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Contents

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

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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).

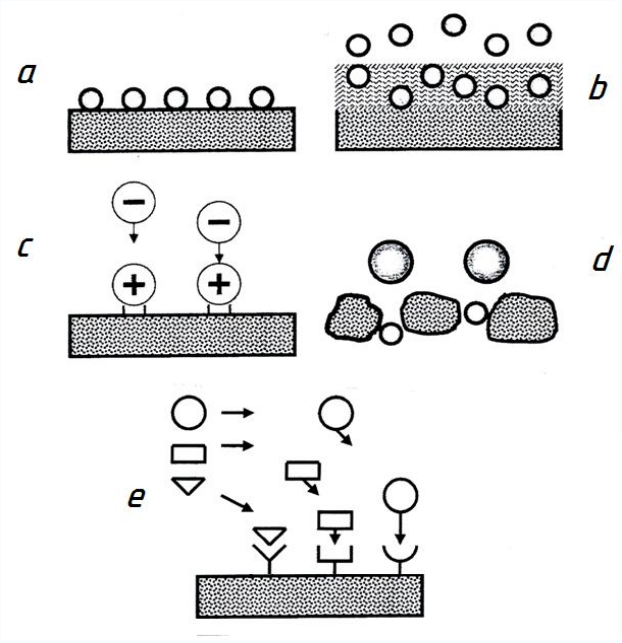

Figure 1. The mechanisms of interaction between the components of the mixture and the stationary phase (explanation in the text)

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).

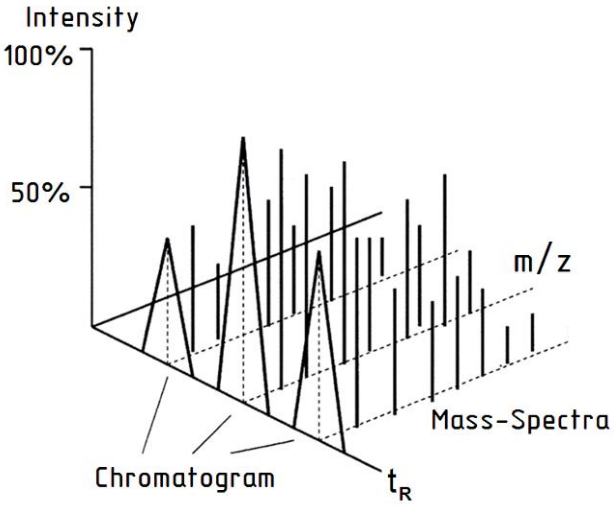

Figure 2. GC/MS spectra: three-dimensional plot of scan number (time) versus mass/charge *(m/z)* versus relative intensity (%)

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.

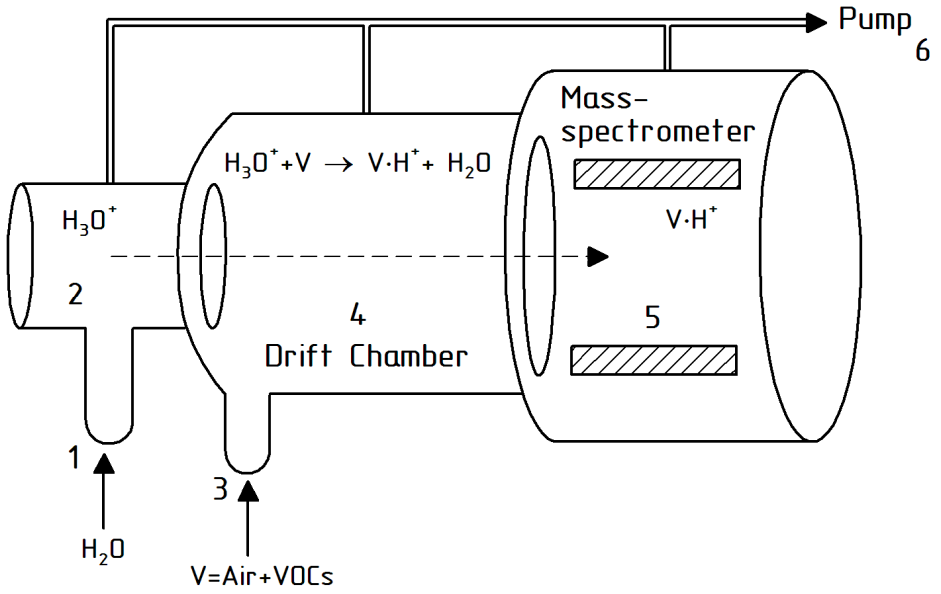

Figure 3. Proton Transfer Reaction Mass Spectrometer (explanation in the text)

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).

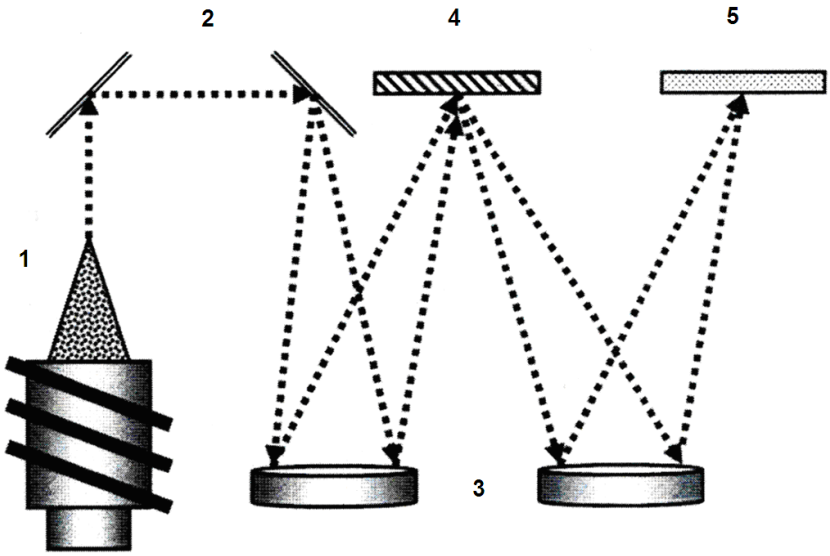

Figure 4. Principle of Optical Emission Spectroscopy with Inductively Coupled Plasma (OES-ICP):
1 – source of plasma; 2 and 3 – mirrors; 4 – diffraction grating; 5 –detector.

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).

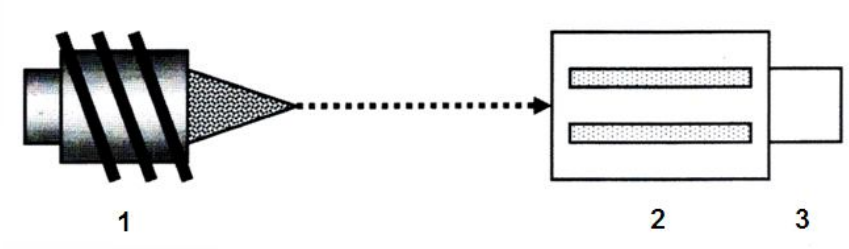

Figure 5. Principle of Mass Spectrometry with Inductively Coupled Plasma (MS-ICP): 1 – source of plasma; 2 – mass-spectrometer; 3 – detector.

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*).

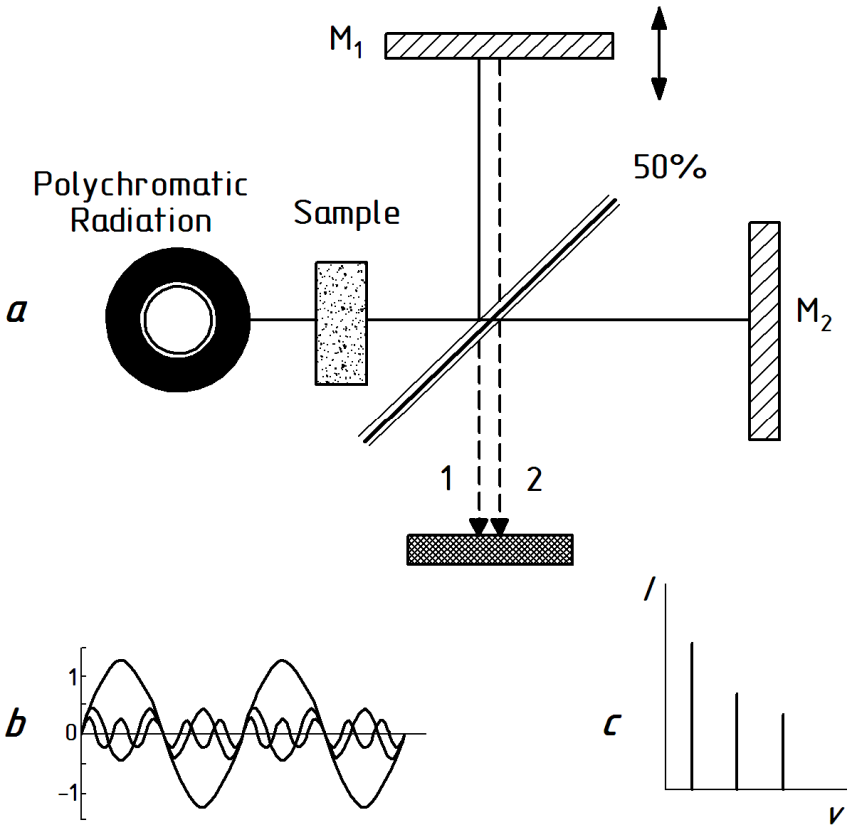

Figure 6. Principle of operation of Fourier transform spectrometer (the explanations in the text)

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.

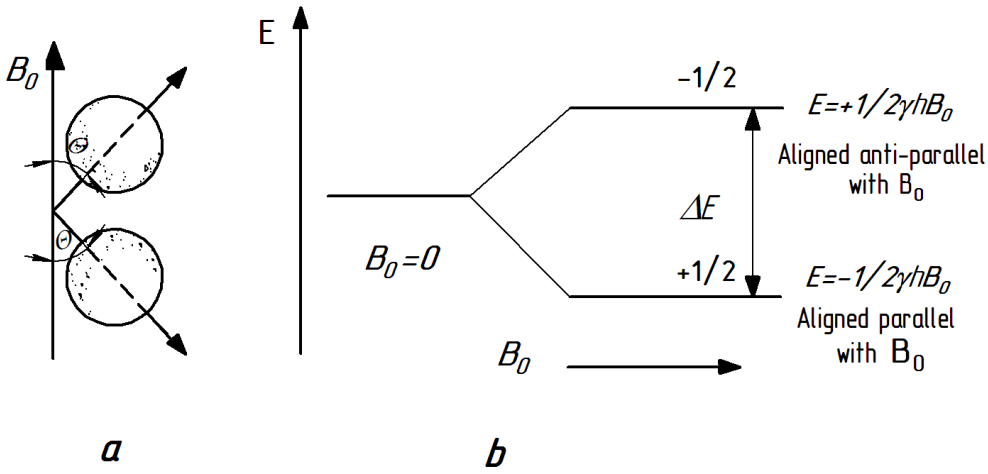

Figure 7. Nuclear Magnetic Resonance:
***a* – possible orientations of magnetic moments relative to the external magnetic field B_0;**
***b* – nuclear splitting ΔE of energy levels in a magnetic field for spins with quantum number ½**

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).

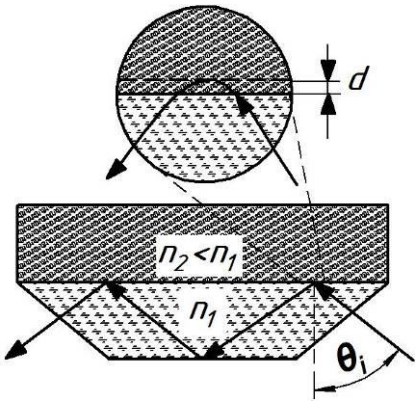

Figure 8. Spectroscopy with Attenuated Total Reflectance (ATR)

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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Perspectives of wedge-shaped dehydration method for evaluation of physical and chemical properties of multicomponent aqueous solutions

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Abstract

Introduction. The relevance of this work is caused by increasing the phenomena research in a droplet due to the development of biotechnology and practical application for assessing the liquid products quality.

Materials and methods. The model blood serum solution, obtained on the base of electrochemically activated solutions, is investigated. Studying the facies in the process of their drying is conducted with a biological microscope equipped with digital photographic lens.

Results and discussion. Analysis of the simulated solutions facies showed that they meet the typical pattern of the protein-salt solution facies, that is, the protein roller is located along the edge of the facies and the protein-salt area is located in the middle of them. It is revealed that the facies based on electrochemically activated water, catholyte, anolyte and their mixture have different protein-salt area structural elements. In particular, lots of regular salt crystals with dendritic branches are found in the protein-salt area. In addition, the facies have the different nature of the created "cells" in the protein-salt area. It is shown that the supersaturated solution structural features influence the crystal growth process. The salts, dissolved in the activated water, crystallize with the regular crystals formation, unlike anisotropic microcrystals, which are formed during drying the plain water solution. As the pH and the catholyte and anolyte mixture redox potential is virtually indistinguishable from distilled water indicators, so the metastable properties of the obtained water namely, a hydrated facies uncompensation – free protons and electrons have a decisive influence on forming the facies structures and the protein roller width. It is shown, that formation time of protein roller depends on the presence of hydroxyl ions and hydronium in the liquid for preparing the solution sample: with increasing the hydroxyl ions content the formation time decreases and with increasing the hydronium ions content it increases in comparison with not activated distilled water.

Conclusions. Using the wedge-shaped dehydration method with the modern computer technology provides a set of indicators to identify different liquids and change their properties due to external influences.

Introduction

One of the most common processes of chemical technology for obtaining solids from the liquid phase is the drying of dispersions – suspensions, emulsions, solutions and crystal forming solutions [1, 2]. Besides drying, many technical processes and devices are connected with the substance droplets – sprays, nozzles, application of coatings, printing industry, aerosols, powders etc. [3–5]. However, recently the interest in the phenomena mechanisms in a droplet sharply increased due to the development of the research in creating the nanoobjects and improving the medical diagnostics and biotechnology [6–8]. One of the applied aspects of such work is the development of rapid methods to determine the physical and chemical properties of multicomponent liquids, which finds its application in assessing the liquid products quality, the compliance with the standards of various technical liquids, pharmaceuticals, food products, and biological liquids in the pharmaceutical, food and chemical industries [9, 10].

The wedge-shaped dehydration in the visible simplicity of the implementation method is the result of the combined influence of the factors, which are different in their nature. It is caused that the droplet on a solid substrate is an open dynamic system. In the droplet drying both the exchange energy processes with the environment and between the components of the solution, and the structural self-organization processes in the very droplet occur [6, 7, 10–12]. The process of drying a droplet can be studied with different physic-chemical methods, but after external perturbation influence – mechanical, thermal, ultrasonic, magnetic, etc. – there is a shift of physic-chemical parameters of the researched environment with the following relaxation [13, 14]. Thus, self-organization processes are very sensitive to external influences, so using nondestructive testing methods (NDT methods), one of which is the wedge-shaped dehydration, is the best to study them.

On the other hand, the outside influence should be also represented in the processes that occur during drying a droplet. However, there are very few works studying facies (dried droplets of solutions), which were exposed to the external factors during drying [13, 15, 16], and even fewer works, where the facies of solutions are studied based on pre-treated water [17]. And these moments are very important in terms of solutions and products analysis, obtained with certain technological processes. So the work object was to study a short-term electric field influence on the water and the effect of this influence during drying the droplets of the colloidal solution, obtained out of the water.

Materials and methods

The influence of electric field on water was carried out with the electrochemical activation (ECA), commonly used in various ecologically safe technologies, including food ones [18–20]. The stationary double-chamber diaphragm electrolyser with a constant voltage on the electrodes was chosen to obtain ECA of water solutions. This electrolyser can be used to activate the solutions of different initial mineralization and chemical composition, and it makes it easy to change the experimental samples volume and the frequency of their selection. The electrolyser housing was made of the organic technical trade glass ТОСП. This material with strong dielectric properties is inert to no concentrated acids and alkalis and can be used at temperatures up to 92°C. To select activated solutions samples in the anode and cathode chambers' bottom of the electrolyser there are two drain cocks that provide a high speed selection and minimal mixing of liquids. To manufacture electrodes the low-ash medium granular graphite plates ГЭ-3 for applying in

electrochemical baths are used. The diaphragm, made of four layers of nonwoven polypropylene FS 2226-14E, is used to separate anode and cathode chambers.

Distilled water is used for the activation. The resistivity of distilled water is not less than 10^4 ohm/m. Thus, according to the directions in [21], ECA of distilled water will be effective at the potential difference of 600V (average field strength in the electrolyser – 17 kV/m), which allows obtaining the highly active solutions even at the low current density.

To measure the hydrogen index of pH basic value and ECA of water (catholyte and anolyte), pH-meter pH-301 with a combined glass electrode ЭСК 10601/7 is used. To control the temperature during the measurement, automatic temperature compensator DT-1000-1, which was immersed with the combined electrode into the test solution, was also used. To measure the redox potential (ORP), ionomer *И*-130 with the platinum electrode and chlorine-silver electrode, was used. The measurements were performed in the automatic temperature compensation mode with using temperature sensor ТКА-7. The hardware permissible absolute error limit during the measurement of ORP with the automatic temperature compensation was ± 2 mV, and the measurement duration – 180 sec. The device calibration was carried out with the standard method using the buffer solutions made from the 2-nd grade standard titres.

For the experimental research of the electric field impact on the structural features of facies from aqueous solutions they used distilled water, anolyte and catholyte ECA of distilled water and the mixed anolyte and catholyte ECA of distilled water at a ratio of 1:1 to produce the sample solutions of blood serum by gradually mixing human blood serum albumin, sodium chloride and investigated liquid. Mixing all the components was performed in the laboratory noncontact mixer for 5 minutes right before forming the facies. In this paper such a ratio of the sample solution components was used as follows: 7 % of serum albumin, 0.9 % of sodium chloride, 92.1 % of water. This simulated solution is chosen, because the most studied facies of biological liquids are the facies of serum. So many effects connected with the influence of external factors on biological objects are studied on the human serum sample. Its protein components can be different proteins – human serum albumin, bovine serum albumin, egg albumin, etc. [7, 22, 24].

For forming the facies the droplets of the simulated solution with the volume of 10–20 ml and the diameter of 5–7 mm were put on the horizontal defatted glass. The study of facies during their drying was carried out with microscope МБС-10, designed to work with bulky items, thin membranes and transparent samples, and digital lens eTREK DCM 220. The studies were carried out in the reflection mode with increasing the optical system from ×21 to ×126. The obtained digital image with a resolution of 1600×1200 was transferred to a computer. The digit image analysis was carried out in two stages in the semi-automatic mode with using program Grafula 3. At the first analysis stage the automatic limit recognition of the individual facies elements was performed: zones of protein roller, contours of salt crystals etc. To do this, with the intellectual mask the extended search area was defined, and the clarification of the individual elements limits was performed in the contrast filtering mode. If necessary, the results of the automatic limit recognition were corrected manually. At the next step of analysis the false (pixel) coordinates of the facies elements were converted to the geometrical ones to determine their actual size. The ratio between the false and geometric coordinates of neighboring marks on the image of an object-micrometer OMO was used as the conversion factor.

Results and discussion

In work [24] it is determined that in the protein-salt solution during the evaporation of free water in droplets there are the following processes:

1) The addition of a droplet to the pad with forming a lower adsorption layer;

2) The redistribution of the colloidal phase inside the droplet due to the centrifugal flow;

3) The formation of different conditions for the phase conversions of protein, located along the edge of a droplet (in the three-phase border) and in its center;

4) The transformation of albumin on the edge of a droplet to the glassy state;

5) The set of transformation phases of albumin (from coacervates to gel) due to increasing ratio of salt concentration to protein concentration in a liquid part of the droplet (in its center);

6) The salt crystallization in the gel pattern.

Thus, the pinning process on the droplet-pad border leads to the rapid change of droplet energy causing the radial movement of the particles dissolved in the liquid. Further, during the evaporation liquid process the droplet becomes more flat and loses the equilibrium shape, and a protein roller appears at the edge of the droplet. Kinetics of phase salt conversions to the solid state is connected with the time of drying and gelling in the droplet of the composed solution, and this time depends both on its composition and the liquid properties, which is the basis of this solution.

For the minimum effect on the ion transference between the electrolyser chambers, the ECA duration of distilled water was 20 sec. As a result of the electric field performance, the water for the subsequent preparation of the protein-salt solutions with the following characteristics was obtained (Table 1).

Table 1

Changing the water properties due to ECA

Used water	pH	ORP, mV
Distilled water	5,76	94,0
Anolyte	5,70	95,7
Catholyte	6,30	67,5
Catholyte + Anolyte	5,74	95,3

As shown in Table 1, the electric field changed strongly the water properties from the electrolyser cathode chamber – catholyte, but the anolyte and catholyte mixture with its indicators within the error is almost identical to the original distilled water. The stages of drying protein-salt solutions droplets are shown in Fig. 1–4.

