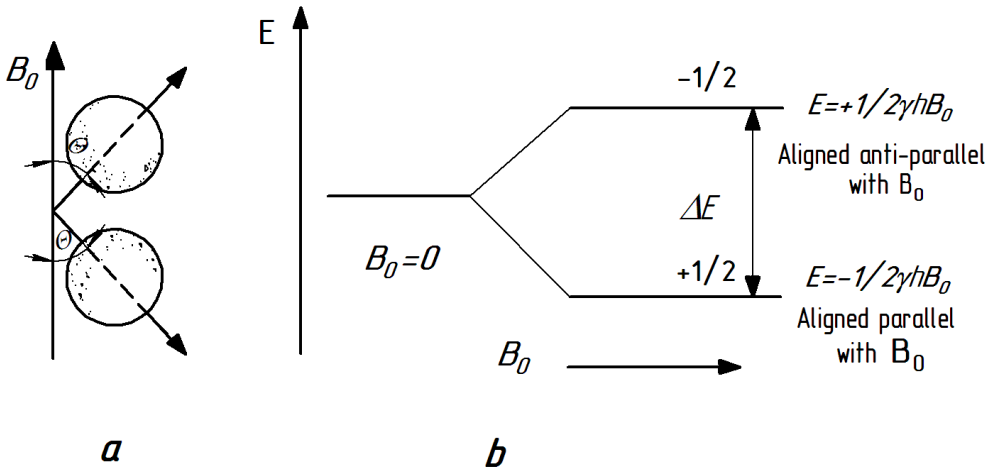

Figure 7. Nuclear Magnetic Resonance:
***a* – possible orientations of magnetic moments relative to the external magnetic field B_0;**
***b* – nuclear splitting ΔE of energy levels in a magnetic field for spins with quantum number ½**

If the electromagnetic radiation of radio frequency (that is equal to the Larmor precession rate) is applied to match the energy difference between the nuclear spin levels, the resonant absorption or emission of the energy by the nuclei takes place. This resonance effect is called *nuclear magnetic resonance* [111].

Electronic screening leads to a shift of the resonance frequency. Generally, nuclear magnetic resonance provides detailed information about the electronic structure of a molecule and its chemical environment.

A typical NMR spectrometer consists of a source of a strong static magnetic field; a solution of the sample in a glass tube located between the poles of the static field; an antenna coil that broadcasts the radiofrequency magnetic field into the sample; a receiver coil that surrounds the sample tube and provides a signal for electronic devices, and a computer.

The advantages of NMR spectroscopy are the ability to qualitative and quantitative detect very fine structural components, and the measurements are non-destructive. Disadvantages are the high cost due to the need for a strong liquid helium-cooled superconducting magnet; measurements are time consuming and not very sensitive; and the sample should be dissolved in a solvent.

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 combined ^{31}P and ^{1}H NMR spectroscopy and with multivariate statistical analysis, which was performed on 13 compositional parameters derived from the spectra [112]. In the Italian oenological industry, a regular practice used to naturally increase the colour of red wines consists in blending them with a wine very rich in anthocyanins, namely Rossissimo. In the Asian market, on the other hand, anthocyanins extracted from black rice are frequently used as correctors for wine colour. This practice does not produce negative effects on health; however, in many countries, it is considered as food adulteration. Ferrari et al., [113] tested FT-NIR and ^{1}H NMR spectroscopy methods

and found that ^{1}H NMR spectroscopy can successfully discriminate wines added with the blending wine Rossissimo from wines adulterated with anthocyanins extracted from black rice to increase their Color Index.

Isotope Ratio Mass Spectrometry

Two or more forms of the same element that contain equal numbers of protons but different numbers of neutrons in their nuclei and correspond to the same atomic number and position in the periodic table are called *isotopes.* Therefore, isotopes have different atomic masses and physical properties. Each chemical element has one or more isotopes.

The term "isotope" is derived from the Greek *ίσος* (iso-, "equal", "same") + *τόπος* ("place") since the same position in the periodic table is occupied by the different isotopes of the element. *Stable isotopes* are those that are stable and do not undergo radioactive decay over time. Carbon, hydrogen, and oxygen have the following stable isotopes: ^{12}C : 98.9% ; ^{13}C : 1.11% ; ^{14}C : <0.1% ; ^{1}H: 99.98%; ^{2}D: 0.015%; ^{16}O: 99.759%; ^{17}O: 0.037%; ^{18}O: 0.204%.

Modern analytical equipment has demonstrated that various isotopes of any element behave differently in both physical processes (i.e., heavier isotopic molecules have a lower mobility and diffusion velocity, and higher binding energy) and chemical reactions since the atoms of different isotopes are of different sizes and atomic weights. The separation of isotopes of an element during naturally occurring processes as a result of the mass differences between their nuclei is called *isotopic fractionation*.

Stable isotope abundances are expressed as the ratio of the two most abundant isotopes in the sample compared to the same ratio in an international standard, using the "delta" (δ) notation. Because the differences in ratios between the sample and standard are very small, they are expressed as parts per thousand or "per mil" (‰) deviation from the standard. The δ notation can be expressed as:

$$\delta_{sample} = [(R_{sample} - R_{std})/(R_{std})] \times 1000. \quad (4)$$

For example, water R_{sample} has a ratio of $^{13}C/^{12}C$, $^{18}O/^{16}O$ or $^{2}H/^{1}H$ in the sample and R_{std} is the ratio of the international standard for carbon, oxygen and hydrogen. The standard is defined as 0‰. International standards and their absolute isotope ratios for several environmentally important isotopes are illustrated by carbon, hydrogen and oxygen. The international standard for carbon is Pee Dee Belemnite, a carbonate formation, whose generally accepted absolute ratio of $^{13}C/^{12}C$ is 0.0112372. Materials with ratios of $^{13}C/^{12}C$ > 0.00112372 have positive delta values, and those with ratios of $^{13}C/^{12}C$ < 0.00112372 have negative delta values.

The ratio $^{2}H/^{1}H$ for hydrogen uses Vienna Standard Mean Ocean Water that has an R value = 0.00015575; and with oxygen the ratio $^{18}O/^{16}O$ is also measured with Vienna Standard Mean Ocean Water and has an R value = 0.0020052. Certain elements, (e.g., oxygen, hydrogen) have more than one international standard.

Because the differences in ratios between the sample and standard are very small, they are expressed as parts per thousand or "per mil" (‰) deviation from the standard. Products of natural and artificial origin display different isotopic abundances. Analysis of stable isotopes such as ^{13}C, ^{2}H and ^{18}O provides an opportunity to detect the adulteration of food.

Plants fix carbon from CO_2 in the atmosphere using three possible carbon fixation pathways and each of these result in carbohydrates with different isotopic compositions.

Most fruits and vegetables utilize the C_3 or Calvin-Benson cycle, while corn and sugar cane utilize the C_4 or Hatch-Slack pathway. Pineapple, in contrast, utilizes the crassulacean acid pathway to fix carbon. Each pathway gives a distinct isotope ratio.

Juice adulteration is achieved by either dilution of juice concentrate with water or addition of exogenous sugars (cane, beet sugar or corn syrup). Addition of water to a product can be detected by measuring ^{18}O, the measurement of the $^{13}C/^{12}C$ ratio, or the deuterium content D/H of sugars isolated from the juice, thus making it possible to distinguish between natural and adulterated juices.

The principles and application of $^{13}C/^{12}C$ analysis for detecting adulteration of juices derived from C_3 plants (those which use the C_3 photosynthetic pathway) with sugars originating from C_4 plants (sugarcane or maize) is explained in a book by L.W. Doner [114]. Adulteration of apple juice with high fructose corn syrup and pineapple juice could be detected by isotopic carbon analysis at the 20% level [115].

Raman Spectroscopy

When light passes through a particular material it may be absorbed, scattered or else simply pass through unobstructed if the photons do not interact with the molecules of the matter. When the energy of the incident photon corresponds to the energy gap between the ground state of a molecule and an excited state, the photon may be absorbed and the molecule promoted to the higher energy excited state. This phenomenon of energy absorption is used in a wide range of absorption spectroscopic techniques such as UV, VIS, NIR and IR spectroscopy. It is also possible for a photon to interact with a molecule and scatter (deflect from the original direction of propagation of incident light) from it. For scattering of photons by a molecule, it is not necessary for the photon to have an energy that matches the two energy levels of the molecule. Such scattered photons can be detected by collecting light at an angle to the incident light beam.

The most common scattering process without a change of frequency is called Rayleigh scattering or elastic scattering where the frequency of photons in monochromatic light does not change upon interaction with a sample. If there is any change in the frequency of the incident light, it is known as Raman scattering [116, 117]. If a sample is illuminated by a monochromatic beam of light, usually by a VIS or NIR laser beam and the frequency of the scattered photons are analyzed, the incident radiation wavelength is mostly observed due to Rayleigh scattering. However, if the 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 vibrational energy levels of the Raman active molecules in the sample. Usually, about 1×10^{-7} of the scattered light is Raman shifted. The change in wavelength of the scattered photon provides chemical and structural information about the sample. The Raman spectrum of the sample is constructed by plotting the intensity of this Raman-shifted light versus frequency. Usually Raman spectra are plotted with respect to the exciting laser frequency such that the Rayleigh band lies at 0 cm^{-1}. Consequently, the band positions will lie at frequencies that correspond to the energy levels of different functional group vibrations. The Raman spectrum can thus be interpreted similar to the infrared absorption spectrum.

Infrared absorption and Raman scattering are governed by completely different selection rules. In general, molecular vibrations symmetric with regard to the centre of symmetry are forbidden in the infrared spectrum, whereas molecular vibrations which are antisymmetric to the centre of symmetry are forbidden in the Raman spectrum. This is known as the rule of mutual exclusion. Infrared absorption can be detected if the dipole

momentum in a molecule is changed during the normal vibration. The intensity of an infrared absorption band depends on the change of the dipole moment during the vibration. A Raman active vibration can be detected if the polarizability in a molecule is changed during the normal vibration. The intensity of a Raman active band depends on the change of polarizability during the vibration.

An adaptation [118] designed to increase the amount of photon scattering is called *Surface Active Raman Scattering* (SERS). Generally, Raman spectroscopy can detect a wide range of compounds from inorganic to organic; however, the detection of organic molecules has been more difficult. It has been observed that, when placed on or near a metal surface, compounds or polyatomic ions can increase the number of Raman photons scattered by a factor of 10^3 to $10^{6.}$ Although this effect appears to be strongest on a silver surface, other metals such as gold or copper also demonstrate this ability to increase the Raman scatter. This process known as SERS enhances the electromagnetic field on the metal surface which, in turn, enhances the vibrational modes of the sample on its surface. Additionally, the SERS method causes a "charge-transfer complex" to be formed between the metal and the sample. This then causes resonance enhancement of the Raman signal to occur. The SERS method is particularly suited for electron rich molecules that contain lone electron pairs or pi electrons. Compounds that respond well to SERS include aromatic amines, phenols, compounds containing oxygen and carboxylic acids.

Raman spectroscopy has several advantages over mid-IR and NIR spectroscopy. Spectra can be obtained with little or no sample preparation therefore, it can be used for non-destructive testing of materials, often those inside glass or plastic containers [119] Since water is a weak scatterer, materials with high moisture levels or aqueous solutions can be easily analyzed using Raman spectroscopy. Raman spectroscopy can be used to measure bands of symmetric linkages which are weak in an infrared spectrum. Raman spectroscopy can also be used for both qualitative and quantitative applications. As in infrared spectroscopy, band areas are proportional to concentration, making Raman spectroscopy open to quantitative analysis. In fact, because Raman bands are inherently sharper than their infrared counterparts, isolated bands are often present in the spectrum for more straightforward quantitative analysis.

Because of the above mentioned advantages, Raman spectroscopic methods have been developed for rapid nondestructive analysis and screening of adulterants in numerous agricultural and food products [120-124]. Zhang et al., [125] used SERS to detect melamine in liquid milk with minimal sample preparation. The limit of detection by this method was 0.01 μg ml^{-1} for melamine standard samples and 0.5 μg ml^{-1} of melamine in liquid milk. The test results for SERS were very precise and as good as those obtained by liquid chromatography/tandem mass spectrometry. The method was simple, fast (only requires about 3 min), cost effective and sensitive for the detection of melamine in liquid milk samples. Therefore, it is more suitable for the field detection of melamine in liquid milk.

Simple and rapid detection of trace amounts of melamine in milk products has been achieved with a portable sensor system based on SERS [126]. The sensor system comprised of high-performance gold nano finger SERS sensor chips and a custom-built prototype portable Raman spectrometer. Compared to the FDA procedure and previously reported studies that were limited to laboratory settings, these sampling and analytical methods are simple (with one sampling step), less time-consuming and cost-effective. The limit of detection of melamine was 120 parts per trillion in water and 100 parts per billion in infant formula, which are well below the FDA's tolerance level of 1 ppm in infant formula.

The most widely practiced approach of adulterating milk is to mix water in it and adding urea to the resultant milk to raise its solid non-fat (SNF) value to give it a concentrated and rich appearance. Depending on the amount of water mixed, urea concentration is adjusted for making the specific gravity of the concocted milk equal to that of the natural milk so that the lactometer fails to detect any difference. Although urea, an end product of nitrogen metabolism, is a normal constituent of milk, a cutoff limit for urea concentration in milk is normally accepted to be ~70 mg/dl. Consumption of milk with a urea concentration above this limit can cause severe health problems for humans. Hence, detection of urea in milk and its quantitative estimation is important from the point of view of not only quality control in the dairy industries but also in human health care.

Khan et al. [127] assessed the applicability of a near-infrared Raman spectroscopy system that incorporates a 785-nm diode laser for Raman excitation to allow quantitative determination of urea adulteration in milk without any preprocessing requirements. The results demonstrated that the method could detect urea mixed in milk samples with an accuracy of >90 % and a detection limit of ~50 mg/dl thereby making it ideally suited for quantitative monitoring of urea adulteration of milk.

Terahertz Spectroscopy

The terahertz region (0.3 to 3 Terahertz frequency (1 THz = 10^{12} Hz) or 1.0 - 0.1 mm wavelength) lies in between microwaves and infrared regions of the electromagnetic spectrum. Terahertz radiation that originates from cosmic background radiation to blackbody radiation from room temperature objects is abundantly found around us. Yet most of these terahertz sources are incoherent and can hardly be utilized. Until recently it was difficult to efficiently generate and detect terahertz waves and due to the lack of good sources and detectors, the terahertz region remained unexplored. Recently, however, there has been a revolution in terahertz technology with the discovery of terahertz generation and detection schemes [128-130]. Terahertz spectroscopy is a non-destructive, non-contact and real-time technique that requires very little sample preparation. Moreover, terahertz radiation can penetrate plastic and paper, which enables the detection of adulterants in packaged foods. Recent developments in time-domain terahertz spectroscopy and related technologies have lead to many applications in a number of fields including food and agriculture [131-133].