After analyzing the stimulated solution facies shown in Fig. 1–4 (photo), we can see that they all meet the typical structure of the protein-salt solution facies – the protein roller is along the edge and the protein-salt area is in the middle [22–24].

In contrast to usual water, the facies based on water ECA are different by this protein-salt area. In Fig. 2 d) and Fig. 3 d) we can see the protein-salt area has a large number of regular salt crystals with dendritic branches in it, and in Fig. 1 d) and in Fig. 4 d) the facies are different by the formed “cells” nature in the protein-salt area.

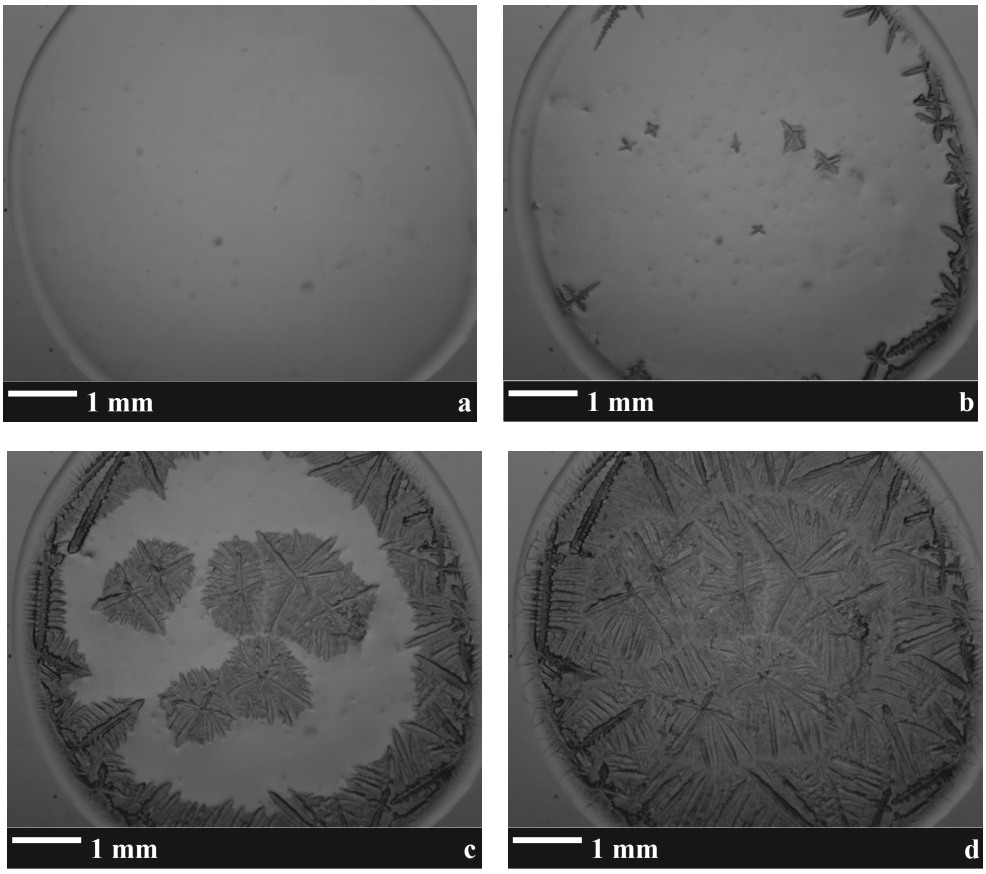

Fig. 1 Morphological evolution during drying the simulated solution droplets based on distilled water:
a) Formation of a protein roller, b) The beginning of crystallization,
c) Crystallization, d) The end of crystallization

The nature of crystals in the protein-salt solutions facies is not cleared up. Some studies [25], consider that protein and salt are separated and on the crystal-solution verge complete protein displacement by crystal is occurring. Resulting crystal growth the protein accumulates near the surface of the crystal. On the other hand, some studies [22] state that the separation into the individual phases does not occur, crystals are the protein-salt mesocomposites, and triangular crystals along the dendrite faces are salt crystals. The study analysis [26] also shows that, most likely, the separation of the protein and salt phase does not occur. However, in Fig. 2 d) and Fig. 3 d) it is clearly shown that along with the dendrites the salt crystals of the correct shape are formed, so the replacement of distilled water to water ECA leads to qualitatively new formation of new facies.

As in the drying process the kinetics of facies formation was studied, it was important to compare the results of computer photo processing regarding the time of protein roller formation and finding out its width (Fig. 1–4 (a)) and the time of protein-salt structures crystallization (Fig. 1–4. (b-d)). The obtained results are shown in Table 2.

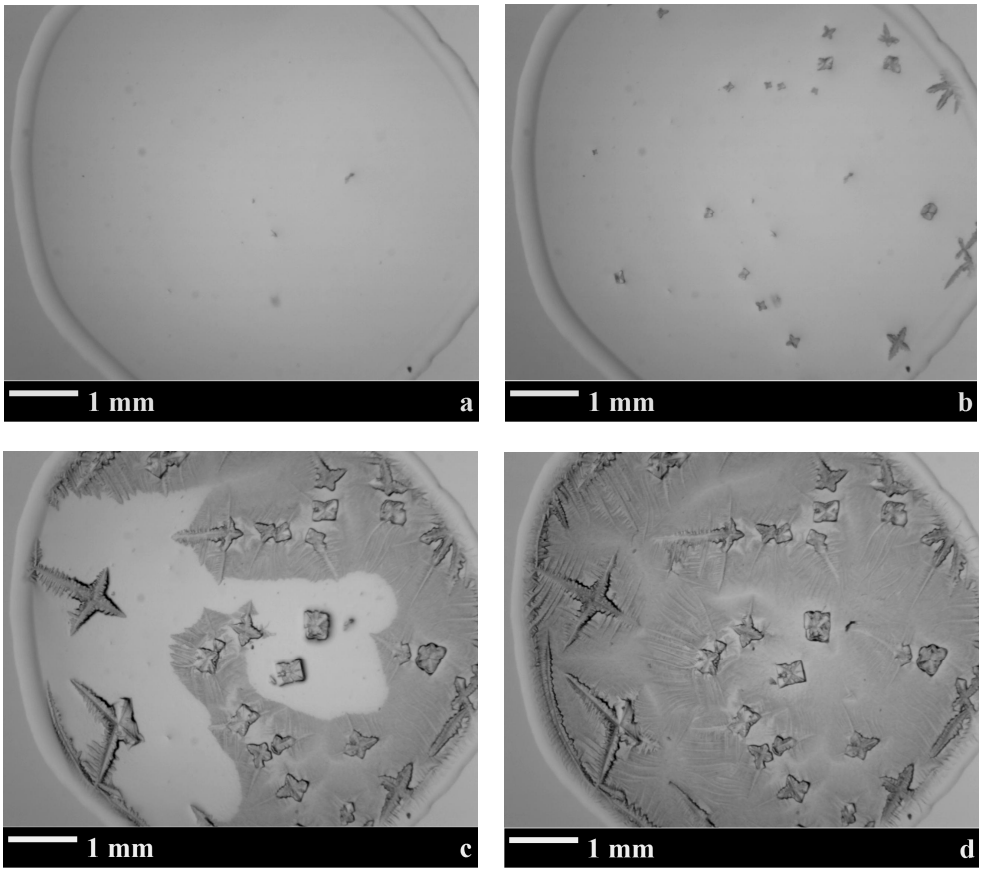

Fig. 2 Morphological evolution during drying the simulated solution droplets based on catholyte:
a) Formation of a protein roller, b) The beginning of crystallization,
c) Crystallization, d) The end of crystallization

Table 2

The change of the facies characteristics depending on the used water

Used water	The facies characteristics		
	Protein roller width, mm	Time of protein roller formation, s	Time of protein-salt area crystallization, s
Distilled water	0,329	1256	55
Catholyte	0,319	1080	84
Catholyte + Anolyte	0,361	1141	121
Anolyte	0,362	1587	103

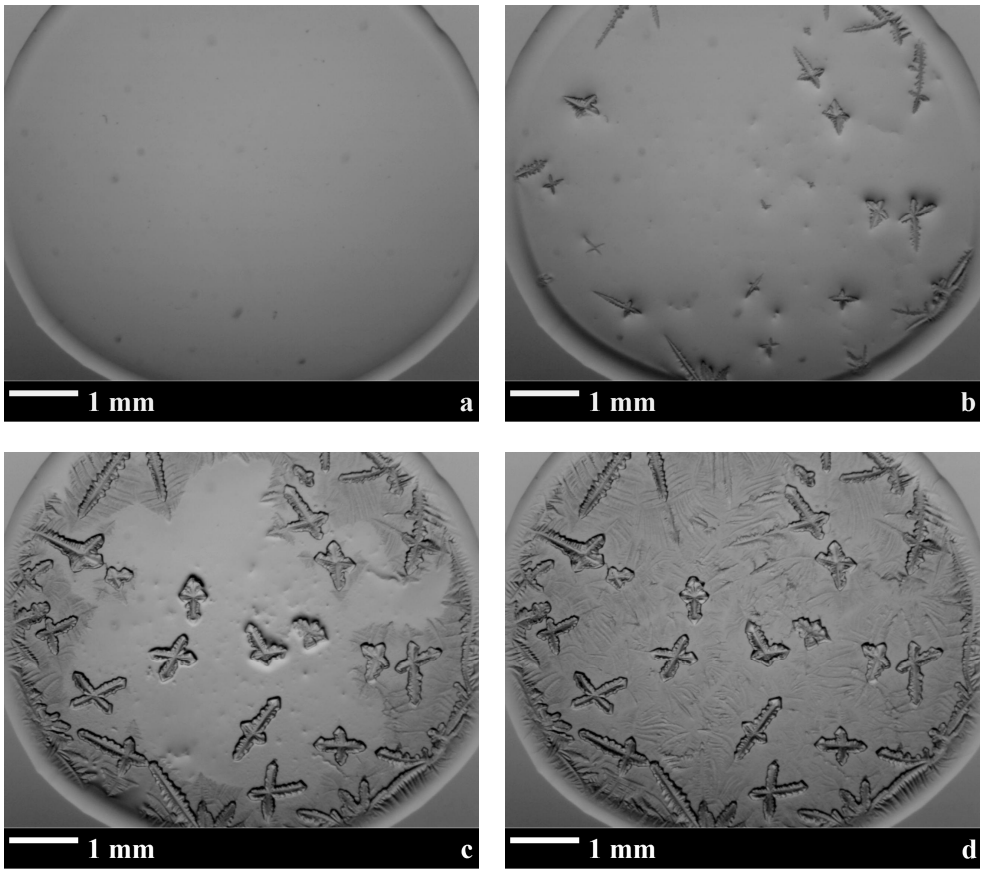

Fig. 3 Morphological evolution during drying the simulated solution droplets based on anolyte:
a) Formation of a protein roller, b) The beginning of crystallization,
c) Crystallization, d) The end of crystallization

Let us consider the possible reasons for such changes. Crystallization process is divided into two stages: the formation of crystal germ and its subsequent growth. The germ can be formed only in supersaturated solution. Initially the crystal germ is considered to be a disordered cluster of atoms, ions or molecules. Gradually inside this cluster, the particles are located at the joints of the crystal lattice. Thus, the structural features of the supersaturated solution have an influence on the process of crystal growth. It should be noted, that the effect of impurities getting into the water during the activation and can make the additional crystallization centers were not considered, because the distilled water used for forming the facies also was previously exposed in the electrolyser in the off mode. The replacement of the activator graphite electrodes to titanium ones did not cause the change in the facies pattern. The luminescence spectrum of water, after being in the activator, did not change either in the comparison with original water.

So the impurities that can get into the water from the electrodes during the activation do not influence the new formations in the facies.

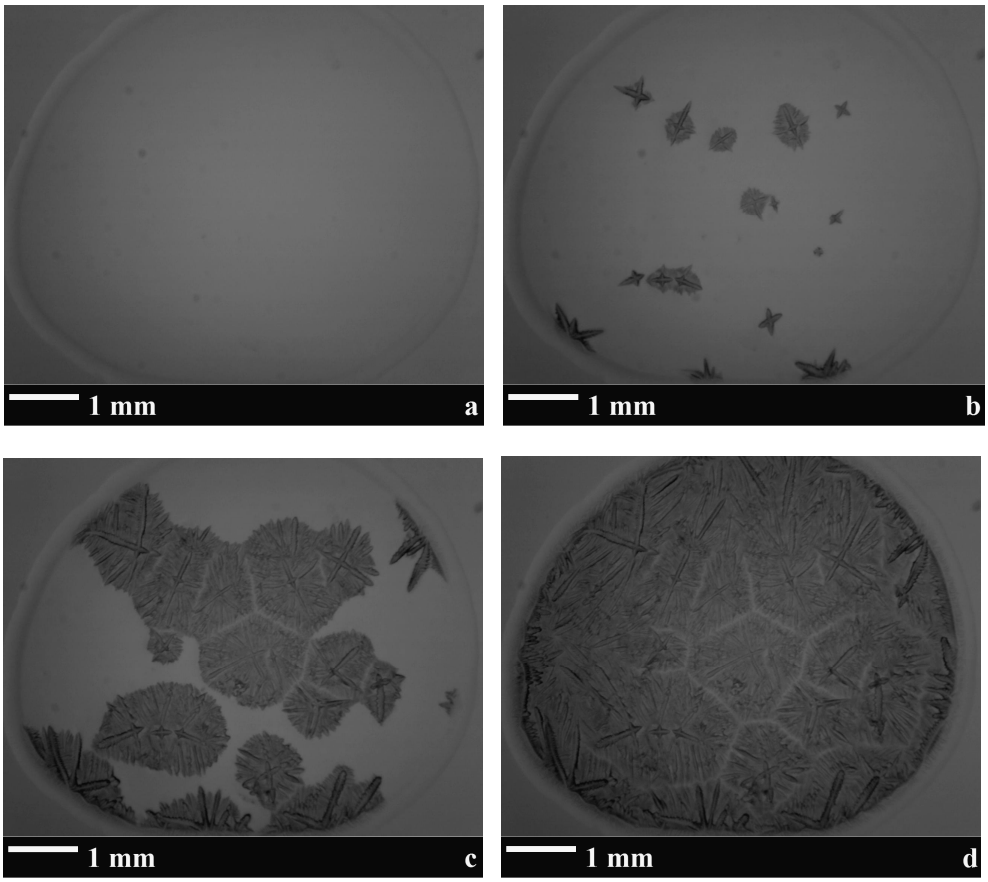

Fig. 4 Morphological evolution during drying the simulated solution droplets based on catholyte and anolyte mixture:
a) Formation of a protein roller, b) The beginning of crystallization,
c) Crystallization, d) The end of crystallization

The observed changes depending on the hydrogen index of water pH can be explained on the basis of the ideas proposed in [27]. Anolyte due to protons H^+ excess slows down the biological processes and the cell growth, that is, it causes such conformational changes of the protein, where the protein cluster structures are formed. As a result there is a slowdown or even a stop of metabolism in the living organism. It is interesting that a slight change in pH (Table 1) causes a significant increase of the time in forming the protein roller (Table 2). Catholyte is enriched by hydroxyl ions OH^-, and it causes the metabolic processes acceleration in the organism. Thus, such water is a natural stimulant and it has anti-carcinogenic properties [27]. These water properties are good for a living organism due to the repulsion between the hydroxyl ions, the opening of the channels in the cell membranes (composed of different proteins) for passing micro and macro elements. This repulsion also causes the better separation of protein molecules manifesting in the reduction of protein roller thickness in the facies, which were obtained from the solutions based on the catholyte, and the reduction of the protein roller formation time (Table 2).

As the pH and ORP of the catholyte and anolyte mixture is identical to the original pH of distilled water, then the metastable properties of the obtained water, namely the noncompensation of hydrated charges – free protons and electrons, are likely to have the influence on the structure formation of the facies and protein roller width. Regarding the structural changes occurring in the water under the influence of an electric field, in [28] it is shown that the hydrogen connections between the molecules are regulated and the large clusters (about 10^4 nm) are formed in the water. The dissolved salts in this water crystallize with forming fractal crystals unlike anisotropic microcrystals, which are formed during drying the solution on ordinary water [29].

Conclusions

The studies have shown that the fixation of spatial-temporal characteristics obtained at drying complex solution droplets is a useful and sensitive tool for assessing the solutions properties. The usage of the wedge-shaped dehydration method with the capabilities of modern computer technology provides a set of indicators to identify different liquids and change their properties as a result of external influences. The further development and technical improvement of the wedge-shaped dehydration method will provide along with other methods to set out the relationship between the molecular structure and physicochemical properties of aqueous solutions. Thus, the comparison of the test solution facies with the standard will provide the quality control and detection of liquid products frauds such as drinks, juices, wines and others.

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Impact of the kind of wine storage on chemical and physical characteristics of the vranec wine

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Abstract

Introduction. Vranec wine is produced from the grape Vranec, which is most important for the production of red wines in Macedonia. Vranec is native Montenegro variety, but is present in all vineyards in the Vardar region and lesser extent in other vineyards.

Materials and methods. There were examined two samples of the wine Vranec, with finished fermentation in tank in the grapes of the same variety - Vranec, in Stobi Winery, located in Tikvesh wine region. The wine Vranec is from vintage 2011 and differs by the method of keeping the wine after its fermentation. One wine is kept in a tank, while the other one which is from the same vintage year is transferred and stored into an oak bundle of 5000L.

Results and discussion. In this work were studied the physical-chemical properties of wine stored in different methods (of wine Vranec kept in a cistern and wine Vranec kept in a Bundle). The concentration of hydrogen ions - pH of the wine samples kept in a tank and bundle are in the limits of 3.33 to 3.42, which is actually allowed pH range for red wines. In the terms of overall acids, the amount of total acids is greater in the wine kept in a tank. Volatile acidity marks higher value in the wine kept in bundle. Malic acid has 0 mg/L in the wine kept in the bundle, which represents complete conversion of malic acid to lactic acid. Citric acid in the wine is more contained in the one kept in a tank (0.38). Acetic acid has higher values in the wine Vranec kept in bundle (0.48). Higher amounts of sugars as total (5.1 g/L) and reducing (0.95 g/L) are noticed in the wine kept in a bundle. The amount of alcohol in the tested samples ranges from 14.53-14.75 % vol, which is consistent with the requirements of the International organization of vine and wine (OIV). Polyphenols and anthocyanins have higher values in wine from bundle (2757 mg/L polyphenols) (989 mg/L anthocyanins), due to material - wood in which the wine is stored. The intensity of the wine kept in a bundle is higher (3.921) than the wine kept in a tank (2.47). The nuance of red wine Vranec stored in tank is higher (1.6) in respect of wine kept in a bundle from the same vintage (0.75). As for the presence of SO_2, it can be said to be "double-edged sword". On one hand the increased presence of SO_2 leads to inactivation of undesirable microorganisms (which is desirable), while on the other hand, increased amounts of SO_2 by a number of scientific research suggests a potential health problem for a certain class of asthmatic individuals. Considering the maximum total content of SO_2 from OIV (350 mg L) in the tested samples are observed three times minor values.

Conclusions. It has been found that the method of storage of Vranec wine from the Tikvesh region has an impact on the physical-chemical properties of the tested wines.

Introduction

The wine represents a product obtained exclusively by full or partial alcoholic fermentation of fresh grapes and grape must, suppressed or unsuppressed [1].

The material of the containers in which wine is kept is extremely important for the quality of the wine. If the material is made of oak, it affects odor and taste of the wine, and affects the wine. Depending on whether the bundle of oak is used once, twice or several times, the wine quality is different. Wine in which the aroma and taste are important, is using a Bundle oak from four to six years [2].

On the other hand, Containers made of stainless steel have shown as best, because they can be easily and effectively cleaned only with a sufficient amount of hot water.

Wooden containers must be kept wet because when they dry, they are flocking, which leads to leaks and loss of fluids [3].

Vranec wine is produced from the grape Vranec, which is most important for the production of red wines in Macedonia [16]. Vranec is native Montenegro variety, but is present in all vineyards in the Vardar region and lesser extent in other vineyards.

Materials and methods

There were examined two samples of the wine Vranec, with finished fermentation in tank in the grapes of the same variety - Vranec, in Stobi Winery, located in Tikvesh wine region. The wine Vranec is from vintage 2011 and differs by the method of keeping the wine after its fermentation. One wine is kept in a tank, while the other one which is from the same vintage year is transferred and stored into an oak bundle of 5000L.

The analyze of samples was conducted by reference methods of International Organisation of Vine and Wine (OIV) [14].

On the analyzed samples are determined the acidity of the wine, as titration acidity and pH titration of wine according reference methods (O.IV-MA-AS313-01, O.IV-MA-AS313-15). Using enzymaticn reference methods (O.IV-MA-AS313-07, O.IV-MA-AS313-09, O.IV-MA-AS313-11) are determined lactic, citric and malic acid. The determination of total acids and volatile acids is done also with the reference methods of International organization of wine (O.IV-MA-AS313-01, O.IV-MA-AS313-02). Reduced sugars like glucose and fructose were determined by the method of Rebelein, while the amount of alcohol is determined with ebullioscopy using the method of Malligand. Total polyphenols were determined according to the reference method O.IV-MA-AS2-10 also examined and the intensity and hue of the wine and the presence of sulfur dioxide by the reference method O.IV-MA-AS323-04B).

Results and discussion

The acidity is one of the factors that influence the most to the quality of wine. The acidity of the wine originates from two sources - acids that are developed in the grapes (tartaric, malic and citric) and acids which are generated in the wine production (lactic, acetic and other) [4].

The actual acidity (pH) represents negative decade logarithm of the concentration of hydrogen ions [5].

The acid taste of wines depends more on the total acidity than of its pH. The boundaries in which range the values of total acidity and pH of the red wines are 5-7 g /L total acidity, and for pH 3.3-3.8 [4].

The volatile acid is generated during the fermentation activity of the acetic-acid bacteria that converts the alcohol into acetic acid and ethyl acetate. All table wines have a certain degree of volatile acidity, which is not noticeable below certain levels [2].

In figure 1 are given the values for pH, total acidity and volatile acidity from the examined samples of wine Vranec kept in a cistern and wine Vranec kept in a Bundle.

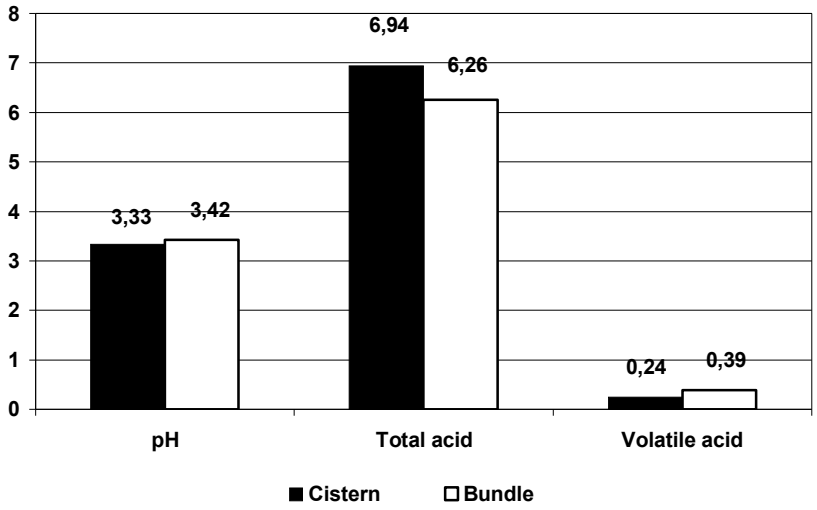

Fig. 1. Values of pH, total acidity and volatile acidity

From the screened in figure 1 it can be seen that wines kept in different ways have large deviations regarding pH, total acids and volatile acidity.

Higher pH values are not recommended due to problems with microbiological stability and for reducing the intensity of the color at a higher pH. On the other hand, a lower pH occurs when picked grapes are not completely ripe. The low pH can prevent malic-lactic fermentation, which is most important in reducing the wine acidity [4].

pH of wine Vranec produced from Biotechnology Faculty of Montenegro showed approximately the same as well as our respondants (3.41) [6].

The total amount of volatile acids in red wine ranges from 0.2 to 0.4 g/L. The increase above this level may represents danger of microbiological failure of the wine [7].

Tests on Vranec wine produced by biotechnical faculty in Podgorica show deviation in respect of the volatile acidity of the predicted values (0.75 g/L) [6].

Comparing the results of the wine vintage 2011 Vranec kept in bundle with our previous researches Vranec wine vintage 2009 and 2010 kept in the tank can be observed that there are no major deviations [8].

Table 1

Amount of acids in the examined samples

Acid	Cistern	Bundle
Malic acid mg/L	0.65	0
Lactic acid mg/L	0.20	0.57
Citric acid g/L	0.38	0.35
Acetic acid g/L	0.30	0.48

From shown in Table 1 it is seen that the wine kept in the bundle have 0 mg/L malic acid, which means that this wine has achieved full conversion of malic acid into lactic acid during the second in importance fermentation after alcoholic fermentation, malic - lactic acid.

In our previous researches made of wine Vranec of different vintage, the wine from vintage 2009 there is almost no conversion of malic acid into lactic acid [8].

Titration difference in acidity due to the conversion of malic acid to lactic acid is easily noticed in taste. The effects on the aroma of the red wine caused by malic - lactic fermentation are subtle and noticeable only in strict tasting conditions [9].

Citric acid represents an organic acid that supports stabilization, ie wines not to create a condensate [3].

In the presence of oxygen, acetic acid bacteria convert the alcohol into acetic acid, which together with the water which is naturally present in the wine, create vinegar [10].

Wines that lack in acid have an insipid and weak flavor to a certain place, where the acid can intensify and contribute to the smell of fruit seems mild. The adjustment in acidity in the countries which allow addition of acid, such as malic, citric and tartaric acid, if titration acidity expressed as tartaric acidity is not more than 0,8 g/L. OIV allows adding tartaric but not the malic acid [7].

Carbohydrates. Carbohydrates are polyhydroxy aldehydes, ketones and their derivatives composed of C, H and O in a ratio of Cn (H_2O). In wine where we have full alcoholic fermentation, the total amount of sugar is relatively small 1 to 2 g/L, a larger amount does not remain if the sugar alcohol fermentation not flow to the end. Glucose and fructose are found equally in grapes as each participate with 10g/100g. Sucrose is one of the three most common sugars. According to the authors, dry table wines have 0% reducing sugars, but in practise usually in analyzing the dry wine samples, have reducing sugars less than 2.0 g/L [7].

In Figure 2 are given values for total sugars and reducing sugars expressed through glucose - fructose, in Vranec wine vintage 2011, kept in a tank and in a bundle.

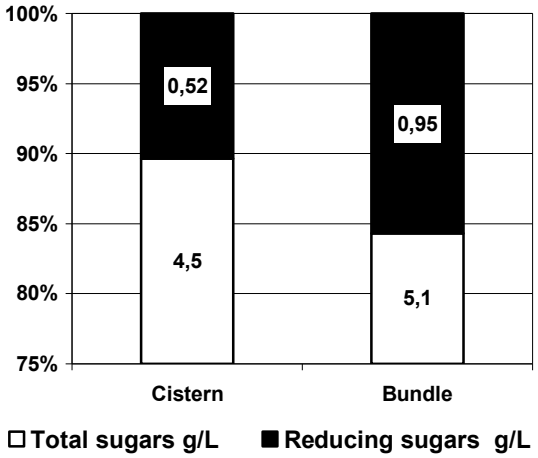

Fig. 2. Total and reducing sugars

Comparing the results shown in Figure 2 can be seen that the wine kept in the bundle has a greater amount of total sugars than the wine of the same vintage kept in the tank, consequently this is expected and a larger quantity of reducing sugars in the wine kept in vats.

Despite the different way of wine storage, it can be concluded that the values in the reducing sugars are ranging in the prescribed framework of 2.0 g/L.

Alcohol. According to the standards prescribed by the International organization of vine and wine (OIV), the wine is required to contain at least 8.5% vol, so that a product can be qualified as one.

Figure 3 is given quantity of alcohol test samples. It can be noticed that the wine kept in bundle contains a large quantity of alcohol.

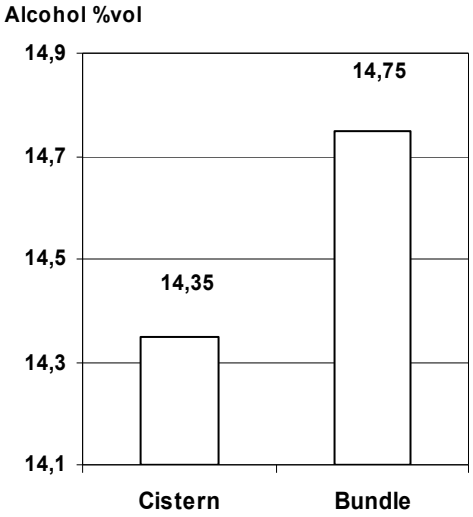

Fig. 3. Quantity of alcohol test samples

In our previous research, related to the year of harvest of wine Vranec, are recorded lower values of alcohol, but supposed that the amount of alcohol with an extension of storage time was reducing the percentage of alcohol [8].

Wines that have a percentage of alcohol more than 14% vol are characterized by warm climate in the areas where vines are grown for obtaining them, have a high degree of maturity and the amount of sugar in the grape juice is more than 26% by weight, while in respect , these wines are Full-bodied, rich in texture [11].

Polyphenols and anthocyanins. Table wines are composed of approximately 85% water, 12% ethyl alcohol and only 3% belong to the color, flavor and body. In these 3% the highest is the presence of phenols which are also called phenolic substances ie tannins. The whole group of phenolic compounds can be called polyphenols. They are mostly found in the seeds, then in the cluster, less in the peels and at least in the seeds. Polyphenols are divided into two guppies: flavonoids and nonflavonoidis [3].

Red, blue, pink, purple, pink purple color due to the presence of anthocyanins. Along with other polyphenolic substances they appear as glycosides and aglycones are also known as anthocyanidins. In nature there are only 6 anthocyanidins, but depending on the modus of glycosylation and acylation, it can be found numerous anthocyanins containing antocyanidins. Of all the six antocyanidins, the only one that is not contained in grapes is pelargonidin [12].

Figure 4 shows the amounts of polyphenols and anthocyanins in the tested samples of wine Vranec stored in a different way.

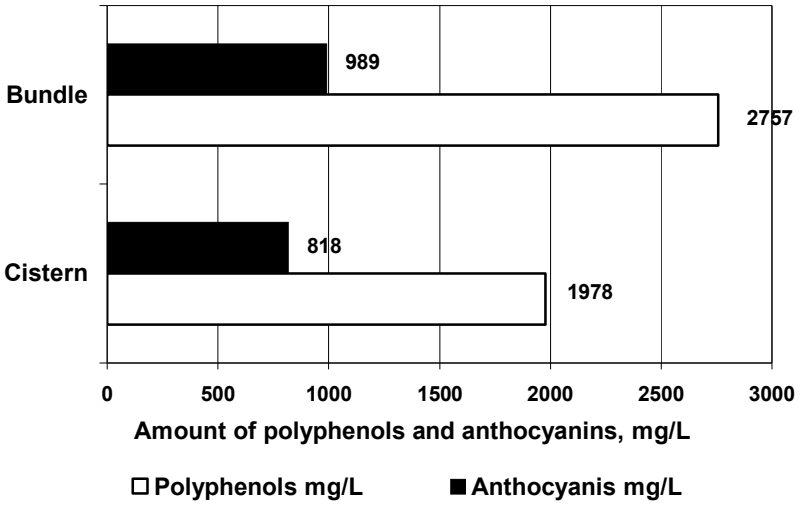

Fig. 4. Amount of polyphenols and anthocyanins

From the submitted, it can be seen that the amount of polyphenols and anthocyanins in wine is higher in the one kept in the bundle, and the reason for this is that wood has a major role in increasing the quantity of polyphenols and anthocyanins.

Comparing these with our previous trials, may be noted that the extension of storage time decreases the amount of anthocyanins and polyphenols, on the other hand, the wood as a material in which the wine is kept, participate in increasing the amounts of polyphenols and anthocyanins [8].

Depending on the variety, maturity of fruit and temperature,the antocyanins are usually extracted in the first 4 to 5 days of fermentation. With progress of fermentation, it comes up a declination in antocyanins and color intensity, and an increasement of the total percentage of extracted phenols [7].

Intensity and nuance of wine. Among the red wines there are 20 shades of red color.The splendor decreases with increasing the pH Value of the wine, and also with low pH value the addition of sulfur dioxide is slight, as negligible affects the color of the red wine. In the life of red wine, the color passes from purple to brown, from dark to light color, these changes are caused by polymerization of antocyanins and colored tannins that eventually come out as sludge [2].

In Figure 5 are given the values of the tested samples of wine Vranec from vintage 2011 with completed fermentation,which are kept in tank and in vats. From the figure it can be seen that the intensity of the wine color kept in the bundle is higher than the values of wine kept in tank, due to the material - wood in which the wine is stored.

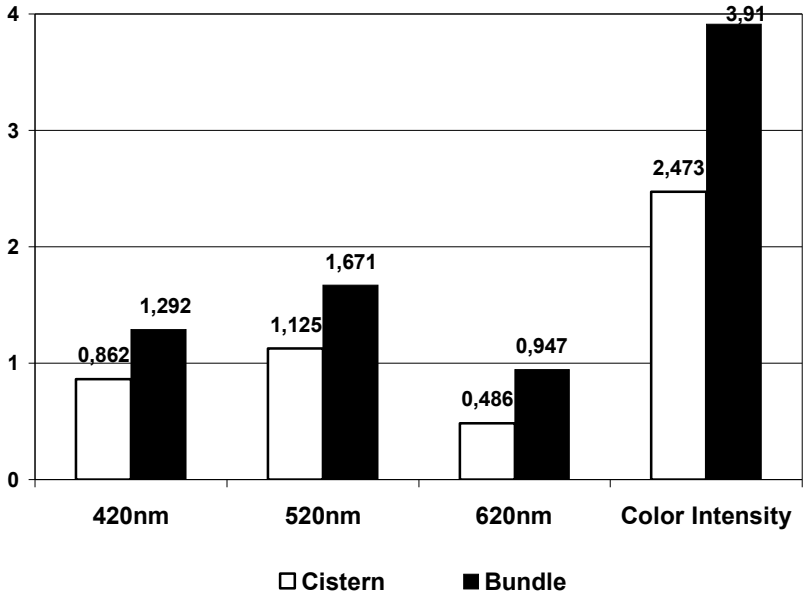

Fig. 5. Results of the test samples for intensity

Comparing these values with the previous surveys it can be concluded that the wine kept in a bundle has the highest values for color intensity of the wine [8].

In Figure 6 are given the values of nuance of burgundy red of the wine Vranec. The determination of the wine Vranec was performed spectrophotometrically at 420 nm and 520 nm.

From the submitted, it can be seen that the Vranec wine's nuance kept in a tank has higher values of shade (texture) of the wine.

Sulphur dioxide. Sulphur dioxide can be in free and bounded state, and the sum of free and bounded condition gives the total content of SO_2. Bound SO_2 binds the bisulfite ion with aldehydes, anthocyanins, protein and aldo - sugars. The maximum permitted level of sulphur dioxide allowed by OIV is 350 mg/L [7].

In Figure 7 are given the values of total and free sulphur dioxide, expressed in mg/L.

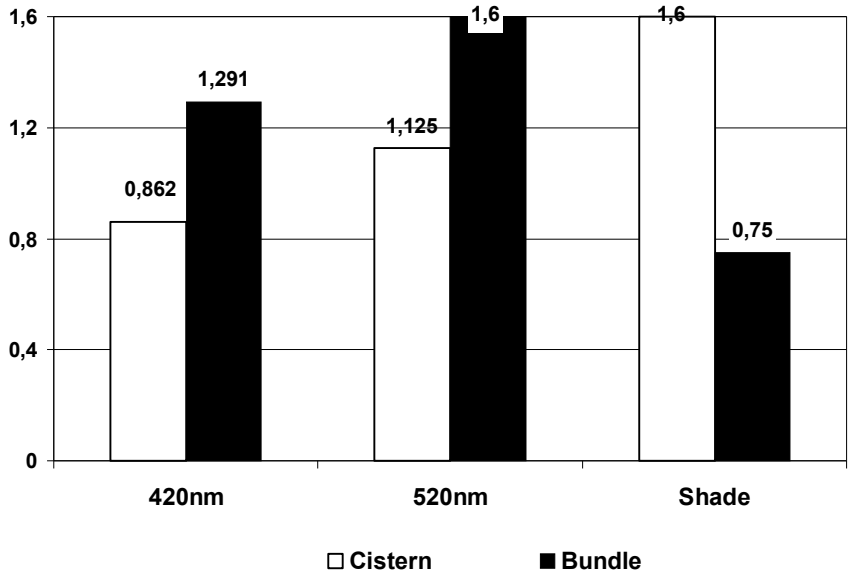

Fig. 6. Results of the test samples for nuance of wine Vranec

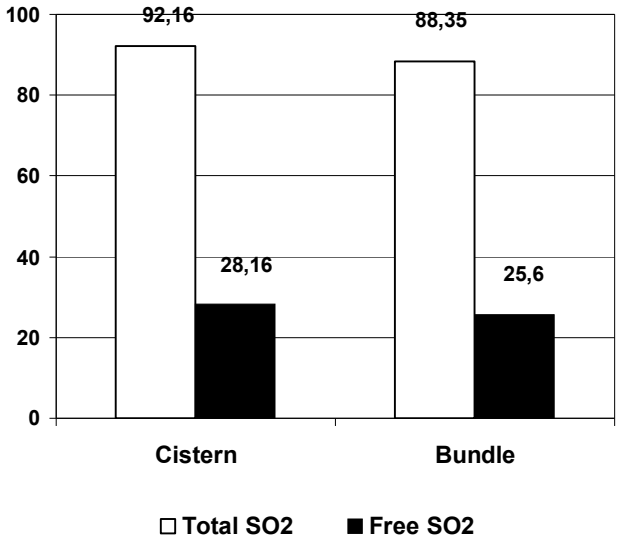

Fig. 7. Values for total and free sulphur dioxide

From Figure 7 it can be seen that the amount of total SO_2 and free SO_2 have higher values.

In the several forms available on the market, SO_2 as chemical antioxidant and an inhibitor of microbial activity is used in wine and related food industries. Although from a

historical perspective sulfites have been assessed as safe for health, the US Administration Food and Drug Administration (FDA) has determined that the presence of non - sulfites in food and beverages represents a potential health problem for a certain class of asthmatic individuals. Due to this the maximum allowed level of total sulfur dioxide allowed by OIV is 350 mg/L. Sulfur dioxide in wine is obtained in two forms, free and bound, and their sum gives the total content of SO_2 [7].

"Bonded SO_2 " refers to binding of bisulfite ion and other substances such as aldehydes, anthocyanins, proteins and aldo-sugar. The amount of bounded SO_2 and the binding rate depend on the response, which depends on pH: Lower pH, slower addition.

Bounded SO_2 has very little inhibitory effect on most of the different types of yeast and bacteria of acetic acid. It is believed that in higher levels of 50 mg/L, SO_2 bound (as a set of acetaldehyde and bisulfate) inhibitory effect in terms of lactic acid bacteria.

Conclusion

The concentration of hydrogen ions - pH of the wine samples kept in a tank and bundle are in the limits of 3.33 to 3.42, which is actually allowed pH range for red wines.

In the terms of overall acids, the amount of total acids is greater in the wine kept in a tank.

Volatile acidity marks higher value in the wine kept in bundle.

Malic acid has 0 mg/L in the wine kept in the bundle, which represents complete conversion of malic acid to lactic acid.

Citric acid in the wine is more contained in the one kept in a tank (0.38).

Acetic acid has higher values in the wine Vranec kept in bundle (0.48)

Higher amounts of sugars as total (5.1 g/L) and reducing (0.95 g/L) are noticed in the wine kept in a bundle.

The amount of alcohol in the tested samples ranges from 14.53-14.75 % vol, which is consistent with the requirements of the International organization of vine and wine (OIV).

Polyphenols and anthocyanins have higher values in wine from bundle (2757 mg/L polyphenols) (989 mg/L anthocyanins), due to material - wood in which the wine is stored.

The intensity of the wine kept in a bundle is higher (3.921) than the wine kept in a tank (2.47).

The nuance of red wine Vranec stored in tank is higher (1.6) in respect of wine kept in a bundle from the same vintage (0.75).

As for the presence of SO_2, it can be said to be "double-edged sword". On one hand the increased presence of SO_2 leads to inactivation of undesirable microorganisms (which is desirable), while on the other hand, increased amounts of SO_2 by a number of scientific research suggests a potential health problem for a certain class of asthmatic individuals. Considering the maximum total content of SO_2 from OIV (350 mg L) in the tested samples are observed three times minor values.

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Effects of processing on the proximate composition and energetic values in two fish species from Iran southern waters

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Abstract

Introduction. The purpose of research – was impact different cooking methods (frying, boiling and baking) on the proximate and mineral composition of fish species *Scomberoides commersonnianus* and *Spyraena jello*.