Antibiotic and pesticide residues in agricultural and food products are of great concern to consumers and legislators. Reliable techniques are necessary for rapid and sensitive detection of pesticide residues to prevent adulteration and ensure food safety. Terahertz spectroscopy, though it is new compared to other methods, is emerging as a new technique for detection and quantification of pesticide residues in agricultural and food products. Redo-Sanchez et al., [134] reported the use of terahertz spectroscopy to explore the spectral properties of eleven antibiotics commonly used in livestock production. Eight of the eleven antibiotics displayed specific fingerprints in the frequency range between 0.1 and 2 THz. The main spectral features of two antibiotics (doxycycline and sulfapyridine) were still detectable when they were mixed with three food matrices (feed, milk and egg powder). These preliminary results indicated that terahertz spectroscopy could be suitable for screening applications to detect the presence of antibiotic residues in the food industry, with the prospect of allowing inspection directly on production lines.

Honey is generally considered to be a natural and healthy product. However, due to improper beekeeping practices antibiotic and acaricide residues has been detected in honey products [135]. Majority of existing analytical methods used for the determination of

residues in honey require pretreatment of the samples. Massaouti et al. [136] demonstrated the potential of Terahertz Time-Domain Spectroscopy for nondestructively detecting antibiotics in concentrations down to 1% w/w. Although the detectable residue levels are still far from those involved in the regulations of food and drug administrations, the technique shows the potential of this emerging technology. Qin et al. [137] investigated detection and quantification of tetracycline hydrochloride (TC-HCl) in powder and solution form using terahertz spectroscopy. Partial least-squares regression (PLSR) was used to build calibration models. The results obtained in this study indicated that the PLSR model for powder samples was excellent and could be used for quality control. However, the PLSR model for solution samples was not robust and needs to be improved. Overall, terahertz spectroscopy combined with PLSR model has the potential for a rapid and non-destructive prediction of TC-HCl residue without sophisticated methods, though the accuracy was not high enough for solution samples.

Suzuki et al. [138] tested the possibility of terahertz spectroscopy for pesticide inspection in agricultural products. Several pesticides show specific absorption in the range of 20-400 cm^{-1} and a high correlation was obtained between the concentration and the second derivative value of the spectra of *cis*-Permethrin. Good prediction performances of PLS and MLR were obtained with R^2 values of 0.95 and 0.96 and RPD values of 3.95 and 5.06, respectively. Broad absorption spectra in vegetables such as tomato, spinach, cabbage and strawberry were observed. When two kinds of material were mixed, absorptions of each material were observed as a superposition. It was confirmed that six pesticides and freeze-dried samples of tomato, spinach, cabbage and strawberry had specific absorption in the terahertz region.

Baek et al. [139] investigated the feasibility of detecting melamine in foodstuffs using terahertz imaging. The terahertz spectra and images of melamine mixtures were obtained in the frequency range of 0.1–3 THz at room temperature using terahertz time-domain spectroscopy (TTDS). Characteristic absorption peaks of melamine were found at 2.0, 2.26, and 2.6 THz, and these peaks had the same frequencies in the different food matrices. At 2.0 THz, the terahertz images of melamine were dose-dependently and distinguishable from those of food components with or without packaging materials present. The calibration curve of melamine had a regression coefficient of >0.913 and a detection limit of <13% suggesting that terahertz imaging has the potential to be used for the qualitative detection of melamine in food as a nondestructive analytical tool.

Powders and Turbid Liquids

Spectroscopy with Attenuated Total Reflectance

Traditional methods of infrared spectroscopy are based on the transmission of infrared radiation that passes from the source through the sample to the detector using a monochromator in the infrared spectrometer or interferometer in Fourier spectrometer. Differences in the energy that is absorbed at specific wavelengths can be used to assess chemical differences.

Spectroscopy with Attenuated Total Reflectance (ATR) is based on a completely different principle [140]. The sample is in contact with a crystal where total internal reflection takes place. Infrared radiation undergoes multiple internal reflections in a crystal with a high refractive index (Figure 8).

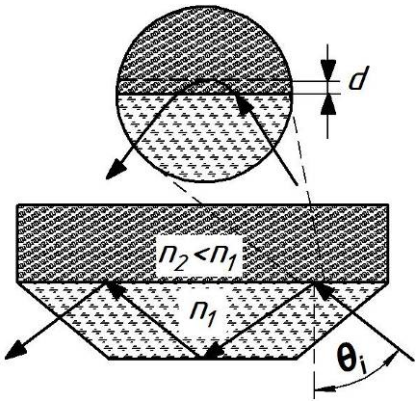

Figure 8. Spectroscopy with Attenuated Total Reflectance (ATR)

A substance with a lower refractive index absorbs radiation which is why the reflected radiation is attenuated exponentially (hence the term "Attenuated Total Reflectance"). This spectroscopy technique involves placement of the sample in contact with a special optical crystal (e.g., ZnSe, Ge or KRS-5).

When radiation passes through a transparent substance with a high refractive index and interacts with another substance with a lower refractive index, it is partially transmitted and partially reflected. However, a total internal reflectance occurs at a certain (critical) angle of incidence θ_{cr}. The value of this critical angle is calculated as:

$$\theta_{cr} = \sin\frac{n_1}{n_2}, \qquad (5)$$

where n_1 and n_2 are the refractive indices of the two substances, and $n_1 > n_2$.

Infrared radiation penetrates into the substance with lower refractive index at a depth d, which depends on the wavelength of the radiation, the refractive indices of two substances and the angle of incidence of radiation at the boundary of these substances. Depth d is calculated as:

$$d = \frac{\lambda}{2\pi n_{cr}\sqrt{\sin^2\theta_i - (n_{cr}/n_s)^2}}, \qquad (6)$$

where θ_i is the angle of incidence; n_{cr} and n_s are the refractive indices of the crystal and the sample, respectively and λ is the wavelength of infrared radiation. A typical value for d is 0.1–5 micrometers.

Since infrared radiation penetrates the sample and interacts with its components, the energy that reaches the detector is attenuated at wavelengths that correspond to the absorption by sample components. Thus, the detector records the dependence of the reflected intensity on the radiation wavelength or the absorption spectrum of components that are present in the sample.

In general, the intensity of the spectral bands depends on the structural composition of the product. Bands at 3700→2850 cm^{-1} (stretching vibrations of OH groups) and at 1640

cm^{-1} (deformation vibrations of the group H-O-H) are due to water; at 2927→2855 cm^{-1} to the joint contribution of fats, proteins and sugars (stretching vibrations of C-H); at 2930 cm^{-1}, 1740 and 1469 cm^{-1} they are associated with lipid components; at 1100 cm^{-1} and below to carbohydrates; at 1660 cm^{-1} with proteins, polypeptides, amino acid salts; and at 3300 cm^{-1}, 1550 and 1400 cm^{-1} to proteins.

The advantage of the ATR-spectroscopy is the ability to analyse various products (e.g., stuffed meat, solid chocolate, viscous liquids and pastes, grease, oil, cheese, juices). Fourier transform infrared (FTIR) technology in conjunction with attenuated total reflectance (ATR) technology is used for the analysis of powders and turbid liquids.