Materials and methods. Fresh Scom beroides lysan (*Scomberoides commersonnianus*), and Sphyraenidae (*Spyraena jello*) were collected from Behbahan market of Iran. They were kept in a plastic container and transported to the Food Chemistry laboratory of Behbahan Technology University. The established AOAC methods were followed for composition bio chemical of fish.

Results and discussion. Protein and lipid content were founded higher in baked and fried in fish *S.commersonnianus* (74.29%) and (20.20%) and fish *S. jello* (88.12%) and (17.77%) respectively. Ash content in fish *S.commersonnianus* varies from 9.80% to 15.34%, and in fish *S. jello* from 5.83% to 7.68% .

Comparison of nutrients contents of boiled fillets of two fish species showed that fish *S. jello* found best. The lower fat content in the boiled and baked *Spyraena jello* is mainly due to absorption of water used in the curry preparation. The absorption of water is evident when compare the fried *S. jello* similar. The protein content was generally high which an expected outcome is since fishes are good sources of protein. The higher protein content in the fried fish is due to meat as a result of moisture loss. Further evidence of this is seen in the fact that *S. jello* cooked in curry and steamed had lower protein content but had higher moisture contents. This can be attributed to absorption of water from the cooking medium thereby causing dilution of the muscle tissue analyzed.

The proximate composition of raw fillets both fish species is similar to earlier reports in tested fish. Proximate composition of protein, Fat and ash of fishes *S. commersonnianus* and *S. jello* was varied in all the cooking methods. There was no significant difference observed in fat content among boiled, baked and raw fish fillets ($P>0.05$). Increased ash content was noticed in all the cooked *S. commersonnianus* fillets when compared to raw fish fillets. Accordingly, the increase in ash, protein and fat content found in cooked silver catfish fillets is explained by the reduction in moisture.

Conclusion. The highest protein, the lowest fat content and calorie value were found in boiled fish; therefore, boiling can be recommended as the best cooking method for healthy diet.

Introduction

Despite its nutritive value, fish is highly susceptible to damage once caught and so have become source of pollution in the environment and growing microorganisms [1]. However, processing methods such as boiling, frying and roasting have been used to preserve and increase its availability to consumers for maximum around two years after caught fish [2]. Most processing methods often times involve removal of the wastes parts of the fish which may have negative effect on the total nutritive values of the fish [3]. Previous works reported the effect of processing methods on different fish types for determination of them nutritive values [4,5,6]. Fish is rarely eaten raw and usually cooked in different ways before consumption. Heating is one of the common methods in food processing. Heat is applied for food in different ways (Boiling, baking, roasting and frying) to enhance their flavor and taste; increase shelf life [7]. However, the effect of different cooking methods invariably affects the nutritive value of fish. The effects of different cooking methods on proximate and mineral composition of some fish species have been reported [8,9,10,11,12,15]. Hence the present study was aimed to investigate the effects of different cooking methods on the proximate composition of Scom beroides lysan (*Scomberoides commersonnianus*) and Sphyraenidae (*Spyraena jello*). The possible effects of different cooking methods on the nutritive value of this species were evaluated; the values obtained in the cooked samples were compared with the values found in raw fish.

Materials and methods

Samples collection and cooking. Fresh Scom beroides lysan (*Scomberoides commersonnianus*), with a length (45-53cm) and weight of (1kg) and Sphyraenidae (*Spyraena jello*) with a length (57-63 cm) and weight of (1kg) were collected from Behbahan market of Iran. They were kept in a plastic container and transported to the Food Chemistry laboratory of Behbahan Technology University. In the laboratory, the fishes were washed with tap water four times to remove wastes materials. The fishes were then placed in ice-cold water for ten minutes prior to eviscerating and beheading. Subsequently the fish samples were filleted and fillets were divided into four groups and each group consisted of four fillets. The first group was uncooked while the other three groups were cooked in the following methods; boiling, baking, and frying. Boiling was performed at 100 °C for 14 min. Baking of fillets was performed in a conventional oven with the temperature set at 210 °C for 25 min. The frying of fillets was performed in a domestic frying pan of 2 L capacity at temperature approximately of 175 °C for 15 min. Sunflower oil was used for frying. The fresh and cooked fishes were ground in a kitchen blender to ensure homogeneity and representative samples taken for analysis. Samples were packed in a polythene bags and kept under frozen conditions (−20 °C) until analysis.

Proximate composition. Proximate composition analysis for homogenized samples of cooked and fresh fish was done in triplicate for protein, lipid and ash content. The protein was determined by the Official methods of AOAC [13]. After cooking and smoking, fish samples were oven dried to constant weight at 60^{o}C, and the flesh of each fish was separated from its bones, skin and head. The fillet alone was homogenized using a kitchen blender and analyzed to determine the proximate composition in each of the fish samples on dry matter basis. The fat, ash and protein of the fish samples were determined following

the method described by AOAC [13]. Five grams of dry ground sample was digested in 100 mL of 1.25% H_2SO_4 for 30 min. The digested sample was cooled and filtered and the residue was collected into a beaker and further digested with 100 mL of 1.25% NaOH. The residue was collected after filtration and oven dried at 100°C to constant weight. Dried residue was incinerated in the muffle furnace at 550°C for 5 h. Moisture content was determined by heating 2.0g each of sample to a constant weight in a crucible placed in an oven maintained at 105ºC. Crude fat was obtained by exhaustively extracting 5.0g of each sample in a Soxhlet apparatus using petroleum ether (40 – 60°C) as the extractant. Crude protein (% total nitrogen x 6.25) was determined by the Micro-Kjeldahl method of AOAC [13]. Ash content was carried out by incinerating 1.0 g of the fish sample in a muffle furnace maintained at 550°C for 5h.

Statistical Analysis. The effect of different cooking methods on the proximate and mineral composition of *Scomberoides commersonnianus* and *Spyraena jello* was analyzed using standard deviation. Significant differences between means of experiments were determined by least significant difference. SPSS 16.0 statistical tool was used to analyze the data obtained. Results were considered statistically significant at $p < 0.05$ with Duncan's multiple range test.

Results and discussion

Proximate composition of raw, fried, boiled and baked of *Scomberoides commersonnianus* and *Spyraena jello* are shown in Tables 1 and 2. Fat minimum content was found to be 5.50%% in raw *Spyraena jello* and highest content in the fried *Scomberoides commersonnianus* (20.20%). The ash content was highest in boiled *Scomberoides commersonnianus* fish (15.34%). Protein content was recorded highest in the baked *Spyraena jello* (88.12%).

Table 1

Proximate (%) composition (DM powder) of raw and cooked fillets samples of *Scomberoides commersonnianus*

	Raw	Boiled	Baked	Fried
Protein	78.78±0.78^a	67.36±0.98^b	74.29±0.33^c	68.56±0.41^b
Lipid	8.46±1.78^a	12.86±0.22^b	11.74±0.69^b	20.20±0.45^c
Ash	9.49±0.57^a	15.34±0.75^b	13.63±0.37^c	9. 80±0.79^a
Carbohydrate	3.27	4.44	0.34	1.44
Energetic value (Kcal/100g)	405.12±1.28^a	402.94±1.22^a	404.18±1.56^a	461.80±1.78^b

Values are shown as mean±standard deviation of triplicates. Values within the same row have different superscripts are significantly different ($p < 0.05$)

Table 2

Proximate (%) composition (DM powder) of raw and cooked fillets samples of *Spyraena jello*

	Raw	Boiled	Baked	Fried
Protein	86.75±1.68[a]	87.16±0.98[a]	88.12±0.47[a]	74.11±0.36[b]
Lipid	6.52±0.24[a]	5.50±0.68[a]	5.71±0.58[a]	17.77±0.34[b]
Ash	9. 50±0.58[a]	7.06±0.57[b]	5.83±0.22[c]	7. 68±0.55[b]
Carbohydrate	0.50	0.28	0.34	0.44
Energetic value (Kcal/100g)	407.68±0.68[a]	399.26±0.48[b]	405.23±0.38[a]	458.13±0.29[c]

Values are shown as mean±standard deviation of triplicates. Values within the same row have different superscripts are significantly different ($p < 0.05$).

Fried fish had a higher level of fat than raw or other cooked fish. The increase in fat content of the fried fish fillets is also related to oil absorption during the cooking process. Fat increase can be due to the oil penetration into the food after water is partially lost by evaporation [14]. Similar results have been reported for African Catfish fried in sunflower oil [15]. The lower fat content in the boiled and baked *Spyraena jello* is mainly due to absorption of water used in the curry preparation. The absorption of water is evident when compare the fried *S. jello* similar reports have been found from Arabian Gulf fish and shrimps [16]. The protein content was generally high which an expected outcome is since fishes are good sources of protein [17]. The higher protein content in the fried fish is due to meat as a result of moisture loss. Further evidence of this is seen in the fact that *S. jello* cooked in curry and steamed had lower protein content but had higher moisture contents. This can be attributed to absorption of water from the cooking medium thereby causing dilution of the muscle tissue analyzed. This higher protein content in fish is important from a dietary point of view since; the quality of fish protein is very high because of its essential amino acid composition [18]. Fish proteins are especially labile and easily denatured than those of meats and the molecules are already stretched to the disruptive action of enzymes that increased in digestion. Adiachi et al. [19] stated that application of heat result in some increase in digestibility that effect on the 10-20 percent of globular proteins in fish muscles. Further, reports also indicate that fish muscle is more digestible than other animal protein due to lower level of connective tissue [20]. The increase in dry matter content was observed in fried fish. The highest moisture content was recorded in fresh and decrease moisture content was noticed in all method of cooked fish when compare to fresh fish. These changes were similar to those reported by [9] in rainbow trout and [7] in sardines. Water losses, occurring during frying resulted in higher protein content in fried fish as compared to the fresh fish [7]. Accordingly, the increase in ash, protein and fat content found in cooked silver catfish fillets is explained by the reduction in moisture. Differences in water contents between fresh smoked rainbow trout were found to be significant [21]. These findings also supported by Gall et al. [22], that deep fried fish fillet. The higher ash content in the cooked fish, might be due to its higher bony consistency and high scaly

nature. Such fish offer minerals in their edible forms more abundantly than large-sized fish do [23].

The proximate composition of raw fillets both fish species is similar to earlier reports in tested fish [24]. Proximate composition of protein, Fat and ash of fishes *S. commersonnianus* and *S. jello* was varied in all the cooking methods. There was no significant difference observed in fat content among boiled, baked and raw fish fillets ($P > 0.05$). Similar results were reported for sardine and African catfish fried in vegetable oil [25]. Increased ash content was noticed in all the cooked *S. commersonnianus* fillets when compared to raw fish fillets. Accordingly, the increase in ash, protein and fat content found in cooked silver catfish fillets is explained by the reduction in moisture.

Conclusions

Several factors influence the nutritional content of the processed fishes and the type and level of losses due to processing. The heat and flow of gases cause drying of the seafood item. This decreases the water content thereby causing the changes associated with dehydration such as increasing the protein and fat concentration of processed fillets. The nutrient changes that occur during concentration will depend on the contents of the mixture and the temperature at which the process takes place. Generally, there is a decrease in water content and corresponding increase in other nutrients. The increased dry matter, protein, ash contents was observed in backed both fish fillets. In this research, the highest protein, the lowest fat content and calorie value were found in boiled fish; therefore, boiling can be recommended as the best cooking method for healthy diet.

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Effect of packaging and storage conditions on retention of ascorbic acid in fenugreek leaves *(Trigonella Foenum-Graecum)*

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Abstract

Introduction. The present investigation evaluated the effect of storage and packaging conditions on retention of ascorbic acid content of fenugreek leaves.

Materials and methods. Fenugreek leaves (*Trigonella Foenum-Graceum*) with and without roots weighing 100 g were made and packed in perforated and non-perforated flexible consumer packets of 30 x 25 cm (750 sq cm) of four different types viz., LDPE -100 gauge, LDPE -200 gauge, PP-100 gauge and PP -200 gauge. For perforations 24 vents of 0.59 cm diameter were made covering an area of 1.87 sq. cm. These samples were stored at ambient (14-35° C, RH 50-60 per cent) and low temperature (0-5° C, RH 80-90 per cent) till acceptable. The samples were analyzed at regular intervals for ascorbic acid content using 2, 6 dichlorophenol indophenol method.

Results and discussion. Fresh fenugreek leaves contained 51.4 mg/100g ascorbic acid. At lower temperature, fenugreek samples without root in non-perforated package (NPWORL) had a shelf life of six days and mean ascorbic acid retention of 80.95%. Packaging the samples with root (NPWRL) reduced the shelf life to four days period and retained 66.05% of ascorbic acid. Perforation in the packaging material also reduced the storage period to four days in both with (PWRL) and without root (PWORL) fenugreek samples. Fenugreek samples without and with roots stored at ambient temperature in non-perforated package (NPWORA and NPWRA) showed a maximum shelf life of two days with mean ascorbic acid retention of 69.99% and 56.47% respectively. A gradual decrease in the mean ascorbic acid content was observed at both low and ambient temperatures with the presence of roots and perforation in the packaging material. This decrease was observed to be significant at both low ($p=0.004$) and ambient ($p= 0.055$) temperatures. The ascorbic acid was also found to decrease with increase in days of storage at both low as well as ambient temperatures.

The flexible packaging materials viz., LDPE and PP of 100 and 200 gauge did not show any significant difference in retention of ascorbic acid. Amongst interaction between perforations, roots, temperature, days of storage and packaging materials, the interactions between days of storage were found to be significant with perforations ($p =0.023$), root ($p=0.053$) and temperature ($p= 0.00$).

Conclusions: Fenugreek samples stored without roots in non-perforated packaging material reflected significantly ($p=0.00$) highest retention of ascorbic acid at low temperatures.

Introduction

Vegetables and fruits are rich sources of micronutrients. These also provide phytonutrients and fibre which are of vital health significance. Vegetables deteriorate quickly when stored for longer periods because of the relatively high moisture content. Huge amounts of losses take place between harvesting and consumption. Around 30,000 million worth of fruits and vegetables get wasted in India, of which vegetables constitute more than 50 per cent. Green leafy vegetables, moisture laden foods are all the more susceptible to spoilage by the attack of fungi and bacteria [1].

Fruits and vegetables are perishable products with an active metabolism during post-harvest period, but the shelf life can be extended by retarding physiological, pathological and physical deteriorative processes after the harvest. Packaging has an important role to play in creating a barrier between environment and food, in addition to preventing pilferage, ease of transport, handling and marketing. Flexible packages are commonly used and are cost effective for various food products especially high moisture foods [2].

Vitamin C, including ascorbic acid and dehydroascorbic acid, is one of the most important nutritional quality factors in many horticultural crops and has many biological activities in the human body. The content of vitamin C in fruits and vegetables can be influenced by various factors such as genotypic differences, preharvest climatic conditions and cultural practices, maturity and harvesting methods, and postharvest handling procedures [3]. In addition to oxidative damage, enzymes may also function indirectly to lower the vitamin C content [4].

Several scientists [5, 6, 7, 8, 2] have studied the effect of treatments and storage conditions on ascorbic acid content of fenugreek leaves. However, studies on effect of presence of roots and perforations in the packaging material on ascorbic acid are scarce; hence it was postulated to study the retention of ascorbic acid when fenugreek is stored with and without roots at low and ambient temperatures in flexible consumer packaging material.

Materials and methods

Selection and procurement of samples. Fresh samples of Fenugreek leaves (*TrigonellaFoenum-Graceum*) of uniform maturity and size were procured form a local farm of Nagpur city in Maharashtra.

Packaging of samples. Samples of fenugreek leaves with and without roots weighing 100 g were made and packed in flexible consumer packets of 30 x 25 cm (750 sq cm) of four different types viz., LDPE -100 gauge, LDPE -200 gauge, PP-100 gauge and PP -200 gauge. An unpacked sample of fenugreek leaves coded as untreated was also kept for storage for comparison. Different studies on pre-packaging of vegetables at different temperature conditions and relative humidity have shown that the shelf life of these commodities could be extended for a considerable period and in some cases the shelf life could even doubled by packing them in polythene bags of suitable gauge with adequate vents. Hence in the present study the packets were used with and without perforations. For perforations 24 vents of 0.59 cm diameter were made covering an area of 1.87 sq cm.

Storage studies. The sample of fenugreek leaves were stored at ambient and low temperature till acceptable. For the ambient temperatures, the samples were kept in a tray in the laboratory. The temperature ranged between 14 to 35°C and the relative humidity between 50-60 per cent. For low temperature, the samples were kept in the incubator and the temperature and relative humidity were maintained between "0° to 5 °C" and 80-90 percent respectively.

Analysis of ascorbic acid. Ascorbic acid was considered as indicator of freshness. The samples were drawn daily for the analysis of ascorbic acid using 2, 6 dichlorophenol indophenol method [8]. The dye, which is blue in alkaline solution and red in acid solution, is reduced by ascorbic acid to a colorless form. The reaction is quantitative and practically specific for ascorbic acid solution in *p*H range 1-3.5. Metaphosphoric acid (HPO_3) extracts of the fenugreek leaves were prepared. The reducing capacity of the extracts was then measured by titrating with 2, 6-dichlorophenolindophenol (DCIP). In this oxidation-reduction reaction, ascorbic acid in the extract was oxidized to dehydroascorbic acid (DHAA) and the indophenol dye reduced to a colorless compound.

The following formula was used for the calculation of ascorbic acid content of fenugreek leaves.

$$\textit{mg of ascorbic acid per 100g or ml} = \frac{\textit{Titre x Dye Factor} \times \textit{Volume made up} \times 100}{\textit{Aliquot of extract taken for estimation} \times \textit{Wt or volume of sample taken for estimation}}$$

Where

- Titre is amount of dye 2, 6-DCIP required to oxidize ascorbic acid of fenugreek leave extract prepared with 3 per cent HPO_3 solution.
- Dye factor is amount of dye solution (prepared by dissolving 50 mg of sodium salt of 2.6- DCIP and 42 gm of sodium bicarbonate , dilute with distilled water to 200ml) required to oxidise standard ascorbic acid solution(prepared by dissolving 100mg of ascorbic acid in 100 ml 3% HPO_3 ,10 ml of which diluted 100 ml).
- Aliquot of extract is prepared by blending 10 gm of fenugreek leaves with 3% HPO_3 and make up to 100 ml with HPO_3.

The estimations for ascorbic acid were carried out in duplicate. The ascorbic acid of fenugreek stored at ambient temperatures were analysed after 24 (1^{st} day) and 48 hours (2^{nd} day) whereas the samples stored at low temperature were analysed on 2^{nd}, 4^{th} and 6^{th} days of storage till the fenugreek leaves were acceptable. The ascorbic acid content of fresh fenugreek leaves was considered as values for 'zero days'. On this basis, the retention of ascorbic acid was calculated.

According to packaging and storage conditions, the fenugreek samples were coded as follows:

- NPWORL: Non perforated packet, without root, low temperature
- NPWRL: Non perforated packet, with root, low temperature

- PWORL: Perforated packet, without root, low temperature
- PWRL: Perforated packet, with root, low temperature
- NPWORA: Non perforated packet, without root, ambient temperature
- NPWRA: Non perforated packet, with root, ambient temperature
- PWORA: Perforated packet, without root, ambient temperature
- PWRA: Perforated packet, with root, ambient temperature

Statistical analysis. The ascorbic acid content of fenugreek leaves was analyzed for t test, one way and two way Analysis of Variance using SPSS version 17. The confidence value was set at 95 %. The t test was computed to assess the significant difference between the means of two groups (for perforations and presence of root) and one way ANOVA was computed to assess the significant difference between the means of more than two groups (for days of storage and packaging materials). To assess the interaction between two variables of storage conditions, two way ANOVA was computed.

Results and discussion

The ascorbic content of fresh fenugreek leaves was 51.4 mg/ 100 g. Other scientists [9,10,2] have reported the ascorbic acid content to be 50.40 to 52/100gm.

The untreated sample of fenugreek leaves remained fresh up to 24 hours of storage at ambient temperature whereas at low temperature the samples were fresh up to 48 hours. The fenugreek leaves stored at ambient temperature within 24 hours showed comparatively higher retention of ascorbic acid when stored without roots (54.08%) than with root samples (51.36%). Similarly fenugreek leaves stored at low temperature also showed higher retention of ascorbic acid when stored without root (49.80 %) as compared to the sample stored with root (48.83) even after 48 hours of storage.

The ascorbic acid content of fenugreek leaves has been discussed below with reference to different packaging material and storage period. The mean ascorbic acid content of fenugreek leaves packed with and without roots, in perforated and non-perforated packets stored at low and ambient temperatures has been presented in Table 1 and Table 2 respectively.

At lower temperature, fenugreek samples without root in non-perforated package (NPWORL) had a shelf life of six days and mean ascorbic acid retention of 80.95%. Packaging the samples with root (NPWRL) reduced the shelf life to four days period and retained 66.05% of ascorbic acid. Perforation in the packaging material also reduced the storage period to four days in both with (PWRL) and without root (PWORL) fenugreek samples. The mean ascorbic acid retention was 66.01% and 53.84% respectively. Statistically significant decrease in the mean ascorbic acid content of fenugreek samples with roots ($p=0.000$) and without roots ($P = 0.000$) with increase in period of storage was observed in both non perforated (NPWORL, NPWRL) and perforated (PWORL, PWRL) packaging. The trend observed was similar in all samples irrespective of the type and gauge of the packaging material as reflected by insignificant differences in samples packed in non-perforated without roots (NPWORL, $p = 0.904$) and with roots (NPWRL, $p = 0.995$) and perforated without roots (PWORL $p = 0.814$) and with roots (PWRL, $P = 0.964$) at low temperature (Table 1).

Fenugreek samples without and with roots stored at ambient temperature in non-perforated package (NPWORA and NPWRA) showed a maximum shelf life of two days with mean ascorbic acid retention of 69.99% and 56.47% respectively. A significant decrease in mean ascorbic acid content with increase in storage period was reflected in samples packed without roots (NPWORA, P =0.000) and with roots (NPWRA, P=0.000.) irrespective of the packaging material which showed insignificant differences (NPWORA, P= 0.895 and NPWRA, P = 0.997 respectively). The mean ascorbic acid retention further decreased with perforation to 54.37% and 46.44% with the two treatments without (PWORA) and with roots (PWRA) respectively. A significant decrease in mean ascorbic acid content was observed in fenugreek samples without roots (PWORA, P = 0.000) and with roots (PWRA, P=0.000) packed in perforated material with increase in storage period. Insignificant differences were observed with respect to the packaging material in both treatments (PWORA, P =0.969 and PWRA, P = 1.00) for without and with root samples respectively (Table 2).

Combined effects of storage conditions on ascorbic acid retention. Table 3 presents the overall mean ascorbic acid values and percentage retention of differently treated samples. A specific trend with respect to the combined effect of temperature of storage, the treatment of the fenugreek samples and the type of packaging was observed. Fenugreek samples stored without roots in non-perforated packages showed maximum ascorbic acid retention at both low (NPWORL, 81.07%) and ambient (NPWORA, 69.98%) temperatures. A gradual decrease in the mean ascorbic acid content was observed at both low and ambient temperatures with the presence of roots and perforation in the packaging material. This decrease was observed to be significant at both low (p=0.004) and ambient (p= 0.055) temperatures.

Table 1

Ascorbic Acid Content of Fenugreek leaves stored at Low Temperatures

Flexible Packaging Materials	Days of Storage	LDPE 100 gauge	LDPE 200 gauge	PP 100 gauge	PP-200 gauge	Mean ± SD	F Value Between Days of storage	F Value Between Packaging Materials
	Zero Day	51.4	51.4	51.4	51.4	51.40 ± 0.0		
Non Perforated Without Root (NPWORL)	DAY 2	48.27 (93.91)	47.58 (92.57)	50.6 (98.44)	49.9 (49.08)	49.08 ± 1.40 (95.49)	F = 58.010, P = 0.000	F = 0.184, P = 0.904
	DAY 4	41.3 (80.35)	41.7 (81.13)	46.8 (91.05)	43.4 (84.44)	43.3 ± 2.50 (84.24)		
	DAY 6	30.6 (59.53)	30.01 (58.39)	35.17 (68.42)	34.09(66.32)	32.46 ± 2.54 (63.15)		
	Mean ± SD	40.05± 8.9 (77.92)	39.76 ± 8.94 (77.35)	44.19 ± 8.03 (85.97)	42.46 ± 7.94 (82.61)	**41.61± 7.46** (80.95)		
Non perforated With Root (NPWRL)	DAY 2	44.6 (86.77)	42.8 (83.27)	44.9 (87.35)	43.6 (84.82)	43.98 ±0.96 (85.55)	F = 336.40, P = 0.000	F = 0.021, P = 0.995
	DAY 4	25.4 (49.42)	21.6 (42.02)	25.7 (50)	23.01 (44.77)	23.93 ± 1.96 (46.55)		
	Mean ± SD	35.00 ±13.58 (68.09)	32.20 ±14.99 (62.65)	35.30± 13.58 (68.68)	33.31 ±14.56 (64.8)	**33.95 ±10.81** (66.05)		
Perforated Without Root (PWORL)	DAY 2	30.5 (59.34)	36.04 (70.12)	41.3 (80.35)	41.6 (80.93)	37.36 ±5.24 (72.68)	F = 20.636, P = 0.004	F = 0.317, P = 0.814
	DAY 4	21.2 (41.25)	24.3 (47.28)	25.03 (48.7)	26.8 (52.14)	24.33 ± 2.34 (47.34)		
	Mean ± SD	25.85 ± 6.58 (50.29)	30.17 ± 8.30 (58.7)	33.17 ± 11.50 (64.52)	34.20 ± 10.47 (66.54)	**30.85 ± 7.91** -60.01		
Perforated With Root (PWRL)	DAY 2	29.9 (58.17)	34.1 (66.34)	33.8 (65.76)	34.6 (67.32)	33.10 ±2.16 (64.4)	F = 75.828, P = 0.000	F = 0.086, P = 0.964
	DAY 4	20.8 (40.47)	21.7 (42.22)	23.6 (22.9)	22.9 (22.25)	22.25 ± 1.24 (43.29)		
	Mean ± SD	25.35 ± 6.43 (49.32)	27.90 ±8.77 (54.28)	28.70 ± 7.21 (55.84)	28.75 ± 8.27 (55.93)	**27.68 ± 6.02**(53.84)		

Numbers in parenthesis indicate per cent retention of ascorbic acid.

Table 2

Ascorbic Acid Content of Fenugreek leaves stored at Ambient Temperatures

Flexible Packaging Material	Days of Storage	LDPE -100 gauge	LDPE -200 gauge	PP-100 gauge	PP -200 gauge	Mean ± SD	F Value Between Days of storage	F Value Between Packaging Materials
	Zero Day	51.4	51.4	51.4	51.4	51.40 ± 0.0		
Non Perforated Without Root (NPWORA)	DAY 1	41.9 (81.52)	38.1 (74.12)	42.1 (81.91)	39.9 (77.63)	40.50 ± 1.88 (78.79)	F = 40.529 P = 0.001	F = 0.195, P = 0.895
	DAY 2	32.6 (63.42)	28.9 (56.23)	33.7 (65.56)	30.6 (59.53)	31.45 ± 2.13 (61.19)		
	Mean ± SD	37.25 ± 6.58 (72.47)	33.50 ± 6.51 (65.18)	37.90 ± 5.94 (73.74)	35.25 ± 6.58 (68.58)	**35.98 ± 5.18**(69.99)		
Non Perforated With Root (NPWRA)	DAY 1	39.2 (76.26)	35.8 (69.65)	40.6 (78.99)	39.1 (76.07)	38.68 ± 2.04 (75.24)	F = 342.38, P = 0.000	F = 0.015, P = 0.997
	DAY 2	19.6 (38.13)	19.1 (37.16)	19.9 (38.72)	18.9 (36.77)	19.38 ± 0.46 (37.69)		
	Mean ± SD	29.40 ± 13.86 (57.20)	27.45 ± 11.81 (53.4)	30.25 ± 14.64 (58.85)	29.00 ± 14.28 (56.42)	**29.03 ± 10.40**(56.47)		
Perforated Without Root (PWORA)	DAY 1	32.1 (62.45)	34.4 (66.93)	36.4 (70.82)	38.1 (74.12)	35.25 ± 2.59 (68.58)	F = 90.942, P = 0.000	F = 0.077, P = 0.969
	DAY 2	18.48(35.95)	21.4 (41.63)	20.4 (39.69)	22.3 (43.39)	20.65 ± 1.64 (40.17)		
	Mean ± SD	25.29 ± 9.63 (49.20)	27.9 ± 9.19 (54.28)	28.4 ±11.31 (55.25)	30.2 ± 11.17 (58.75)	**27.95 ± 8.06**(54.37)		
Perforated With Root (PWRA)	DAY 1	31.3 (60.89)	34.09 (66.32)	31.9 (62.06)	32.06 (62.37)	32.34± 1.21 (62.91)	F = 485.134, P = 0.000	F = 0.002, P = 1.000
	DAY 2	15.3 (29.77)	14.1 (27.43)	16.1 (31.32)	16.1 (31.32)	15.40 ± 0.95 (29.96)		
	Mean ± SD	23.30 ± 11.31 (45.33)	24.10 ± 14.14 (46.88)	24.00 ± 11.17 (46.69)	24.08 ± 11.29 (46.85)	**23.87 ± 9.10**(46.44)		

Numbers in parenthesis indicate per cent retention of ascorbic acid.

Table 3

Combined effects of storage conditions on mean Ascorbic acid content of Fenugreek

Temp of storage	Vitamin C Content	Non Perforated Without Root (NPWOR)	Non Perforated With Root (NPWR)	Perforated Without Root (PWOR)	Perforated With Root (PWR)	F Value
Low Temp (L)	mg/100gm	41.61 ± 7.46^{ab}	33.95 ± 10.81	30.84 ± 7.91^{b}	27.67 ± 6.02^{a}	F = 5.473
	Retention (%)	81.07 %	66.05 %	60.00 %	53.83 %	P= 0.004
Ambient Temp (A)	mg/100gm	35.97 ± 5.18^{ab}	29.02 ± 10.40	27.94 ± 8.06^{b}	23.86 ± 9.10^{a}	F = 2.861
	Retention (%)	69.98 %	56.45 %	54.35 %	46.42 %	P= 0.055

Superscript values with similar letters differ significantly.
t value between NPWORL and NPWRL=1.883, P= 0.076
t value between NPWRL and PWORL = 0.656, P = 0.523
t value between NPWRL and PWRL = 1.434, p=0.173
t value between NPWORL and PWRL = 4.400, p= 0.000
t value between NPWORL and PWORL=3.088, p = 0.006
t value between PWRL and PWORL =0.902, P = 0.382
t value between NPWORA and NPWRA=1.691, P = 0.113
t value between NPWRA and PWORA = 0.232, p= 0.820
t value between NPWRA and PWRA = 1.055, p = 0.310
t value between NPWORA and PWRA = 3.26, p=0.006
t value between NPWORA and PWORA=2.369, P = 0.033
t value between PWRA and PWORA =0.948, P = 0.359

The fenugreek leaves packed in different packaging materials and stored at ambient conditions were comparable to fresh samples only up to two days whereas at low temperature the shelf life of samples could be extended up to six days (Table 1 and 2). Raw minimally processed vegetables are living entities. Temperature control after processing and during storage is critical in reducing deteriorative processes damage induced metabolic activity, thus maintaining product quality [11]. Refrigeration is one of the foremost tools for inhibiting damage induced metabolic reactions and also growth of pathogenic microorganisms [12]. Several scientists [13, 14, 15, 16] have observed the extended shelf life of fruits and vegetables when stored under refrigerated condition.

The present study revealed that fenugreek leaves retained maximum ascorbic acid when packed in non-perforated packets and stored without root at low temperature. The presence of root have reduced the ascorbic acid content of fenugreek which may be due to deterioration of leaves due to small particles of soil attached to roots. The small particle of soil detaches itself from the roots and then stuck to the leaves, making it unacceptable and in few instances led to microbial spoilage during prolongs storage. Vitamin C is most sensitive to destruction when the product is subjected to unfavorable handling and storage conditions. Losses are enhanced by extended storage, higher temperatures, low relative humidity, physical damage and chilling injuries [3].

In the present study fenugreek leaves stored in perforated packets also showed higher loss of vitamin C. This may be due to excessive loss of oxygen due to large area covered due to perforations. Reduced O_2 and high CO_2 levels have also been proved to effectively control enzymatic browning, firmness and decay of fresh-cut fruits and vegetables. Besides, the proliferation of aerobic spoilage microorganisms can be substantially delayed with reduced O_2 levels [17]. Perforation of the packaging is a solution to control the atmosphere inside the packaging, as the holes is a way of steering a continued transport of oxygen into the packaging. At the same time carbon dioxide can get out of the packaging. The size of the holes must be adapted to the product, the packaging film and not least the distribution temperature [18]. According to FAO leafy vegetables require a high relative humidity level to prevent wilting and only a few holes in the package are recommended [19].

The present investigation revealed that ascorbic acid decreased with increase in days of storage at both low as well as ambient temperatures. Several scientists [2, 19, 20] have also reported loss of ascorbic acid with the increase in days of storage in leafy and other vegetables.

The present study also reveals that amongst the non-perforated packets, PP 100 gauge and amongst the perforated packets, PP 200 gauge retained maximum ascorbic acid. However packaging materials showed insignificant difference in retaining ascorbic acid of fenugreek leaves in different storage conditions.

Interaction of storage conditions variables. Table 4 presents the combined effects of storage condition variables. Amongst the interaction between perforations, roots, temperature, days of storage and packaging materials, the interactions between length of storage were found to be significant with perforations (p =0.023), root (p=0.053) Temperature (p= 0.00).

Table 4

Interaction among variables of storage conditions

	Temperature	**Perforation**	**Root**	**Days of storage**	**Packaging**
Temperature	-	0.059 P=0.809	0.000 P=0.995	34.57 P=0.000	0.102 P=0.981
Perforation	-	-	0.201 P=0.655	3.324 P= 0.023	0.215 P=0.930
Root	-	-	-	2.637 P= 0.053	0.086 P=0.987
Days of Storage	-	-	-	-	0.301 P=0.993

The days of storage interacted significantly with the temperature of storage, which was also indicated by increasing the shelf life of fenugreek leaves and retention of higher amounts of ascorbic acid when stored at lower temperatures. The presence of roots and presence of perforations in the packets also showed significant interactions with the days of storage with respect to ascorbic acid content of fenugreek leaves. This indicates that only perforations in the packet or presence of root alone does not decrease ascorbic acid content of fenugreek, but it is due to the days of storage which interacts with the ascorbic acid content of fenugreek leaves.

Conclusion

The present study revealed that fenugreek leaves without root packed in non-perforated packets and stored at low temperature retains highest amount of ascorbic acid. The present study also revealed insignificant difference in retaining ascorbic acid of fenugreek leaves in different packaging materials. Perforated packages need evaluation in terms of the total area of vents for the optimum retention of ascorbic acid. Amongst the interaction between the packaging and storage conditions, the interactions between lengths of storage were found to be significant with perforations, root and temperature with respect to ascorbic acid content of fenugreek leaves.

Thus it can be concluded from the study that for the retention of maximum ascorbic acid in fenugreek leaves, it may be stored without root in non-perforated LDPE/PP, 100/200 gauge packaging material at lower temperatures.

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Application of infrared spectroscopy for quantitative analysis of new food emulsifiers

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Abstract

Introduction. Spectroscopic study of the new emulsifiers synthesized under the mild conditions with the purpose of determination of mono- and diacylglycerines of fatty acids and proof of the conservation of essential bioactive components in them gains actuality.

Materials and methods. For the current studies the emulsifiers of acylglycerine origin were synthesized by transesterification of the refined sunflower oil in the binary solvent under the mild conditions (35...40 °C). A qualitative and quantitative study of these emulsifiers was performed by using infrared spectroscopy on Perkin-Elmer Spectrum One FTIR Spectrometer by the method of a crushed drop.

Results and discussion. Infrared spectra of the new emulsifiers of acylglycerine origin were studied and an analysis of the characteristic absorption bands assigned to the respective types of valence and deformation vibrations of triacylglycerines (1110 cm^{-1}, 1173 cm^{-1}, 1244 cm^{-1} - ν(C=O) of esters; 1377 cm^{-1} and 1416 cm^{-1} - δ_s(C–H) in groups $–CH_3$ and$–CH_2–$; 1736 cm^{-1} - ν(C=O) of esters; 2855 cm^{-1} and 2927 cm^{-1} - ν(C–H) in $–CH_2–$ groups; 3009 cm^{-1} - ν_{as}(C–H) in groups –CH=CH– in the *cis*-form), the hydroxyl groups of mono-, diacylglycerines of fatty acids (3435 cm^{-1}), primary alcohols (1061 cm^{-1}) was made. The presence of mono- and diacylglycerines of fatty acids in the new emulsifiers was proved. It was also established that due to the mild conditions of their obtaining these emulsifiers didn't contain *trans*-isomers and unsaturated acids in the native form were preserved in them. On the basis of calculated spectral characteristics the calibration graph of *S* on the mass concentration of mono-, diacylglycerines in the model compositions E471 with the refined sunflower oil was plotted. With the help of the obtained equation of the line the total content of mono-, diacylglycerines of fatty acids was determined as 52,6±0,2% in the samples of emulsifiers of acylglycerine origin synthesized in the binary system hexane:isopropanol with the ratio of volume fractions of the solvents 0,4:0,6. This ratio was accepted as appropriate for obtaining new food emulsifiers with the content of mono-, diacylglycerines 54±1,2%.

Conclusions. Using the method of infrared spectroscopy for solving the problems of quantitative determination of mono-, diacylglycerines of fatty acids in the emulsifiers of series of acylglycerines E471 is suggested.

Introduction

Currently there is an increasing demand for high quality foodstuff that is made with using additives based on natural raw materials that are absolutely harmless to the human health and the environment. Such additives include mono- and diacylglycerines (MAG and DAG) of fatty acids (E471) - safe additives of the GRAS status (Generally Regarded as Safe - completely safe) that are applied without restrictions. Being surfactants with an indicator of hydrophilic-lipophilic balance (HLB) 3...5 they are widely used as lipophilic nonionic emulsifiers, emulsion stabilizers, baking powders, and amendments. In publications [1-3] significant advantages of the emulsifiers of acylglycerine series are noticed.

Sagalowicz L. and co-authors reviewed the typical characteristics of monoacylglycerine self-assembly structures, the most common characterisation techniques, how introduction of guest molecules influenced the self-assembly structures, their use for drug delivery and how commercial food grade monoacylglycerines obtained from sunflower oil could be applied to achieve unique delivery functionalities in food systems. Such emulsifiers can also improve the consistence, marketable state of the finished meat products including those ones on the basis of frozen raw meat [4-7].

In spite of the quite wide assortment of these emulsifiers there are significant drawbacks in the technology of their obtaining. First of all, these drawbacks are associated with the hard conditions of the synthesis of emulsifiers [8]. Moreover, their industrial production in Ukraine is absent.

The technology of producing emulsifiers of E471 series is based on two chemical processes that are carried out in industry at 210...245 °C: glycerolysis of fats (transesterification with glycerin) and esterification of glycerin with high molecular fatty acids. A mixture of the products obtained is separated by centrifugation and molecular distillation at temperatures 205...210 °C. Along with the high yields of MAG (40...50%) industrial technologies are notable for hard conditions of glycerolysis and molecular distillation thus causing the intensification of thermal oxidation and thermal polymerization processes in the emulsifiers [8]. New technologies of production of emulsifiers also have the similar drawbacks as they assume the technological processes to be carried out at temperatures not below 120 °C [9-10]. For example, Pakamas Chetpattananondh and co-authors describe the process of obtaining MAG from the palm stearin. The optimum conditions for the glycerolysis of palm stearin and crude glycerol derived from biodiesel process were found to be as follows: a reaction temperature of 200 °C with a molar ratio of crude glycerol to palm stearin of 2,5:1, and a reaction time of $20 \cdot 60^2$ s [11].

The enzymatic synthesis technologies which are being actively developed nowadays have such a distinctive feature as a duration of the process (2 to $8 \cdot 60^2$ seconds) [12]. Researchers Yong-Ching Yang, Shaik Ramjan Vali, Yi-Hsu Ju carried out a synthesis of high-purity (> 99%) monostearin using a two-step process. The first step involved lipase-assisted enzymatic esterification of fatty acid with glycerol catalyzed by immobilized lipase *Candida antarctica* (Novozym 435) in acetone. The second step involved the removal of fatty acids by a mild alkali treatment, and it produced MAG with purity greater than 99 wt% and an overall yield of 66,8% [12].

The domestic market of food emulsifiers is mainly represented with additives E471 and their derivatives (E472a-g) of foreign production for using primarily in confectionery and perfume industry [13]. Usually emulsifiers E471 don't contain polyunsaturated fatty acids as they are produced in industry by means of glycerolysis of palm oil with formation of MAG of saturated fatty acids [11].

Thus development of the technology of producing domestic food emulsifiers from the natural raw materials under the mild conditions was an important task. In the previous works authors based the technology for obtaining food emulsifiers with mono-, diacylglycerines of fatty acids under mild conditions (at 35...40 °C). New food emulsifiers of acylglycerine origin for meat products including the frozen ones were obtained as an oil phase with MAG, DAG by means of transesterification of the refined sunflower oil in the hexane-isopropanol system [14].