The disadvantage of ATR-spectroscopy is that it is limited to only homogeneous samples. Furthermore, the procedure requires for reliable measurements contact between the crystal and the product (this applies primarily to solidified powders). After measurements the crystal should be thoroughly washed, removing any residual product (especially those containing oil).

The technology can be applied to detect honey adulteration [141, 142]. For example, it was used to quantify three different adulterants (corn syrup, high fructose corn syrup and inverted sugar) in honey from four different locations in México [143]. FTIR-ATR spectra has also been successfully used for the detection of olive oil adulteration with corn oil [144]. Fourier transform infrared spectroscopy and attenuated total reflection sampling have also been used to detect adulteration of apple juice samples [145].

Single bounce attenuated total reflectance (SB-ATR) FTIR was used as an effective and rapid tool for the detection and quantification of melamine in liquid and powder milk [146]. The limit of detection and limit of quantisation of the proposed SB-ATR–FTIR method was 0.00025% (2.5 ppm) and 0.0015% (15 ppm) respectively. Little or no sample preparation is required for measurement and the procedure takes 1-2 min. Santos et al. [147] used attenuated total reflectance mid-infrared microspectroscopy as a rapid method for the detection and quantification of milk adulteration. Partial Least Squares Regression (PLSR) showed standard errors of prediction of 2.33, 0.06, 0.41, 0.30 and 0.014 g/L for estimation of levels of adulteration with whey, synthetic milk, synthetic urine, urea and hydrogen peroxide respectively, demonstrating that MIR-microspectroscopy can provide an alternative screening method to the dairy industry for fraudulent adulteration of milk.

NIR Spectroscopy

Near infrared spectroscopic methods have been developed for the detection and quantification of adulteration of flour made from durum wheat [148], oats [149] and Chinese glutinous rice [150]. Adulteration of these flour types with cheaper substitutes such as common bread wheat flour, non-glutinous rice flour and talcum powder were successfully detected and quantified by NIR spectroscopy. Gaspardo et al. [151] tested a method using a FT-NIR spectrophotometer equipped with an integration sphere to predict Fusarium mycotoxin Fumonisin $B_1 + B_2$ contents in corn meal. Coefficients of correlation, root mean square error and standard error of a calibration model were 0.964, 0.630 and 0.632, respectively and the external validation confirmed a fair potential of the model for predicting $FB_1 + FB_2$ concentrations, suggesting that FT-NIR analysis is a suitable method to detect $FB_1 + FB_2$ in corn meal and to discriminate safe meals from those contaminated.

Chili powder is a globally traded commodity which has been found to be adulterated with Sudan dyes. Haughey et al. [152] tested NIR reflectance spectroscopy and Raman spectroscopy to quantitate Sudan I dye in chili powder at the concentration range of 0.1 – 5.0%. For the quantitative models, coefficients of determination (R^2) were found to be

0.891–0.994 depending on which spectral data (NIRS/Raman) was processed, the mathematical algorithm used and the data pre-processing applied. The limit of detection (LOD) based on analysis of 20 blank chili powders against each calibration model gave 0.25% and 0.88% for the NIR and Raman data, respectively. In addition, it was also possible to discriminate between adulterated from non-adulterated chili powders.

Near- and mid-infrared spectroscopy methods (NIR, FTIR-ATR, FTIR-DRIFT) were evaluated by Mauer et al. [153] for the detection and quantification of melamine in infant formula powder. Partial least-squares (PLS) models were established for correlating spectral data to melamine concentration: $R^2 > 0.99$, RMSECV = 0.9, and RPD = 12. Factor analysis of spectra was able to differentiate unadulterated infant formula powder from samples containing 1 ppm melamine with no misclassifications, a confidence level of 99.99%, and selectivity > 2.

These nondestructive methods require little or no sample preparation and the NIR method has an assay time of 1 min and a 2 min total time to detection. The FTIR methods require up to 5 min for melamine detection. Therefore, NIR and FTIR methods enable rapid detection of 1 ppm melamine in infant formula powder. Balabin and Smirnov [154] found that infrared spectroscopy is an effective tool to detect melamine in dairy products, such as infant formula, milk powder or liquid milk. However, the relationship between MIR/NIR spectrum of milk products and melamine content is nonlinear. Thus, nonlinear regression methods are needed to correctly predict the melamine content of milk products. A limit of detection below 1 ppm (0.76±0.11 ppm) can be reached with correct spectrum preprocessing and a correct multivariate algorithm.

Raman Spectroscopy

A portable compact Raman spectrometric system was used by Cheng et al. [155] to detect melamine adulterantion in milk powder. Melamine fortification of milk powder was identified with good reproducibility by two characteristic vibration modes at 673 and 982 cm^{-1}. The intensity of the first mode was used to quantify melamine levels in milk powder with a detection limit of 0.13%.

Melamine has been discovered in many types of food in addition to milk powder [156] and causing enormous economic losses to the food industry. Lin et al. [157] measured melamine concentration in wheat gluten, chicken feed, and processed foods (cake and noodle) by surface enhanced Raman spectroscopy (SERS) in combination with SERS-active substrates. SERS was able to rapidly detect 0.1% melamine in wheat gluten, 0.05% in chicken feed, 0.05% in cakes, and 0.07% in noodles, respectively. A partial least squares (PLS) model was established for the quantification of melamine in foods by SERS: R= 0.90, RMSEP = 0.33. Compared with HPLC, the SERS method is much faster and simpler, requires minimum sample preparation, but still yields satisfactory qualitative and quantitative results.

Hyperspectral /Multispectral Imaging Spectroscopy

Machine vision and image processing techniques [158, 159] has long been used to evaluate quality and safety of food and agricultural products. Likewise, spectroscopic techniques such as VIS-NIR spectroscopy have also been used to measure certain chemical/physical quality parameters of food and agricultural products [160, 161]. However, such conventional imaging and vision techniques cannot acquire spectral information while conventional spectroscopy cannot differentiate spatial differences in a

sample in relation to spectroscopic properties. To overcome these problems when the image processing or spectroscopic techniques are used alone, spectral imaging techniques such as hyperspectral and multispectral imaging has emerged as a better tool for safety and quality assessment of various agricultural commodities. Spectral images are three-dimensional in nature having two spatial dimensions and one spectral dimension. Based on the continuity of the data stored in the wavelength domain, spectral imaging can be divided into two main techniques: hyperspectral imaging and multispectral imaging. The hyperspectral technique acquires images with numerous continuous wavebands, while the multispectral technique acquires images with a few discrete wavebands. A full spectrum can be extracted from each pixel in hyperspectral images. Multispectral images produce a set of isolated data points for each pixel due to the separate wavebands stored in the data set.

These spectral imaging techniques combine capabilities of conventional imaging and spectroscopy techniques allowing obtaining both spatial and spectral information from the product. The technique has developed rapidly during the past decade with many applications for quality and safety assessment of food products [162-166]. Moreover, a portable hyperspectral imaging system has been developed for monitoring sanitation procedures in produce processing plants to assure food safety [167].

September [168] used NIR hyperspectral imaging for the detection of millet and buckwheat flour in ground black pepper. Black pepper and adulterant (either millet or buckwheat flour) mixtures were made in 5% (w/w) increments spanning the range 0→100% (w/w). The mixtures were imaged across the spectral range of 1000–2498 nm. The model created with millet adulterated black pepper samples had a classification accuracy of 77%; a classification accuracy of 70% was obtained for the buckwheat adulterated black pepper samples.