Foreign scientists [15, 16] studied the problem of quality and falsifications of vegetable oils. They accumulated a broad experience of using IR spectroscopy in such kind of studies. Thus, according to S.F. Hamed and Mousa A. Allam, Fourier transform infrared (FTIR) spectroscopic technique could be applied well in the determination of the antioxidant activity of synthetic or natural antioxidants in sunflower oil [15].

In the work [16] Ersilia Alexa and co-authors intended to identify the adulteration of some olive, peanut, corn germ and pumpkin oils with sunflower oil using FTIR spectroscopy. Their experimental results showed the presence of subtle spectral differences in the spectra of various types of vegetable oils. This enabled to identify the addition of foreign oil in an oil sample using calibration curves established for certain characteristic frequencies in known mixed oils.

Therefore qualitative and quantitative studies of the composition of food emulsifiers for the purpose of determination of the content of surface active components - mono- and diacylglycerines of fatty acids and proof of the conservation of essential bioactive components and deceleration of thermal-oxidative processes in these emulsifiers gain actuality.

Materials and Methods

Materials. For the quantitative determination of MAG, DAG and plotting the calibration graph the model compositions of emulsifiers with the total mass fraction of MAG, DAG of 10, 20, 30, 40% were prepared by mechanical mixing of the refined sunflower oil (Ukraine) and the emulsifier E471 (Malaysia) with a known composition (content of mono- and diacylglycerines - 95,5±2,5% and 3,5±0,1% respectively).

The current studies deal with emulsifiers of acylglycerine origin (EAGO) obtained with using the laboratory equipment under the mild conditions according to the authors' developed technology of transesterification of the refined sunflower oil in a binary system of organic solvents as follows (Fig. 1).

Prepared 1.5...1.6% solution of potassium hydroxide in isopropanol, based on the mass ratio of refined sunflower oil:hexane:isopropanol - 1:2,5:2,5, was introduced into the miscella with a mass fraction of 28...30% (refined sunflower oil in hexane) and transesterification was performed under the constant stirring within (10...12)·60 seconds at temperature 35...40 °C. In order to complete transesterification water was introduced into the binary system in amount 16...18% from the system mass while stirring. The diphase system was kept at 23...25 °C until complete separation of the water-isopropanol layer with soaps, partly MAG, DAG *etc.* from the hexane layer containing TAG, DAG, MAG. Evaporation of hexane from miscella was performed in the rotary evaporator ИР-1М2 within (5...10)·60 seconds at 40 °C under the pressure of 335 mbar. Emulsifiers of acylglycerine origin were obtained as an oil phase (with MAG, DAG) of a light yellow color (this is typical for glycerines of unsaturated fatty acids) with a neutral taste, without smell.

In the current paper using the term transesterification is based on the fact that the formation of mono-, diacylglycerines of fatty acids occurs precisely at the stage of alcoholysis (a kind of transesterification reaction).

Physical and chemical indexes of EAGO obtained under the rational technological conditions in comparison with E471 are shown in Table 1.

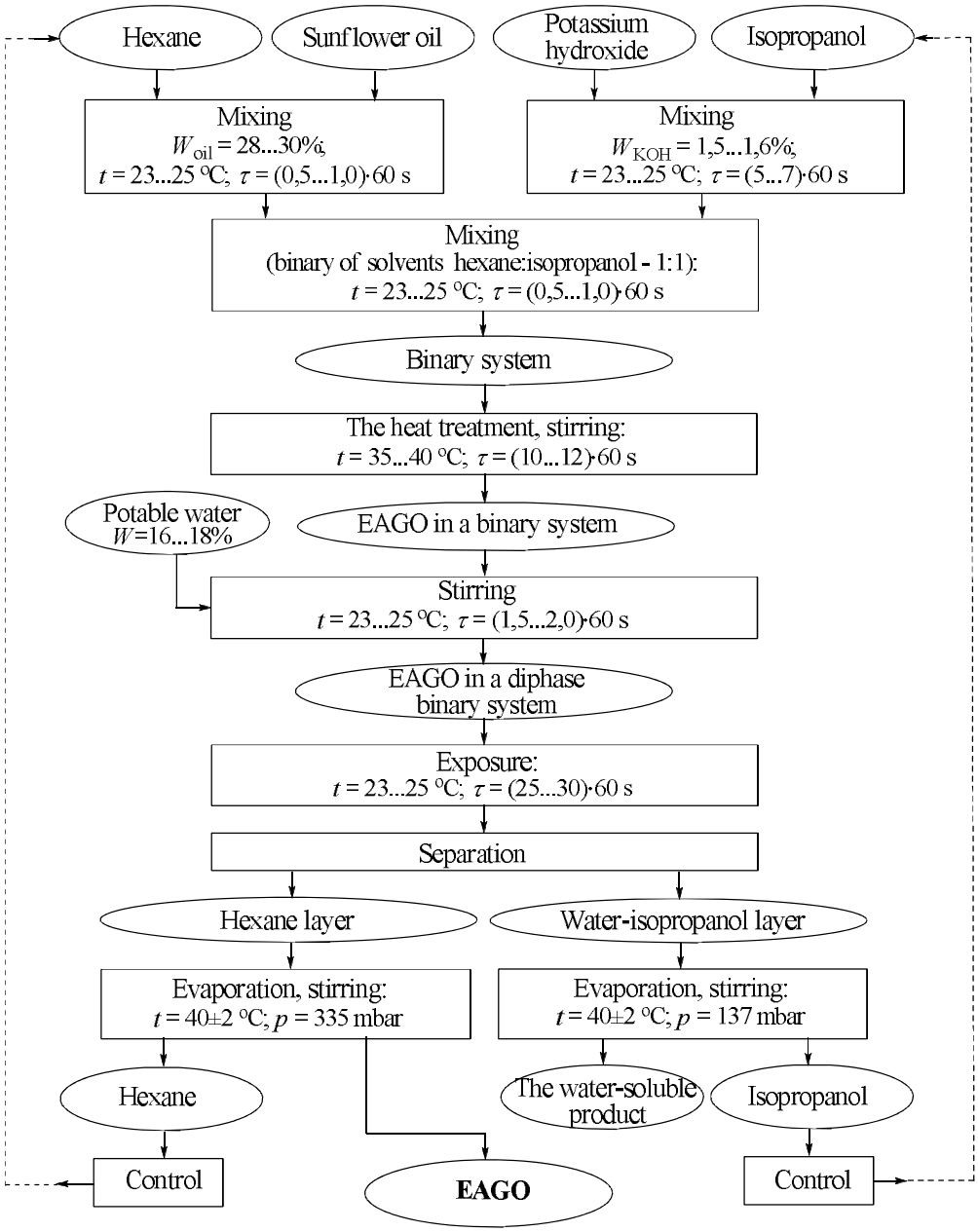

Fig. 1 Technological scheme of obtaining emulsifiers of acylglycerine origin

Table 1

Physical and chemical indexes of emulsifiers of acylglycerine series (*n*=3, P≥95)

Name of index	EAGO	E 471
Acid value, mg KOH	0,20±0,01	1,80±0,02
Saponification value, mg KOH	163,0±0,5	162,0±0,5
Iodine value, g I_2/100 g	121,0±0,2	3,0±0,1
Peroxide value, mmol0,5O/kg	3,34±0,01	3,67±0,01
HLB	6,1±0,1	3,8±0,1
Refractive index at 20 °C	1,474±0,001	1,454±0,001

For determination of MAG, DAG the samples of emulsifiers of acylglycerine origin synthesized by the method described above at different ratios of volume fractions of hexane and isopropanol in a binary solvent were also used. The temperature of transesterification was in the range 35...40 °C, the temperature of extraction - 23…25 єC. The duration of transesterification was (10...12)·60 s. The other technological parameters varied during the experiment (Table 2).

Table 2

The accepted ratios of the components in the transesterification reaction of the refined sunflower oil

N standard	Ratio		Mass fraction, %		
	volume fraction, hexane: isopropanol	mass, sunflower oil:hexane: isopropanol	potassium hydroxide in isopropanol	sunflower oil in hexane	potable water
1	0,6:0,4	1,0:2,5:2,5	1,6	28,6	16,2
2	0,7:0,3	1,2:3,0:1,8	2,7	28,6	7,5
3	0,7:0,3	0,7:3,3:2,0	2,7	16,7	18,0
4	0,5:0,5	1,5:2,2:2,2	2,7	40,0	13,0
5	0,4:0,6	1,2:1,8:3,0	1,6	40,0	17,3

Procedure of the studies. Firstly a study of the structure of the new emulsifiers synthesized was made by means of infrared (IR) spectroscopy. For quantitative analysis and plotting the calibration curve the model compositions of emulsifiers were made. These compositions were obtained by mechanical mixing refined sunflower oil and emulsifier E471 in such a proportion that the total mass fraction of MAG, DAG in them was 10, 20, 30, 40%. Then on the basis of calculated spectral characteristics and the calibration graph the mass fractions of MAG, DAG in the samples of emulsifiers of acylglycerine origin synthesized in the binary system of solvents with different ratios of hexane:isopropanol were determined. The content of MAG, DAG in the emulsifiers of acylglycerine origin synthesized under the rational technological parameters was also determined.

Methods and equipment. A qualitative and quantitative study of emulsifiers of acylglycerine origin and model compositions was performed by using infrared spectroscopy on Perkin-Elmer Spectrum One FTIR Spectrometer by the method of a crushed drop. The

drops of samples were placed in a thin layer between the plates from Zinc Selenide while recording IR spectra.

Treatment the results of the studies. For an objective judgment about the degree of probability of the data obtained the mathematical treatment of the obtained results was made. The reliability of the results obtained was determined with the help of Student's coefficients for the taken statistical significance level of P = 0.05 and corresponding (n-1) degrees of freedom.

Results and discussion

Study of the structure of the new food emulsifiers. After carrying out the synthesis according to the technological scheme (Fig. 1) the samples of emulsifiers of acylglycerine origin were obtained and their infrared spectra were studied.

IR spectra of the new emulsifiers of acylglycerine origin (Fig. 2) are represented with characteristic absorption bands assigned to the respective types of valence ν and deformation δ vibrations of triacylglycerines: a triad of bands 1110 cm^{-1}, 1173 cm^{-1}, 1244 cm^{-1} ν(C=O) of esters; 1377 cm^{-1} and 1416 cm^{-1} - δ_s(C–H) in groups –CH_3 and –CH_2– ; 1736 cm^{-1} - ν(C=O) of esters; 2855 cm^{-1} and 2927 cm^{-1} - ν(C–H) in groups –CH_2–; 3009 cm^{-1} - ν_{as}(C–H) in groups –CH=CH– in *cis*-form.

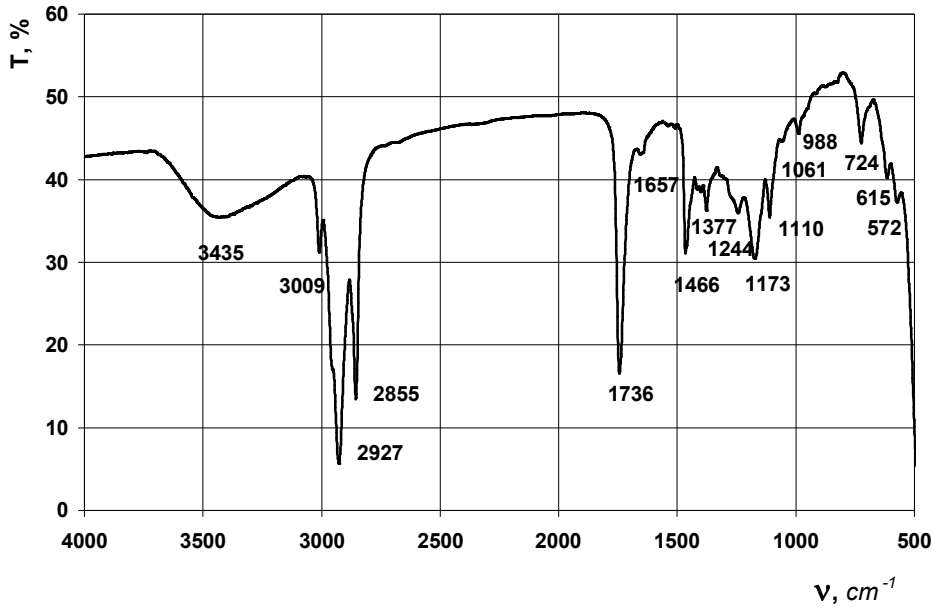

Fig. 2. IR absorption spectrum of the sample of emulsifier of acylglycerine origin

The absence of absorption bands at 970 cm^{-1}, 1675…1665 cm^{-1} indicates that obtained under mild conditions emulsifiers don't contain *trans*-isomers. The presence of absorption bands at 1657 cm^{-1} and 3009 cm^{-1} proves the conservation of unsaturated acids in the native state on the level of their content in the sunflower oil [17].

The presence of mono- and diacylglycerines of fatty acids in the emulsifiers is confirmed by the broad band registered at 3435 cm^{-1} (Fig. 1) that is characteristic for the valence vibrations of hydroxyl groups associated by hydrogen bonds (3350±100 cm^{-1}), by band at 1061 cm^{-1} that is characteristic for the valence vibrations of hydroxyl groups of the primary alcohols.

Application of IR spectroscopy in a quantitative analysis of emulsifiers of E471 series. IR spectroscopy allows solving problems of quantitative analysis. Therefore it was applied for determining the mass fraction of MAG and DAG in the test emulsifiers of E471 series in the spectral area that was characteristic for the valence vibrations of associated hydroxyl groups - 3350±100 cm^{-1}. IR spectra of the samples of model compositions of emulsifiers on the basis of the refined sunflower oil and E471 with the total mass fraction of MAG, DAG - 10, 20, 30, 40% were obtained (Fig. 3).

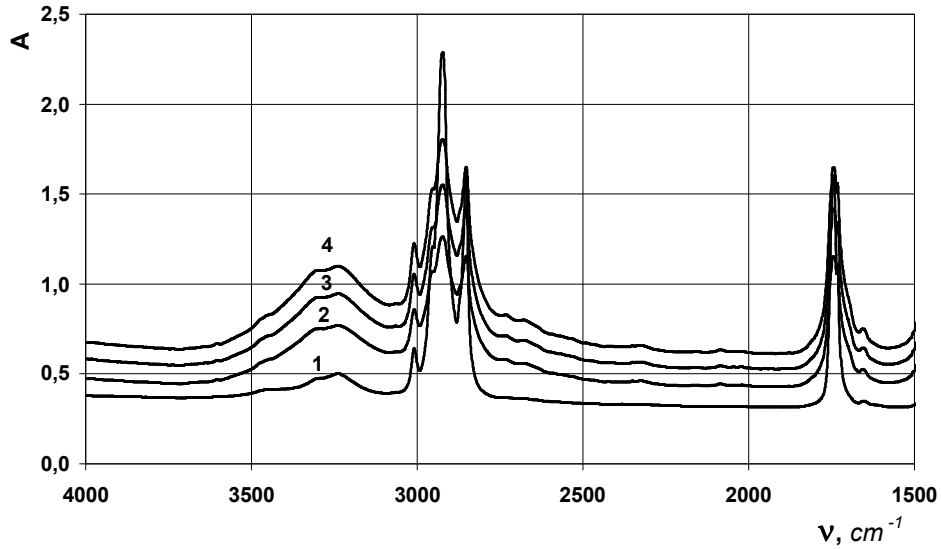

Fig. 3. IR spectra of the samples of model compositions of emulsifiers with different mass fractions of MAG, DAG, %:
1 – 10; 2 – 20; 3 – 30; 4 – 40

It is known [18] that IR spectroscopy uses integral intensity (absorption coefficient) that is considered as the sum of all the values of the extinction coefficient ε within the whole absorption band regarded, *i.e.* the area bounded by the curve and the x axis. The integral intensity is equal to the area of the band and, in case if the absorption coefficient and wave number ν (cm^{-1}) are chosen as coordinates; it is expressed [18] by the integral:

$$A_\nu = 2{,}304 \int_{\nu_1}^{\nu_2} \varepsilon \mathrm{d}\nu \quad (1)$$

The integral intensity is less dependent on the apparatus resolution than the intensity at the maximum and is better reproduced. The dependence of the optical density on the wave number ν by the outline of the band assuming the band is symmetrical with respect to the

maximum and does not overlap with the other bands is described by Lorentzian function [18]:

$$A_\nu = a/[(\nu - \nu_{max})^2 + b^2], \quad (2)$$

where a, b - are constants.

The function 2 describes the band better the broader is the band. Since this approximation is satisfactory for the broad band of associated hydroxyl groups at 3350±100 cm^{-1}, the area S bounded by the curve and the horizontal zero line ($A = 0$) can be described by the equation [18]:

$$S = (\pi/2) \cdot \Delta\nu_{1/2} \cdot A_{max}, \quad (3)$$

where $\Delta\nu_{1/2}$ - the width of the absorption band between the points of the curve where the optical density is equal to the half of the maximum one;

A_{max} - peak intensity.

Based on the calculated spectral characteristics (peak intensity, the width of the absorption band, the area S bounded by the curve and the horizontal zero line) the calibration curve representing the dependence of S value on the mass fraction of MAG-DAG ($w_{MAG\text{-}DAG}$) in the model compositions of emulsifiers E471 with the refined sunflower oil was plotted (Fig. 4).

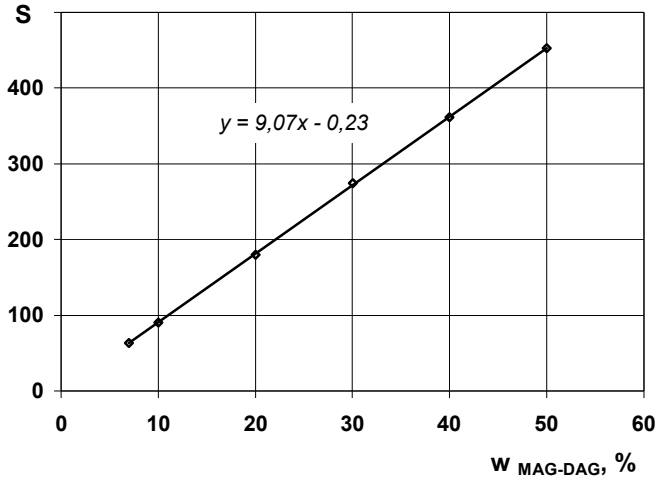

Fig. 4. Calibration curve of the dependence of MAG, DAG content in the model compositions of emulsifiers E471

The obtained dependence is well described by a linear function:

$$S = 9{,}07 \cdot w_{MAG,\,DAG} - 0{,}23, \quad (4)$$

that allows using it as a calibration curve for determining the mass fraction of MAG and DAG contained in the emulsifiers of E471 series which the emulsifiers of acylglycerine origin obtained under mild conditions also belong to [19].

Determination of the content of MAG, DAG in the synthesized emulsifiers of acylglycerine origin. The results of the studies were used for solving several problems of quantitative determination of MAG, DAG in EAGO.

The content of MAG, DAG (Table 3) was determined in the samples of emulsifiers of acylglycerine origin synthesized at temperatures 35 ... 40 °C in the binary system of solvents with different ratios of hexane:isopropanol (volume fraction φ was 0,6:0,4; 0,7:0,3; 0,5:0,5; 0,4:0,6). For this purpose on the basis of obtained IR spectra of the samples of EAGO being studied the spectral characteristics were determined and the area S was calculated according to the formula 3 (Table 3). The value $w_{MAG\text{-}DAG}$ was calculated according to the equation 4. The relative deviation δ of the results of determining the content of MAG, DAG by the methods of IR spectroscopy and thin-layer chromatography didn't exceed 2,7 %.

Table 3

Comparison of the spectral characteristics of the samples and the content of MAG-DAG in them depending on the technological parameters of obtaining EAGO (n=3, P≥95)

Sample	$\varphi(C_6H_{14}):\varphi(C_3H_8)$	ν, cm^{-1}	A_{max}	$\Delta\nu_{1/2}$, cm^{-1}	S	$w_{MAG\text{-}DAG}$*, %	δ, %
1	0,6:0,4	3457	0,94	321,1	476,9	52,6±0,2	1,3
2	0,7:0,3	3453	0,75	367,2	432,4	47,7±0,4	2,7
3	0,7:0,3	3450	0,73	370,2	424,3	46,8±0,3	2,5
4	0,5:0,5	3454	0,63	400,5	396,1	43,7±0,4	2,7
5	0,4:0,6	3448	0,55	390,1	336,9	37,1±0,3	2,4

Note. * - calculated on the basis of IR spectroscopy data

The results of the studies indicate that with an increase of the nonpolar agent hexane in the binary solvent the tendency of increasing the content of MAG-DAG in EAGO is observed. The obtained regularity is explained by an increase in thickness of the layers of the nonpolar solvent in a polar one to the sizes comparable to those ones of the fatty acids radicals. This fact prevents the shielding and facilitates the accessibility of ester-groups for attack by nucleophilic agent (isopropoxy-anion) during the reaction of MAG, DAG formation. The obtained results showed that the maximum quantity of MAG, DAG 52,6 ± 0,2% (sample 1) was formed in a binary system of solvents with the ratio of hexane: izopropanol - 0.6: 0.4. This ratio was chosen for determination of the rational technological parameters for obtaining EAGO [14].

The problem of quantitative determination of MAG, DAG was also solved for EAGO synthesized according to the rational technological parameters (Fig. 1, 2).

The content of MAG, DAG in the new emulsifiers obtained at temperature 35...40 °C in the system hexane-isopropanol from the refined sunflower oil was 54,2±1,2%. The data obtained correlates with the results of determination by thin-layer chromatography with a relative deviation of the mass fraction of MAG and DAG within 1,1...2,4%. The results of the

studies confirm the possibility of using IR spectroscopy for solving the problems of quantitative determination of mono-, diacylglycerines of fatty acids in the emulsifiers of acylglycerine E471 series.

Conclusions

With using infrared spectra the presence of the characteristic absorption bands assigned to the respective types of valence and deformation vibrations of triacylglycerines in the new emulsifiers of acylglycerine origin was proved: ν(C=O) - 1110 cm^{-1}, 1173 cm^{-1}, 1244 cm^{-1}; δ_s(C–H) - 1377 cm^{-1} и 1416 cm^{-1}; ν(C=O) - 1736 cm^{-1}; ν(C–H): 2855 cm^{-1} и 2927 cm^{-1}; ν_{as}(C–H) in groups –CH=CH– in the *cis*-form - 3009 $см^{-1}$), hydroxyl groups of mono-, diacylglycerines of fatty acids associated by hydrogen bonds - 3435 cm^{-1}, primary alcohols - 1061 cm^{-1}.

The fact of the absence of absorption bands at 970 cm^{-1}, 1675…1665 cm^{-1} proves that obtained under mild conditions emulsifiers don't contain *trans*-isomers. The presence of absorption bands at 1657 cm^{-1} and 3009 cm^{-1} indicates on the conservation of unsaturated acids in the native state on the level of their content in the sunflower oil.

On the basis of calculated spectral characteristics (peak intensity, width of the absorption band, area S bounded by the curve and the horizontal zero line) the calibration graph of S on the mass concentration of mono-, diacylglycerines in the model compositions was plotted and the equation of the line $S = 9{,}07 \cdot w_{\text{MAG-DAG}} - 0{,}23$ was determined.

By means of IR spectroscopy the total content of mono-, diacylglycerines of fatty acids in the food emulsifiers obtained under mild conditions (35...40 °C) from the refined sunflower oil was determined. This data correlated with the results obtained by means of thin-layer chromatography. The relative deviation of the mass fraction of MAG and DAG between two methods was not more than 2,7%.

Using the method of infrared spectroscopy for solving the problems of quantitative determination of mono-, diacylglycerines of fatty acids in the emulsifiers of series E471 was suggested.

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Biologically activated wheat grain as a functional component of glazed bars

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Abstract

Introduction. The biologically activated wheat grain contains a significant amount of B vitamins, vitamin E, minerals, dietary fiber and a promising material for creating health food.

Materials and methods. Wheat varieties of Poliska, Myronivska 137, Bezosta and Bars samples that are based on biologically activated what are studied. Vitamin C is determined by titration, the content of polyphenols is determined by spectrophotometric analysis.

Results and discussion. The most promising varieties of wheat on the physical properties is Poliska. A crop of this variety are aligned in size, its volume weight is 788 g/l; energy and germination capacity of grain, respectively, are 97.2% and 98.8%; the viability of the embryo is 100%.

In the long process of intensive humidification and subsequent germination of wheat at the temperature of 16˚S the content of water-soluble vitamins increases from 8 to 66%. The amount of vitamin C increased more than twice. The content of tocopherols increases tenfold.

With regard to the principles of health food are developed recipes and calculated rates of consumption of raw materials for 1 ton production of glazed bars which are base on biologically activated wheat. Bars recipe does not contain sugar, so this product may be included in the diet of people suffering from metabolic disorders. The proposed regime of thermal treatment of the main raw material provides microbiological stability of the product. Bars Energy value is 190.3 kcal; the ratio of basic substances enerhohennyh is 11 ... 13% (fibers): 21 ... 23% (fat): 66% (carbohydrates). The degree to ensure the daily requirement in certain minerals through consumption of 100g bars is from 13.1 to 53.6%.

Number of microbial samples were stored in sealed conditions for 10 days without exceeding the standard norms.

Conclusions. We recommend to use the biologically activated wheat grain in technology of health food products, particularly glazed bars.

Introduction

The development of functional purpose production is a key issue. Receiving such an important product is the maximum preservation of natural compositions of biologically active substances foodstuffs.

Grain raw materials is one of the main bases for food production in our country. Chemicals that make up the grain, determine its nutritional and biological value. Wheat, compared with other crops, has the widest range of use.

Given the high nutritional value of raw grain it is developed very intensively new advanced technologies of grain products. Expanding production of functional cereal products in the form of semi-finished products, breakfast cereals, structured products and other fast food.

Multiple use of grain-based increases in order to reduce the energy value and the cost of food while preserving natural bioactive components.

One of the promising directions of grain raw material is freeze dried food establishment powder compositions with a high content of cellulose and natural biologically active compounds [1].

Sprouting grains as a method of biological activation is used to improve the nutritional value of grain and other raw materials.

The process of germination of seeds is influenced on several factors: temperature, humidity, light, availability of substrate, maturity and physiological grain age. Important role in the preparation of raw grain quality plays a genetic samples varietal characteristics [2, 3, 4]. During the germination of seeds produced a significant amount of class peptidases enzymes that catalyze the splitting of starch, proteins, lipids [5].

Germination of wheat is rather complicated process. Established that Australian wheat varieties with greater speed germination compared to European and North American black fertile land varieties. This is due to the presence of membranes black fertile land grain wheat anthocyanins that affect the level of calm grain. The optimum temperature for germination of seeds is 12-25° C [6].

The influence of temperature regimes on seeds germination of different varieties of wheat is proved that this process is most effective at 15-22° C is researched. Significant influence is the genetic potential of grain [7, 8]. Low temperature of 5° C as too high - 45° C inhibits peroxidase activity. Effects of high temperature is reasonable for the first two hours of grain germination for stimulating the rate of swelling [9].

Based on the investigations of amaranth seeds germination it set its increase of nutritional content of vitamins, including riboflavin and ascorbic acid. The starch degradation, changes in the quantitative content of sugars are followed [10].

The possibility of improving the nutritional value of sweet lupine by Australian germination is analysed. The process of seed germination in 9 days, an increase in the number of crude fiber, increasing the total content of proteins, lower fat context is described in the article. Recommended the application of germination to improve food raw profile [11]. It is noted that the thermal treatment of germinated soybeans and lupine seeds increases digestibility of protein and promotes the breakdown of phytic acid [12].

It is proved that peanuts germination increases the bioactive compounds. Peanut sprouts propose to use as a functional ingredient to enrich foods [13].

Polish scientists investigated the effect of iron sulfate solution on the degradation degree of starch and sugar content sugar during soybeans germination, alfalfa seeds and wheat. Decreasing the quantitative content of starch and sugar beans germinated soybeans, alfalfa seed and wheat grain as a result of abiotic stress caused by ferrous iron ions. Add

flour of this grain to the bulk material will provide a meal with desired technological properties [14].

The effect of aqueous extract of Apera spica-venti energy and ability sprouting grain triticale is determined. It was established that these extracts inhibit the germination of seeds physiological parameters [15].

The study of pulse magnetic field influence on hulless oat seedlings shown that treatment significantly reduces the total number of microorganisms increases the content of polyphenolic compounds and antioxidant activity of the samples [16].

The content of phenolic compounds, including rutin, quercetin, chlorogenic acids in native buckwheat and germinated for 6 - 10 days is studied. Established that during germination the phenolic compounds content in grains significantly increased. It is proved that buckwheat sprouts have a high antioxidant activity and a valuable source of phenolic compounds [17].

The scientists are conducted the researches on the impact of the germination duration on the nutritional value of grain. Thus, the analysis of the chemical composition of wheat, sprouted within seven days. Investigated that the content of crude protein, lipid and mineral substances, respectively, are 20.8; 1.6; 1.3%. Seedlings content of polyunsaturated fatty acids linoleic and oleic, respectively, are 45.9 and 18.4% of the total fat context is researched. During wheat germination the change in the proportion of amino acids increased content of vitamins A, C, E, routine is marked [18].

Biologically active wheat is a promising raw material for making health food. During grain germination the chemical composition is changing, resulting in the supply of nutrients partly converted into a ready to use form, peptides and proteins to amino acids, starch is in sugar, fat is a fatty acid also produced significant amounts of vitamin E, B vitamins, inositol [19].

Given the high nutritional value, sprouted grain cereals used for malting, enrichment of products not subject to long-term storage; in baking, pasta and food concentrates production; in the manufacture of mixtures for baby food. Biologically activated grain as valuable food raw materials is used abroad for the production of health orientation [20].

The quality of food is determined by organoleptic, physical, chemical and microbiological parameters. Significant impact on customer value products has technological parameters of processing raw materials and original quality. Studying the impact of Phytoextracts on the microorganisms' growth that develops during the grain germination, and to replace the content of biologically active substances is an urgent problem for determining the mode of heat treatment product and to establish the product storage.

The purpose of the research is to study the functional properties of biologically activated wheat and indicators as new chopped recreational purposes - Bars glazed, the main component of which is biologically activated grain.

Objectives of research:

- Examine indicators of physiological values of wheat;
- Examine the biological value of sprouted wheat;
- Investigate the effect of Phytoextracts to change the biologically active substances content in the sprouting grain;
- Develop of Grain Bars recipes;
- To determine the nutritional value of corn snacks;
- Determine the organoleptic properties of the product;
- Identify indicators of microbiological stability bars.

Materials and methods

During experimental studies we researched wheat varieties of Poliska, Myronivska 137, Bezosta; Bars samples are based on biologically activated wheat. The selection of promising varieties of wheat for researching is the process of grain germination and later use it as a main component of Bars glazed carried out with the advice of Ukrainian central laboratory of qualitative evaluation studied agricultural crop varieties.

Moisture content of the samples was determined by drying to constant weight at temperature of 105° C.

Indicators of physical properties of grains were determined by conventional methods. The volumetric weight of grain was determined using metric purky. Energy and grain germination capacity are determined by the number of sprouted grains for three and five days.

Determination of vitamin C is performed by titration method. The method is based on extraction of vitamin C with sample solution acid (hydrochloric, metafosfornoyi or a mixture of acetic and metaphosphoric) followed visually or potentiometrically titrating solution 2,6 - dyhlorfenolindyfenolyat sodium.

Determination of polyphenols was performed by using spectrophotometric analysis by Folin-Denis' method. This method provides for up to 1 cm^3 0.3 cm^3 test Folin – Denis's solution reagent (is prepared by mixing 100 g of sodium tungstate $Na_2Wo_4 \cdot 2H_2O$ 20 g of fosfornomolibdenova acid 50 cm^3 share 85% of H_3PO_4 and 750 cm^3 water, mixture is boiled with reflux for 2 hours, filter and dilute with water to 1 dm^3), thoroughly shaken and exactly 20 seconds add 5 cm^3 of 20 % solution of Na_2CO_3 (crystalline); in 30 seconds optical density measured at a wavelength of 725 - 730 nm on the photocolorimeter in a ditch with a working length of 5 mm; control of this is water while serving with all these reagents adding.

Number of phenolic compounds are on the calibration curve, built by hlorohenniy acid (the solution contains 0.025; 0.075; 0.10; 0.185 mg / cm^3). According to the presence of polyphenolic compounds present alkaline reagent changes its color. For optical density of measuring value and the previously constructed calibration graph to find Galloway acid concentration of phenolic compounds.

Energy bars value determined by the content of protein, fat, carbohydrates, taking into account the relevant factors and caloric expressed in kcal per 100 g.

Microbiological bars from sprouted wheat was determined immediately after preparation and during 10 days storage.

With this aim the studied samples were plated on agar surface of nourishing source: meatpepton agar (detection of mesophilic aerobic and facultative anaerobic microorganisms - MAFAnM) wort-agar (yeast and fungi).

Cups of crops were incubated for 2 - 3 days at 37° C for determining the total number of microorganisms (MAFAnM). Crops in the cup of the wort-agar medium for detection of fungi and yeast were incubated at a temperature of 28° C for 5 - 7 days.

We determined the change of microbiological grain bars at different storage conditions (sealed and unsealed) at 5° C.

Organoleptic cereal bars were determined by specialized sensory analysis.

Results and discussion

Based on the study of different varieties of wheat, the physical properties that are important in the processing of raw materials for health products, is selected the most promising class it's Poliska. Grains of this sort are aligned in side: they have large fractions content, medium and small, respectively, are 90, 8.3, 0.7%; have high values of bulk density, index which adequately reflects the quality of grain and its quality factor - 788 g / l.

The indicators of physiological values of wheat, which determine its suitability for the production of glazed bars from sprouted grains and allow predicting the length of the main raw material preparation, are established in the article. Value vigor and germination capacity for wheat varieties Poliska, respectively, are 97.2 and 98.8%. The viability of the embryo, the potential ability to grain germination is 100%. This is a great quality grain for use in food products for health improvement.

Water sensitivity of wheat germination time is 24, 48 and 72 h, respectively, are 73, 91 or 98 pieces. The results indicate that the wheat variety is not water sensitivity because grain germination should not be held by the regime of low moisture.

We asked to prepare wheat, which includes intensive humidifying for 24 hours at temperature of 14 - 16° C and germination for 24 h at the same temperature.

Experimental studies have established the intensification of the synthesis of vitamins and vitamin-like substance in the wheat germination. Determined that the long process of intensive humidification and subsequent wheat germination of Poliska varieties in temperatures of 16˚C of water-soluble vitamin content increases by 8 - 66%. The amount of vitamin C increases more than twice. The content of tocopherols increases in ten times.

To improve the biological value of raw materials in the preparation of the Phytoextracts solutions influence to change the content of biologically active substances in the sprouting grain. As a result, analytical studies of Phytoextracts selected plant material: are horseradish root and fennel seed. These raw materials contain minor bioactive substances, such as essential oils, phenolic compounds, glycosides, saponins, volatile, which determine its pharmacological properties as antiseptic, antibacterial, anti-inflammatory.

The effect of plant material extracts, including the horseradish root and fennel seeds to replace the contents of vitamin C and phenolic compounds wheat in the germination process. To prepare the aqueous extract of horseradish root and fennel seed hydrological was, respectively,1: 100 and 1:20.

The increasing content of polyphenolic compounds in wheat grown in using Phytoextracts on 2 - 4% compared with grain germinated in water.

Investigated that during wheat germination aqueous extracts of horseradish root and fennel seeds using is intensification of the synthesis of vitamin C, the content increases by 15 - 20% compared with the content in the grain germinated in water. This is due to activation of the enzyme complex grain under the influence of biologically active Phytoextracts substances. The results make it possible to predict the intensification of the synthesis of other biologically active substances in the sprouting grain using Phytoextracts.

Thermal processing sprouted grain mode pasteurization ensures inactivation of enzymes and enzymatic processes cease and prevents the development of microorganisms when stored outside sprouted grain for several days. The thermal treatment of sprouted wheat and products based on it at 80 - 100 degrees respectively for 30 minutes allows inactivate existing flora and ensures proper storage of these samples at 10 degrees C in sealed conditions within two weeks is envestigated. In preparing sprouted grains we used mode specified thermal processing.

Agar is almost insoluble in cold water, but swells well, connecting plenty of water (one part of dry agar and 4-10 parts of water). In hot water when boiling agar dissolves almost completely. When cooled agar solution, contains more than 0.2% the jelly is formed. A strong jelly with cpecific vitreous fracture is obtained by the content of 0,3-1,0 % agar in solution.

In preparing the agar solution we take into account good practice and organoleptic properties of the product. Agar solution heated to the temperature not exceeding of 50° C, because when heated agar solution contains acid to 60-70° C and above, hydrolysis of agar loses jelly creating power.

Preparation of dried fruits included inspection, washing, scalding and crushing of required size. Flax seeds are sieved; visually inspect the content for impurities.

On the basis of biological value ingredients and taking into account the principles of health food recipes of glazed bars samples from sprouted wheat are developed and investigated in the laboratory. The recipe of glazed bars is shown in Table 1.

Table 1

The recipe and norms of raw material expenditure for making the glazed bar

N	The name of raw material	Content of dry substances,%	Expence of raw material on 1t of the prepared products, kg	
			In nature	In dry substances
1	Sprouted grain of wheat	75	550,0	412,5
2	Dried fruit	80	120,0	96,0
3	Honey	78	55,0	42,9
4	Agar	85	12,0	10,2
5	Seed of flax	90	9,0	8,1
6	glaze	98	100,0	98
7	Water	-	200,0	-
8	All	-	1046	667,7
9	Exit		1000	638,3

The basic constituents value of coated bars is 11 ... 13% (fibers): 21 ... 23% (fat): 66% (carbohydrates), corresponding to the WHO recommendations regarding content energetic substances in the diet for health food.

Caloric bars from sprouted wheat are 190.3 kcal.

Formula of integral swift is calculated degree of providing daily needs of individual minerals by consumption 100 g of grain bars (tab. 2).

The given data show that the introduction of diet bars, when main ingredient is wheat sprouted grain, will replenish the body potassium, phosphorus, magnesium, iron, zinc, magnesium. The daily requirement for these minerals, except Ca is provided from 13.1 to 53.6%. The developed grain bar can be classified as functional foods for mineral composition.

The bars' recipe doesn't contain sugar that's why we recommend this product to a diet of people suffering from metabolic disorders.

Table 2

The integral fast and minerals bars, mg%

Indicator	Minerals, mg / 100g							
	Na	K	P	Ca	Mg	Fe	Zn	Mn
The daily requirement	300	400	1200	1100	350	15	17	7
Mineral content in Bars	39,33	529,05	522,97	55,26	182,6	5,48	9,13	2,42
Integral fast	13,1	53,6	42,5	5,02	52,2	36,5	53,6	34,6

For objectiv identifying changes in organoleptic characteristics of the finished product during the storage was applied the relevant sensory analysis method.

Sensory evaluation test and profile, characterized the expiry grain bars standard is developed. The analysis presented in the form of a profile diagram, which is used to visualize the organoleptic characteristics of bars (Fig. 1).

The intensity of the organoleptic characteristics assessed on a 5-point scale as follows: 0 points are no sign; 1 point is only felt; 2 points are weak intensity; 3 points - moderate intensity; 4 points are strong intensity; 5 points arevery strong intensity.

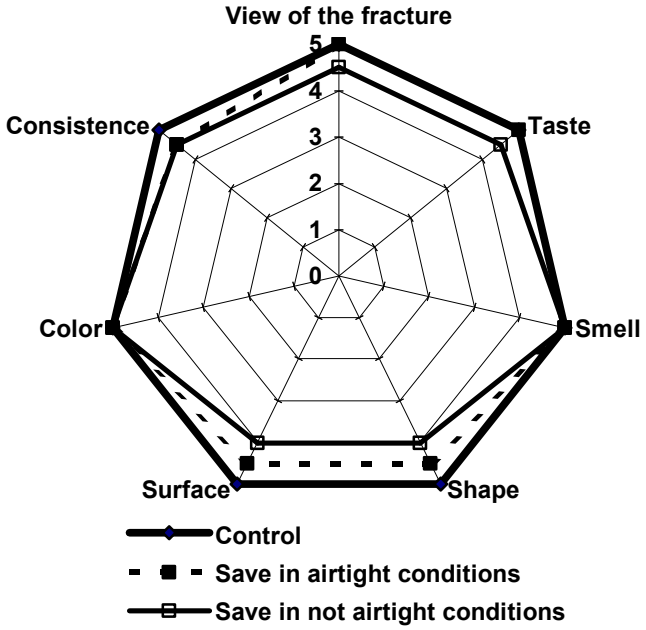

Fig. 1. Profile changes as bars storage

This profile shows that the bar, which stored for ten days in airtight conditions are not significantly different from control. There was a slight moisture influenced the glaze that was not dry and shiny. Gray hair samples did not happen. The overall positive impression of the appearance of the product is not spoiled.

Qualitative indicators of finished product was evaluated on the basis of microbiological analysis of samples. We studied samples bars prepared from sprouted wheat which is used in the preparation:

1) water;
2) fennel seed extract;
3) horseradish root extract;
4) solution of lactic acid.