The potential of Raman chemical imaging for simultaneously detecting multiple adulterants in milk powder was investigated by Qin et al. [169]. Potential chemical adulterants, including ammonium sulphate, dicyandiamide, melamine and urea, were mixed into skim dry milk in the concentration range of 0.1–5.0% for each adulterant. Using a 785-nm laser, a Raman imaging system acquired hyperspectral images in the wave number range of 102–2538 cm^{-1} for a 25 × 25 mm^2 area of each mixture sample, with a spatial resolution of 0.25 mm. Self-modelling mixture analysis was used to extract pure component spectra, by which the four types of the adulterants were identified at all concentration levels based on their spectral information divergence values to the reference spectra. Raman chemical images for effective visualization, identification and spatial distribution of the multiple adulterant particles in the dry milk was also demonstrated. Fu et al. [170] investigated a NIR hyperspectral imaging technique to detect low levels (<1.0%) of melamine particles in milk powders as an effective method for melamine adulteration discrimination.

Fruits, Vegetables and Nuts

Nitrate Tester

Marketing fruit and vegetables may be accompanied by qualitative adulterations (e.g., the addition of water, the introduction of antibiotics and preservatives, the addition of nitrate and other compounds that are intended to modulate the rate of ripening). For example, most greenhouse plants are given nitrate fertilizer and are treated with pesticides. Exceeding the admissible concentrations of these potentially harmful substances in the soil often leads to their accumulation in the plant. Nitrates dominate usually in large-sized fruit.

The most nitrates can be found in watermelons, melons, cabbage, potatoes, parsley, dill, black radishes, lettuce, spinach, rhubarb, celery, carrots, radishes and beets. The consumption of excess nitrates by humans leads not only to poisoning, but also to oxygen starvation of cells and tissues (tissue hypoxia) and even to the formation of carcinogens in the body.

Assessment of the nitrate content of fresh fruit and vegetables can be achieved using a nitrate-tester (e.g., the Soeks nitrate detector which has a range from 20 to 5,000 mg/kg). The principle of operation of such a device is based on the measurement of electric conductivity of the fruit or vegetable tissue, which contains the salt ions (nitrates, phosphates, etc.) required for vital functions and the normal development of the plant.

Advantages of the Soeks nitrate-tester include quick and relatively accurate measurements, compactness, lightweight, easy control and numerical and graphical presentation. The disadvantage is that graphs of the measurements on the screen are rather small and cannot be easily read.

Infrared Spectroscopy

A VIS-NIR spectroscopy method was tested with contact and reflectance scanning modes to measure nitrate content of radish [171]. Multiple linear regression (MLR) of the non-contact mode gave a multiple correlation coefficient (MR) of 0.929, and a standard error of the calibration sample set (SEC) of 675 ppm. MLR on spectra of the contact mode gave a calibration equation with a MLR of 0.927, and a SEC of 686 ppm. The single correlation coefficients at 560 nm and nitrate concentration were high (R= -0.888 for the contact mode, -0.858 for the non-contact mode, respectively). Although the RMSEs of these results were not satisfactory the data showed the possibility of using NIR methods for the determination of nitrate content in Japanese radishes.

Salguero-Chaparro et al., [172] tested the feasibility of using NIR spectroscopy as a swift and non-destructive screening method for intact olives that contain levels of the pesticide diuron that were higher than the Maximum Residue Limit (MRL) stipulated by the European Union (0.2 ppm). The best model developed correctly classified 85.9% of samples used in the validation set of olives with diuron contents above and below the MRL.

Mold infection is a significant postharvest problem for processors of chestnuts (*Castanea sativa* Miller). Fungal diseases cause a direct loss of product or reduced value due to the lower-quality grade of the chestnuts. In most cases, fungal infection is not detectable using traditional sorting techniques. Moscetti et al. [173] demonstrated the feasibility of using NIR spectroscopy to detect hidden mold infection in chestnuts. Classification error rates as low as 2.42% false negative, 2.34% false positive, and 2.38% total error were achieved. The results represent an important step toward the development of a sorting system based on multispectral NIR bands, with the potential to rapidly detect and remove chestnuts contaminated by fungi, thereby reducing the incidence of hidden mold in chestnuts.

Olive fruit fly infestation is a significant problem for the milling process. In most cases, damage from the insect is not visually detectable on the fruit surface. Consequently, traditional visual sorting techniques are generally inadequate for the detection and removal of olives with insect damage. Moscetti et al. [174] tested the feasibility of using NIR spectroscopy to detect hidden insect damage. The classification error rates were as low as 0.00% false negative, 12.50% false positive, with 6.25% of total error.

Peppers are a frequent object of food safety alerts in various member states of the European Union owing to the presence of unauthorized pesticide residues in some loads.

The feasibility of using NIRS for the measurement of pesticide residues in peppers was tested using commercially available spectrophotometers and different sample-presentation methods [175]. Classification accuracies of 75 and 82% were obtained for pesticide-free and pesticide-containing samples respectively for intact peppers using a diode-array spectrometer. These results confirmed that NIRS technology may be used to provide a rapid, non-destructive preliminary screening for pesticide residues in peppers. Suspect samples may then be confirmed using another analytical method.

Near-infrared spectroscopy was used byVitale et al. [176] to develop an analytical protocol to authenticate the origin of pistachio nuts (*Pistacia vera* L.) coming from Bronte (Sicily), the only protected designation of origin (PDO) pistachio production in Europe. Six different origins (Sicily, India, Iran, Syria, Turkey and U.S.A.) were analyzed by NIR spectroscopy. Classification accuracies higher than 90% were achieved for most of the classes with only exception being samples from Turkey and Iran, whose heterogeneity resulted in a poorer specificity, though the identification was still higher than 80% accuracy. In particular, the results obtained for the samples coming from Bronte, a high value-added food product, were very promising from the viewpoint of the authentication of this product.

Raman Spectroscopy

Residual pesticides in fruits and vegetables are one of the major food safety concerns around the world. Recently, Raman spectroscopic techniques have been widely tested for detecting and quantifying pesticide residues in fruit and vegetables.

Fan et al. [177] tested SERS for quantitative analysis of trace levels of carbaryl pesticide in apples. The lowest detectable level for carbaryl in apple was 0.5 μg g^{-1}, which was sensitive enough for identifying apple contaminated with carbaryl above the maximum residue level. Carbaryl levels in apples could be predicted by a low root mean square errors (RMSE = 0.44 μg g^{-1}) and a high ratio of performance to deviation (RPD = 8.11) value, indicating that SERS has the potential to quantify carbaryl pesticide in complex food matrices reliably. Dhakal et al. [178] explored the application of Raman spectroscopy for detection of a commercially available organophosphate pesticide (chlorpyrifos) on apple surfaces. The results showed that the system could detect chlorpyrifos residue to minimum limit of 6.69 mg/kg on apple surfaces at less than 4 seconds/fruit.

Surface-enhanced Raman spectroscopy was also used to detect and characterize three types of pesticides (carbaryl, phosmet, and azinphos-methyl which are widely used on apples and tomatoes) extracted from fruit surfaces [179]. Significantly enhanced Raman signals for the pesticides were acquired by SERS from the extract of fruit samples and exhibited characteristic patterns of the analytes. SERS was able to detect all three types of pesticides extracted from fruit samples in the parts per million level. The study of detection limits demonstrated that at 99.86% confidence interval, SERS can detect carbaryl at 4.51 ppm, phosmet at 6.51 ppm, and azinphos-methyl at 6.66 ppm spiked on apples; and carbaryl at 5.35 ppm, phosmet at 2.91 ppm, and azinphos-methyl at 2.94 ppm on tomatoes. This study showed that using SERS coupled with novel gold coated nano-substrates, pesticides residues can be quantitatively measured and qualitatively distinguished and characterized. With a few preparation steps, trace amount of pesticides on apples and tomatoes can be rapidly extracted and detected by SERS, and the detection limits meet the MRLs set by FAO/WHO.

The quality of olive oil produced depends largely on the quality of the olives. In an enterprise aimed at producing high-quality oils, olives with defects (“ground”; i.e., fallen to

the ground) need to be separated from healthy fruit ("sound"; i.e., collected directly from the tree) in that a very small portion of low quality fruit can ruin the whole batch. The fruit falls partly because of its maturation process, but also because of pests, diseases or weather conditions (e.g., strong wind). Fruit that has fallen to the ground generally suffers a rapid deterioration in quality. Guzman et al. [180] developed a low-resolution Raman spectroscopy method for the discrimination of olives before the oil processing stage in order to detect whether they have been collected directly from the tree (i.e., healthy fruit) or not. The best results were obtained with prediction of 100% for "sound" and 97% for "ground" in an independent validation set. These results demonstrated the potential of this method as a rapid, nondestructive tool for checking the quality of olives before they enter the oil production process. This allows producing good quality oil by creating more controlled production processes and saving considerable expense by avoiding unwanted mixing.

Li et al. [181] reported a new approach, shell-isolated nanoparticle-enhanced Raman spectroscopy in which the Raman signal amplification is provided by gold nanoparticles with an ultra-thin silica or alumina shell. Given the availability of portable Raman spectrometers, this very simple method can be widely applied to probe surface composition, adsorption and processes in diverse objects and morphologies (e.g., single-crystal surfaces, cell walls, semiconductors, fruits). The potential of this method for detection of pesticide residues on fruit was illustrated with citrus fruits contaminated with parathion residues.

Hyperspectral Imaging

Hyperspectral imaging is rapidly gaining ground as a non-destructive, real-time detection tool for produce quality and safety assessment. Hyperspectral imaging could be used to simultaneously obtain large amounts of spatial and spectral information on the objects being studied [182]. Hyperspectral techniques are used to detect pathogens, defects and contaminants and also to evaluate certain quality attributes of fruits and vegetables. Since the quality attributes of fruit and vegetable products show significant variation within the product unit [183], hyperspectral techniques that can encompass spatial variability may be more suitable for such products. Therefore, these techniques may be useful to detect intentional adulteration or prevent unintentional contamination of produce with poor quality product units.

Bruising is the most common type of mechanical damage affecting fresh horticultural produce. It reduces quality to the consumer and income to fruit and vegetable industries. Bruising can occur during harvest and at all stages of postharvest handling, especially during packhouse operations, transport and storage, and is one of the major physical defects contributing to downgrading and postharvest losses in fresh horticultural produce. Novel and emerging non-invasive technologies for bruise measurement of fresh horticultural produce include NIR spectroscopy, hyperspectral imaging, thermal imaging and nuclear magnetic resonance imaging [184].

The early detection of bruises in apples was studied using a system that included hyperspectral cameras equipped with sensors working in the visible, near-infrared (400→1000 nm) and short wavelength infrared (1000→2500 nm) ranges and a thermal imaging camera in the mid-wavelength infrared (3500→5000 nm) range [185]. Principal component analysis (PCA) and minimum noise fraction (MNF) analyses of the images that were captured in particular ranges made it possible to distinguish between areas with defects in the tissue and sound tissue. Fast Fourier analysis of the image sequences after pulse heating of the fruit surface provided additional information not only about the

position of the area of damaged tissue but also about the depth of damage. Results confirmed that broad spectrum range (400–5000 nm) fruit surface imaging can improve the detection of early bruises of varying depths.

Lee et al. [186] used hyperspectral imaging in the 950–1650 nm range for detecting bruise damage underneath the surface of pears. A classification algorithm based on *F*-value was applied for analysis of the image to find the optimal waveband ratio for discrimination between bruised and sound surfaces. The results demonstrated that the best threshold waveband ratio for detecting bruises had an accuracy of 92%, illustrating that the hyperspectral infra-red imaging technique could be a potential detection method for pear bruising.

Hyperspectral imaging (400–1000 nm) was investigated by ElMasry et al. [187] for the detection of chilling injury in Red Delicious apples. A hyperspectral imaging system was established to acquire and pre-process apple images, as well as to extract apple spectral properties. Feed-forward back-propagation ANN models were developed to select the optimal wavelength(s), classify the apples, and detect firmness changes due to chilling injury. The five optimal wavelengths selected by ANN were 717, 751, 875, 960 and 980 nm which had an average classification accuracy of 98.4%. This allowed distinguishing between normal and injured fruit with a correlation coefficient between measured and predicted firmness values of 0.92 for the validation. The results demonstrated the potential of the technique for detecting chilling injury and predicting apple firmness.

Yu et al. [188] presented a method for the identification of fresh jujube surface cracks using hyperspectral imaging in the visible and near infrared (VIS/NIR) regions (380–1030 nm) combined with image processing. Partial least squares regression (PLSR) and least-squares support vector machine (LS-SVM) discrimination models were established to correctly distinguish between cracked and sound fresh jujube. The results demonstrated that the PLSR–LS-SVM discrimination model had an accuracy of 100 % indicating that hyperspectral imaging combined with an image processing technique could rapidly identify surface cracking in fresh jujube fruit.

Crack defects in cherry tomatoes is an important quality aspect as this type of damage can harbor pathogenic microbes that may have detrimental consequences on consumer health. A multi-spectral fluorescence imaging technique was presented by Cho et al. [189] as a diagnostic tool for non-destructive detection of defective cherry tomatoes. Fluorescence intensity in the area of a cracked cuticle was significantly higher in the blue-green spectral region than that of the sound surfaces, suggesting the multi-spectral fluorescence imaging technique may be an effective classification tool for detecting surface cracking defects in cherry tomatoes. This technique is capable of detecting defective cherry tomatoes with >99% accuracy.

Detection of surface defects and/or contamination that included side rots, bruises, flyspecks, scabs and molds, fungal diseases (such as black pox), and soil contamination of Red Delicious, Golden Delicious, Gala, and Fuji apples were compared using a high spatial resolution (0.5–1.0 mm) hyperspectral imaging system [190]. Differences in spectral responses within the 430–900 nm spectral range were analyzed using monochromatic images and second difference analysis methods for sorting wholesome and contaminated apples. An asymmetric second difference method using a chlorophyll absorption waveband at 685 nm and two bands in the NIR region was shown to provide excellent detection of the defective/contaminated portions of apple fruit, independent of the apple colour and cultivar.

Hyperspectral imaging in the visible and near-infrared (400–1000 nm) regions was tested for the nondestructive determination of moisture content (MC), total soluble solids (TSS), and acidity (expressed as pH) in strawberries [191]. The correlation coefficients (*r*)

with the whole spectral range (400–1000 nm) for predicting MC, TSS, and pH were 0.90, 0.80, and 0.87 with SEC of 6.085, 0.233, and 0.105 and SEP of 3.874, 0.184, and 0.129, respectively for the PLS calibration models.

A rapid method based on hyperspectral imaging for detection of *Escherichia coli* contamination in fresh packaged spinach was developed using a hyperspectral system in the 400–1000 nm wavelength range, with a spectral resolution of 5 nm [192]. Reflectance spectra were gatherd from various positions on the sample surface. Principal component analysis (PCA) and artificial neural network (ANN) models were then used to build models where PCA was implemented to remove redundant information in the hyperspectral data. ANN was capable of correlating hyperspectral data with number of *E. coli.* Once trained, the ANN was also used to construct a prediction map of all pixel spectra of an image to display the number of *E. coli* in the sample. The results suggested that this hyperspectral imaging method provided a rapid and innovative approach for the detection of *E. coli* contamination in packaged fresh spinach.

The appearance of fresh fruits and vegetables is considered as a primary criterion in making purchasing decisions [193]. Hyperspectral imaging techniques can be successfully used to evaluate important quality attributes by assessing each product unit identifying defective or poor quality units for removal whereby improving the overall appearance of the product and assuring product quality and safety.

Granules and Grains

Mass Spectrometry with Inductively Coupled Plasma (MS-ICP)

This method is described in section “Analysis of Gaseous Phase of Products”. It is based on spraying particles (granules and grains) in the form of an aerosol, its evaporation and breakage into fragments and/or atoms which are ionized at a high temperature and directed to the mass spectrometer. The output signal of provides information on the concentration of the particles.

MS-ICP was used for testing different rice (*Oryza sativa* L.) genotypes and demonstrated its efficiency for determining the authenticity and adulteration of food products [81]. The method has also been used for the detection of adulteration of rice products. The discrimination of geographical origin of rice is practically useful to prevent possible mislabelling and adulteration of rice products. Inductively Coupled Plasma Mass Spectrometry and discriminant analysis was applied to 31 Thai jasmine rice and 5 foreign (France, India, Italy, Japan and Pakistan) rice samples [80].

Fluorescent Detection of Simple Sequence Length Polymorphisms

Simple Sequence Length Polymorphisms (SSLPs) are used as genetic markers with Polymerase Chain Reaction (PCR) that permits the analysis of any short sequence of DNA (or RNA).

Fluorescent simple sequence length polymorphisms (SSLPs) between known Basmati rice cultivars and non-Basmati long-grain rice within samples of Basmati were used to detect the presence of any adulterant [194].

Visible and Infrared Spectroscopy

A great deal of public attention has been focused on problems associated with *Fusarium* head blight (FHB) of wheat and barley and fungal metabolite vomitoxin (also known as DON or deoxynivalenol). In the Northern Plains of USA, the epidemic which began in 1993 persisted for several consecutive years, lowering yields and subjecting producers to large quality-related price discounts [195]. Instrumentation using single kernel NIR spectroscopic techniques have been developed to detect, quantify DON levels and sort *Fusarium* infected wheat grains [196-198]. The instrumentation and analysis technique can be run at a speed of about one kernel/s and is suitable for evaluation of small grain samples, for example, plant breeding materials to help plant breeders identify FHB resistant wheat cultivars. For this single kernel grain evaluation instrument, singulation of kernels to feed the spectrometer viewing area was achieved using a nearly vertical 15 cm in diameter vacuum wheel with eight evenly spaced 0.7-mm vacuum ports located 0.6 cm from the edge of the wheel. The vacuum wheel picks up one kernel at a time from a kernel bin and deposits it into a V-shaped trough for the acquisition of kernel spectrum. After the kernel has been analyzed, the trough is rotated by a stepper motor to drop the kernel through a series of gates that led to one of four sorting bins based on predefined sort settings.

Recently, Pearson et al. [199] developed a high speed multispectral sorting device constructed using three visible and three NIR light emitting diodes (LED) with peak emission wavelengths of 470 nm (blue), 527 nm (green), 624 nm (red), 850 nm, 940 nm, and 1070 nm (near-infrared) with a throughput of approximately 20 kernels/s which could detect and remove approximately 90% of the kernels with visible symptoms of FHB damage. Saito et al. [200] tested two types of commercial optical sorters: a full colour belt sorter (model CS-300, Satake Corp., Hiroshima, Japan) which measures a material's optical characteristics in the RGB wavelength range, and an optical sorter (model RMGS561, Satake Corp.), which measures a material in the NIR wavelength range over 1400 nm to reduce deoxynivalenol (DON) and nivalenol (NIV) concentrations in wheat. The results showed that the 2.29 ppm DON concentration of the material wheat can be reduced below the tentative DON regulation level in Japan (1.1 ppm) at 95% product yield after sorting while the 1.20 ppm NIV concentration of the material wheat can be reduced by 50% to 60% using the same optical sorter.

Karnal bunt is a fungal disease of wheat, durum, and triticale caused by the smut fungus *Tilletia indica* Mitra. Wheat infected with *T. indica* is subject to international regulation by 78 countries. To rapidly sort and remove infected wheat kernels, Dowell et al. [201] investigated the use of ScanMaster II SM100IE (Satake USA Inc, Houston, TX) sorter which has 10 parallel channels that singulate kernels before each is viewed from two sides by a high-resolution CCD camera with a 675-nm filter. The filter maximizes the colour difference between asymptomatic and kernels with Karnal bunt. When the sorter removed about 8% or more of the sample, the reject portion contained 100% of the bunted kernels. Concentrating the bunted kernels in a smaller sample size will reduce sample inspection time and should reduce inspection errors. The sorter can process up to 8,800 kg/h; thus, bunted kernels can be rapidly removed from samples or large lots. Each sample was sorted in less than 1 min. The high speed sorter consists of several steeply inclined chutes where kernels descend by force of gravity. Immediately below the channel exit, kernels are illuminated while the sensors observe each kernel in freefall and gather its spectra for evaluation based on the calibration. Thereafter, using the sort criteria an air ejector diverts the kernel from its normal trajectory to a bin for rejected material while the non-diverted kernels fall into a separate accept bin. This technology provides the wheat industry with a tool to rapidly inspect samples to aid in regulating Karnal bunt, and to remove bunted grains from seed wheat and wheat destined for food or feed use.

Fish, Meat, and Seafood

Infrared Spectroscopy

Adulteration level of meat products, especially minced beef, is estimated using non-destructive spectroscopic methods. Mixtures of minced beef adulterated with turkey meat in the range 5–50% (w/w) were prepared and analyzed through the methods of UV–visible, near infrared (NIR) and mid infrared (MIR) spectroscopy [202]. The best results were obtained with NIR and MIR spectroscopy.

Methods of visible and short wave near infrared (VIS/SW-NIR) spectroscopy were used for the rapid, non-destructive detection of beef adulteration [203]. This spectroscopic technique was applied to the samples of pure minced beef pork and beef liver, beef and pig fat trimming as well as the mixture samples in the form of minced beef adding different proportion of others, respectively. The results demonstrated that the VIS-SW-NIR spectroscopy can be used to detect and classify the amount and level of adulterants added to the minced beef with acceptable precision and accuracy. Likewise, the results of application of near infrared spectroscopy (NIRS) for detecting and quantifying different adulterants (pork, fat trimming and offal) in fresh minced beef demonstrated good performance [204].

The adulteration of pork in beef meatball was studied by Rohman et al. [205]. The application of Fourier transform infrared (FTIR) spectroscopy and partial least square (PLS) calibration made it possible to distinguish pork fat (PF), beef fat (BF), and their mixtures in meatballs.

Ding and Xu [206] developed a NIR spectroscopic technique to detect beef hamburgers adulterated with 5–25% mutton, pork, skim milk powder, or wheat flour with an accuracy up to 92.7%. The accuracy of detection increased with the increase of adulteration level. When an adulterant was detected, the adulteration level was further predicted by calibration equations. The established calibration equations for predicting adulteration levels with mutton, pork, skim milk powder, and wheat flour had standard errors of cross-validation of 3.33, 2.99, 0.92, and 0.57%.

Zhao et al. [207] demonstrated MIR-ATR technique for detecting offal-adulterated beefburger from authentic product comprised either only lean meat and fat (higher quality beefburgers) or lean meat, fat, rusk and water (lower quality product). Beef offal adulterants comprised heart, liver, kidney and lung. 100% correct classification accuracies were obtained separately for fresh and frozen-then-thawed material. Separate class-models for fresh and frozen-then-thawed samples exhibited high sensitivities (0.94 to 1.0) but lower specificities (0.33–0.80 for fresh samples and 0.41–0.87 for frozen-then-thawed samples). When fresh and frozen-then-thawed samples were modelled together, sensitivity remained 1.0 but specificity ranged from 0.29 to 0.91 indicating a role for this technique in monitoring beefburger compliance to label.

Ottavian et al. [208] tested the possibility of using near-infrared spectroscopy for the authentication of wild European sea bass (*Dicentrarchus labrax* L.). NIRS can be used reliably as a nondestructive rapid method to discriminate between wild and farmed sea bass, achieving the same classification performance as classification methods that use chemical properties and morphometric traits.Visible and near-infrared spectroscopy (VIS/NIR) has been used by Gayo et al. [209, 210] to detect economic adulteration of crab meat with surimi-based imitation crab meat. Both Partial least squares (PLS) and principal component analysis (PCR) models were able to perform similarly in predicting crab meat adulteration with a standard error of prediction (SEP) of 0.25% and 0.24%, respectively suggesting that VIS/NIR technology can be successfully used to detect crab meat samples adulterated with surimi-based imitation crab meat.

Raman Spectroscopy

A Raman spectroscopic method was developed by Boyaci et al. [211] for the rapid determination of beef adulteration with horse meat. Meat samples were classified successfully according to their origins while the presence of different concentrations (25%, 50%, 75%, w/w) of horsemeat in beef was also differentiated. This study offers a rapid assay for determination of meat adulteration by discriminating beef and horsemeat with high accuracy, a short analysis time (30 s) and no requirement for time-consuming sample preparation procedures.

A noninvasive portable system has been developed that monitors meat quality in terms of soluble protein content, microbial load, and biogenic amine content [212]. This new device is based on standard analytical techniques coupled with Raman and fluorescence spectroscopy. Moreover, a hand-held Raman sensor head using an excitation wavelength of 671 nm was developed as a tool for *in situ* characterization of meat quality. It has proven capable of detecting microbial spoilage on the meat surface even through the packaging foil [213].

Hyperspectral Imaging

Near-infrared (NIR) hyperspectral imaging technique was developed by Kamruzzaman et al. [214] to detect the level of adulteration in minced lamb meat. Minced lamb meat samples were adulterated with minced pork in the range 2–40% (w/w) at approximately 2% increments. Good prediction model was obtained using the whole spectral range (910–1700 nm) with a coefficient of determination (R^2= 0.99; RMSECV = 1.37% demonstrating that the laborious and time-consuming tradition analytical techniques could be replaced by spectral data in order to provide rapid, low cost and non-destructive testing technique for adulterate detection in minced lamb meat.

Reliability and accuracy of hyperspectral imaging was investigated by Wu et al. [215] for detection of gelatin adulteration in prawn. The combination of uninformative variable elimination (UVE) and successive projections algorithm (SPA) was applied to select the optimal wavelengths in the hyperspectral image analysis. The UVE–SPA–LS–SVM model had a coefficient of determination) of 0.965 and was transferred to every pixel in the image for visualizing gelatin in all portions of the prawn. The results demonstrate that hyperspectral imaging has a great potential for detection of gelatin adulteration in prawn.

Conclusions

Product adulteration is an acute and critical problem that impacts the health and financial well-being of consumers worldwide. It is evident from the history of adulteration that the methods being used to circumvent detection have become progressively more subtle and sophisticated and increasingly require the use of cutting-edge non-destructive methods for identification. The character and nature of the product and the adulterant, as well as the distribution of the adulteration among and within samples, are critical in selecting the most appropriate and effective analytical method. New rapid and accurate non-destructive analytical methods capable of assessing individual product units are needed and are becoming increasingly important.

Abbreviations

ANN – artificial neural networks, ATR – attenuated total reflectance, ATR – attenuated total reflectance, BCE – before the Common Era, synonymous with BC, CE – Common Era, synonymous with AD, eNOSE – electronic nose, eTONGUE – electronic tongue, F – fructose, F/G – fructose to glucose ratio, FAO – Food and Agriculture Organization of the United Nations, FDA – Food and Drug Administration, FFAS – free fatty acids, FTIR – Fourier transform infrared spectroscopy, FTIR-ATR – Fourier transform infrared spectroscopy with attenuated total reflectance, FTIR-DRIFT – Fourier transform infrared spectroscopy with diffuse reflectance Fourier transform, FT-NIR – Fourier transform near infrared, G – glucose, GC – gas chromatography, GC-MS – gas chromatography with mass spectrometry, HFCS – high fructose corn syrup, HPLC – high performance liquid chromatography, IRMS – isotope ratio mass spectroscopy, LDA – linear discrimination analysis, LOD – least detection limit, MIR – mid-infrared, MLR – multiple linear regression, MNF – minimum noise fraction, M-PLS – multiway partial least squares regression, MRL – maximum residue limit, MS-ICP – mass spectrometry with inductively coupled plasma, MS-IPC – mass spectroscopy with inductively coupled plasma, NDQE – nondestructive quality evaluation, NIR – near infrared, NIRS-RAMAN – near infrared spectroscopy with Raman spectra, NMR –nuclear magnetic resonance, OES-ICP – optical emission spectroscopy with inductively coupled plasma, OES-IPC – optical emission spectroscopy with inductively coupled plasma, PDO – protected designation of origin, PLS – partial least-squares, PLSR – partial least-squares regression, PLSR-LS-SVM –partial least squares regression - least-squares - support vector machine, PTR-MS – proton transfer reaction mass spectrometry, r – correlation coefficient, R^2 – coefficient of determination, RMSE – root mean square error, RMSECV – root mean square error of cross validation, RPD – ratio of performance to deviation, SB-ATR-FTIR – single bounce attenuated total reflectance with Fourier transform infrared spectroscopy, SERS – surface active Raman scattering, SNF – solid non-fat, SPME – solid-phase micro-extraction, SPME-MS – solid-phase micro-extraction with mass spectrometry, TC-HCL – tetracycline hydrochloride, TPM – total polar materials, TTDS – terahertz time-domain spectroscopy, UV – ultra violet, VIS – visible, VOCs – volatile organic compounds, WHO – World Health Organization.

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