The total number of colonies creation units of mesophilic aerobic and facultative anaerobic microorganisms (CFU MANFAnM) in all bars' samples was determined for fresh samples and within 10 days store them in airtight and leaky conditions at temperature of 5° C. Research results of microbiological samples bars shown in Table 3.

Table 3

Microbiological bars' change at different storage conditions

Duration storage	Sample	Unsealed conditions		Sealed conditions	
		Quantity MAFAnM, CFU / g	Yeast, fungi CFU / g	Quantity MAFAnM, CFU / g	Yeast, fungi CFU / g
1 day	1	$<10^2$	$3 \cdot 10$	$<10^2$	$<10^2$
	2	$<10^2$	$<10^2$	$<10^2$	$<10^2$
	3	$<10^2$	$1{,}3 \cdot 10$	$<10^2$	$<10^2$
	4	$<10^2$	$1{,}1 \cdot 10$	$<10^2$	$<10^2$
3 days	1	$2{,}1 \cdot 10^2$	$8 \cdot 10^3$	$1{,}1 \cdot 10$	$2 \cdot 10^2$
	2	$5 \cdot 10$	$<10^2$	$<10^2$	$1{,}2 \cdot 10$
	3	$1{,}3 \cdot 10$	$1{,}1 \cdot 10^2$	$<10^2$	$1{,}4 \cdot 10$
	4	$1 \cdot 10^2$	$2 \cdot 10^2$	$1{,}3 \cdot 10$	$3 \cdot 10$
10 days	1	$2{,}9 \cdot 10^2$	$5 \cdot 10^4$	$1 \cdot 10^2$	$2 \cdot 10^2$
	2	$7 \cdot 10^2$	$1{,}7 \cdot 10^2$	$8 \cdot 10$	$5 \cdot 10$
	3	$1{,}1 \cdot 10^2$	$1 \cdot 10^2$	$3 \cdot 10$	$1{,}1 \cdot 10$
	4	$1{,}7 \cdot 10^3$	$5{,}1 \cdot 10^4$	$1{,}2 \cdot 10^2$	$2{,}9 \cdot 10^2$

When storing the bars from sprouted wheat for leaky conditions for one day the growth of microorganisms is absent.

With further storage on the 3 day revealed that the samples bars, made from sprouted grains using plant extracts horseradish root and fennel seed microorganisms on two orders lower of magnitude compared with the sample control and bars made from grains germinated of using breast acid. On the 10th day of the studied bars samples, were made from sprouted grains using plant extracts, growth MAFAnM lower order of magnitude, and yeast and fungi of two orders of magnitude compared with the control.

When storing bars for tight conditions for one day and the growth of microorganisms is ansent in all samples. On the third day, compared with samples that were stored in leaky

conditions the growth of microorganisms in samples of bars wasn't revealed, made from sprouted grains using plant extracts, and an order of magnitude less than the microorganisms growth in control. As for further storage bars in tight conditions, compared with storage in leaky conditions on the 10^{th} days in all samples were reduced the total number of microorganisms in bars samples, made from sprouted grains using plant extracts, the growth of microorganisms in twice smaller than in control. The number of MAFAnM samples were stored in sealed conditions for the 10^{th} days within the set rules standards; it allows you to recommend this bar for safe consumption during 10 days of storage.

Antimicrobial effect of plant extracts that have been used, due to the presence in the horseradish roots volatile and enzyme lysozyme, which have antibacterial properties; fennel seeds contain phenolic compounds and their glycosides which exhibit antibacterial activity.

Thus, it is reasonable to use plant extracts horseradish root and fennel seed for the purpose of suppression of the growth of microorganisms during grain germination for its use as a food base.

Conclusions

Biological activation of wheat by continuous heavy humidification and subsequent germination within 24 - 28 hours at temperature 12 - 15° C promotes dramatic growth of water-soluble vitamins, vitamin E and vitamin compounds. Manufacture of grain by Phytoextracts horseradish root and fennel seeds intensifies the formation of biologically active substances, including vitamin C and polyphenolic compounds during germination of grain.

The proposed treatment of benign modes in the preparation of prescription components ensure the maximum preservation of biologically active substances of raw materials that have immunomodulating, and antioxidant effect of sorption.

Using extracts from horseradish root and fennel seed grain during the preparation of raw materials reduces the growth and development of microorganisms.

Bars storage based on biologically activated grain in airtight conditions at a temperature of 5° C extends its suitability for ten days.

Whole biologically activated wheat usage as a basis glazed bars, allows preserving the valuable substances weevil, enriching the product complex of B vitamins, vitamin E, vitamin and minerals, natural food sorbents; and enhances the range of functional cereal products.

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Iodine content determination in dried talli of laminaria by galvanostatic coulometry

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Abstract

Introduction. Dried seaweeds are well-known food source with rich iodine content that can be used for the prevention of iodine deficiency disorders (IDD) independently as well as functional ingredients in dietary foods. Considering the above, analysis of total iodine content in seaweeds is an important pursuit.

Materials and methods. The total content of iodine in samples of dried thalli laminaria, known as a commercial product Kombu, was determined by galvanostatic coulometry with potentiometric indication of the end point of the titration in aqueous solution obtained by mineralization samples.

Results and discussion. Contained in the samples iodinated compounds such as organic and inorganic nature, by a dry alkaline mineralization were transferred to the aqueous solution in the form of iodides. The procedure was carried out at the optimal temperature conditions within 420-480ºC which provides maximum yield.

Standard aqueous solutions of sodium iodide in the concentration range of 15-300 mg / 100 g of solution used for the analytical method validation of determining the concentration of iodide by galvanostatic coulometry with electrogenerated bromine. These key characteristics of validation procedure, such as the specificity, linearity, range of analytical procedure, accuracy and precision, led to the conclusion about the possibility of using galvanostatic coulometry for the determination of total iodide in the solutions. Was confirmed that the electrogenerated bromine reacts with iodide in the ratio 1:1.

The iodine content surveyed for four series of kombu was 394, 476, 587 and 743 mg/100 g dry algae, respectively.

Conclusions. Using the coulometric method for solving the problems of quantitative determination of iodine content in popular seaweed products as Kombu and others is suggested.

Introduction

Many different analytical techniques have been developed for iodine speciation in food, environmental and biological matrices but they are characterized as difficult procedures. It is associated with the complexity of the analysis: low levels of iodine in the study of multicomponent arrays, its volatility and polyvalent in redox reactions. Among these methods modern highly informative and sensitive methods are used. Interfacing various separation techniques, such as reversed-phase high-performance liquid chromatography, ion chromatography, size-exclusion chromatography and capillary electrophoresis with element selective ICP-MS (inductively coupled plasma- mass spectroscopy) has been employed in speciation studies of iodine to separate and characterize iodine species of different nature [6-10]. At the same time, we have not lost their relevance and affordable traditional titrimetric, spectrophotometric and electrochemical methods [11-16]. Among them, it should be isolated by coulometric titration as an absolute and rapid method, which gives a sufficiently high statistical certainty of outcome and sensitivity in the analysis of objects of vegetable origin [17].

One of the important sources of iodine in the human body is seafood, among which an important place belongs to the algae. Recent represented a large number of species, among which the most popular are the brown algae. The brown algae is the largest amount of iodine in the form of iodides and iodates, as well as the iodinated amino acids that can be regarded as an iodine-containing additive for the human diet [1-3]. On the recommendation of WHO, the recommended dietary allowance (RDA) of iodine is 150 μg/day for healthy humans [4]. This is an important issue for our country, which in terms of this indicator is epidemic [5].

Edible brown algae as a good dietary source of iodine have consumed in many countries. Furthermore, in Ukrainian Pharmacopoeia (Addition 4) dried thalli of laminaria are medicine. According to article "Laminaria thalli" of Pharmacopoeia, as the primary method for determining the iodine content using volumic titration. However, the visual indicator fixing the end-point of titration and the need for pre-standardization of the titrant, significantly increase the time of analysis, it should be known, it refers to the disadvantages of this method. Therefore, rapid procedure method of galvanostatic coulometry as an absolute method with low economic parameters of the tools design and the ability to automate of determining iodine process method gives clear advantages for the measurement.

Materials and methods

Materials. Objects of the present research was samples of seaweed as a food supplement – marine algae Kombu (thalli of Laminaria saccharina and Laminaria japonica). They were obtained from local drug stores. All seaweed samples were dried. In our work used samples from four parties with different series number on the package ("Lektravi" plant, Ukraine).

The above mentioned marine algae were analyzed for total iodine content after complete mineralization using by dry alkaline ashing technique to convert iodine into iodide [11,12,16,18]. Previously, the dried algae samples were ground in a household coffee grinder for 5 minutes. After weighing 1-2 g dry seaweed sample were putted into a porcelain crucible, 4 mL 0,5 N KOH solution was added with followed by soaking for 6-10 hours and drying at 105 ° C. The sample solution was heated on a hot plate into a slurry state. The sample slurry should be kept heated until it is completely dry. Then the crucible was placed into the ashing furnace to avoid loss of iodine. A complete and smooth

combustion is essential for a good recovery of iodine. In heating procedure the ashing temperature was 420–460 °C and lasted 7-8 hours. This values allowed to optimize the standard ashing technique. The maximum iodine contents is obtained in the temperature range 420-460 ° C, whereas, at 400 ° C there is no complete convert of organic compounds with too low a yield of 40% and at temperatures of 500 - 600 ° C ashing gives 50% final result .

After cooling down in a desiccator, 15 mL deionized water was added into the crucible. The sample crucible was placed on a hot plate to heat up and dissolve the ash. The ashing solution was then suction filtered. The ash was dissolved again in 15 mL hot water. Them the filtrated solutions were combined, and water was added volumetrically to 50 mL and that solution was weighted. The sample solution were analyzed for total iodine content.

Standard solutions of sodium iodide were prepared by dissolving precise portions in water with followed by masse diluted method.

In research was used dry reagent of chemically pure grade, bidistilatted water with pH=6,8 and electric conductance less 4 μSm/m.

Methods. The total iodide content in solutions was estimated by galvanostatic coulometry with electrogenerated bromine.

The electrogeneration of bromine as coulometric titrants–oxidants was performed using a T-201M1 titrator or PU-1 polarograf as potentiostat device in 0.2 M solutions of potassium bromide in a 0,1 M solution of sulfur acid (pH=1,1) with a platinum electrode (S = 200 mm2) at a constant current intensity of 2,0-5,0 mA. The cathode was a coiled platinum wire (l = 10 mm). A cathode chamber, wherein the auxiliary electrode was set, was separated from the anode chamber by a porous glass septum. A constant current intensity were carried by the combined V7-21s instrument with accuracy 0,2%.

Before each determination, platinum electrodes were stored in solution of potassium bromide and subjected to chemical cleaning (in nitrate acid 1:1) and electrochemical cleaning (in sulfur acid 0,2 M under 5 mA) [17].

A 80.0 mL portion of a supporting electrolyte was charged in a 100 mL electrochemical cell with the working, auxiliary, indicator and reference electrodes, and the generating circuits were switched on. The solution in the cell was stirred with a magnetic stirrer.

The aliquot portions (in g) were selected so that the titration time took no more than 300-400 seconds which provided express and the necessary accuracy of measurements.

The end-point of titration was established potentiometrically with indicator and reference electrodes: platinum redox electrode EPV-1 and Ag/AgCl system EVL-1M3.1 (Gomel ZIP, Belarus), respectively. The solution samples contains ions which are incompatible with the reference electrolyte, a double junction electrode were used.

Time that responsibility to the end-point of titration was controlled by two procedure: 1) the achievement of the initial value by the indicator redox potential ; 2) by an inflection in the titration curves with the regard for electrolysis time of a supporting electrolyte. Both procedures were yielded identical results. The theoretical quantity of substances released on the electrode (g) was established according to Faraday's law.

Redox potential, pH and temperature measurements of solutions were performed using a 692 pH/Ionmeter (Metrohm, Swiss) with accuracy 0,1 mV, 0,002 pH and 0,1° C, respectivelly. In this research using a combined glass electrode with temperature sensor Pt1000 (Combined LL pH glass electrode with Pt 1000 temperature sensor, № 6.0238.000 Metroohm, Swiss).

Potentiometric data of titration in form (voltage-time) were monitored and recorded in electronic file produced by a computer software PicoLog Recorder v.5.24 (PicoScope Ltd.,

UK). The statistical treatment of results was carried out for four measurements at a confidence level of 0,95. Results are presented as X ± ΔX, where X is the mean value and ΔX is the confidence interval. The corresponding values of the relative standard deviation (RSD) were also calculated. All calculations were performed using program Excel (Microsoft Office 2010) and IBM SPSS Statistic v.20.

Results and discussion

The validation procedure of the quantitative determination of total iodine content by galvanostatic coulometry was performed. In practice, it is usually possible to design the experimental work such that the appropriate validation characteristics can be considered simultaneously to provide a sound, overall knowledge of the capabilities of the analytical procedure, for instance: specificity, linearity, range, accuracy and precision. For this purpose was prepared the model solutions of sodium iodide aqueous solutions in the range of 15-300 mg, which corresponds to the level of concentration in the range from 70 to 130% of the possible concentration. This concentration was estimated on the basis of the following condition: 1) the amount of iodide in dried thalli of laminaria is the interval from 100 to 1000 mg / 100 g of dried algae, with an average value of about 150 mg [3,19-20]; 2) Ukrainian Pharmacopeia regulates the content of iodine in dried thalli of not less than 0.11%; 3) converting coefficient at procedure of the filtrated solution dilution.

The total iodide content in samples g (mg/100 g solution) was calculated from coulometric data by the equation (1):

$$g = \frac{100ItM}{nFm_p}, \quad (1)$$

where *I* is current, A; t is the time at which the end-point of titration is reached, s; M is the molar weight of the substance, g/mol; n is the number of electrons participating in the reaction; F is Faraday's constant, Coul/mol; is the weight of the aliquot portion, g; and m is the weight of dry sample, g.

To establish the stoichometry of the interaction iodide with electrogenerated bromine reactions, the coulometric titration of sodium iodide standard solutions was performed. When converting the equation (1) concerning the quantity of electricity Q required to generate bromine, we obtain the following equation (2):

$$Q = It = n\left(\frac{100F}{Mm_p}\right) = nf(g), \quad (2)$$

where *f(g)* is parameter equal to expression in brackets.

Figure 1 shows the dependence between the quantity of electricity Q and a function of f(g) for standart solutions of NaI for ten iodine concentration (25 measurements). The curve is linear. The correlation coefficient and slope of this curve are 0,9946 and 2,01, respectively. The slope value is numerically equal to the number of electrons n in the oxidation reaction of bromine. This confirms that electrogenerated bromine reacts with iodide in the ratio 1:1 [17]. So, the numbers of electrons participating in the reactions of iodide with titrants is two (n=2 in equation 1).

Figure 2 shows the dependence between the quantity of electricity Q and iodine concentration g for 6 standart solutions of NaI. The curve is linear over the iodine concentration range of 12-150 mg/100g of solution. The correlation coefficient of curve is 0.9996, as evidenced by the condition of linearity and the possibility of quantitative determination of iodide in the area of the proposed analytical methodology.

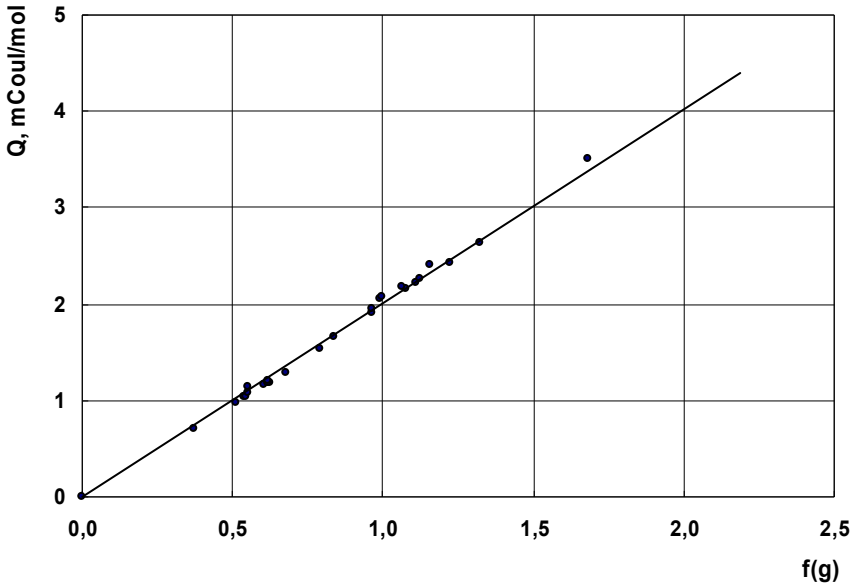

Fig. 1. The quantity of electricity Q as a function of f(g) for standard solution of sodium iodide

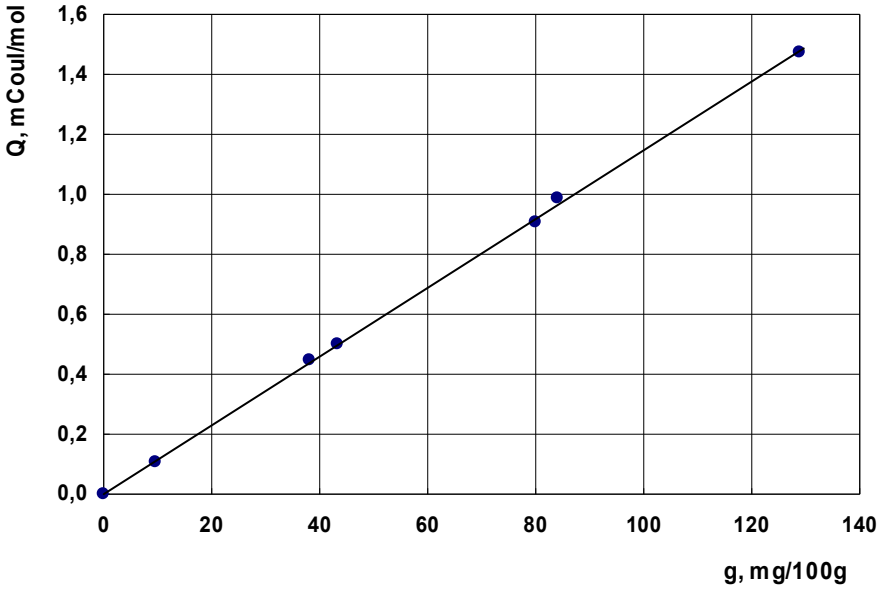

Fig. 2. The quantity of electricity Q as a function of concentration g for sodium iodide standard solution

Specificity was evaluated by the method of "added-found". The obtained values of the relative standard deviation is less than 0,05 (Table. 1).

Table 1

Coulometric determination of sodium iodide in standard solutions (n=5, P=95%)

Sample	Added g, mg/100 g of solution	Found g, mg/100 g of solution	RSD S_r
Sodium iodide	12,00	12,07	0,019
	59,60	58,34	0,014
	184,9	184,5	0,009
	318,3	322,1	0,053

The accuracy and precision were evaluated by varying the weighed portions at three levels of concentration using three portion on each level in comparison with iodinemetry method wich the recommended by Ukrainian Pharmacopoeia. Comparing dispersions series of measurements using F-test indicates statistically significant difference between the two methods and means the absence of significant systemic error. The calculated values of T-test is less than the tabular data. That facts corresponds to the validity of analytical procedure on characteristics of accuracy and precision.

The characteristics of validation procedure was showed that reliable experimental results are obtained. Adding in model solutions of chlorides and bromides at concentrations that may be present in the mineralized samples did not significantly alter these parameters do not affect the selectivity of the determination.

The total content of iodine in the ashing solutions was determinated for four manufacturer's serial numbers of dried algae at the level of the three samples in each series. The results of the measurements with the metrological characteristics are shown in Table. 2.

Table 2

Total iodine content for kombu (n = 4, P = 0.95)

Number of manufacturers series	Number of samples in series	Iodide amount g, mg/100 g solution	S_x	S_r	Mean value g±Δg, mg/100 g dry algae
10415	1	117,3	0,421	0,011	587 ± 21
	2	118,0	0,659	0,018	
	3	116,8	0,451	0,012	
50414	1	96,8	0,396	0,011	476 ± 9
	2	95,1	0,174	0,013	
	3	93,8	0,269	0,010	
30613	1	149,5	0,851	0,025	743 ± 19
	2	147,6	0,771	0,024	
	3	148,8	0,672	0,029	
30314	1	75,7	0,639	0,025	394 ± 8
	2	81,2	0,772	0,026	
	3	79,5	0,671	0,028	

As seen from Table. 2, the iodide content within the same lot is within measurement error, but there is a significant difference in the iodide content between manufacturer's series. The iodine content surveyed for four series of kombu was 394, 476, 587 and 743 mg/100 g dry algae, respectively. Apparently, the discrepancy confirms the fact that the iodine content in algae varies depending on the season and geographical location preform vegetable raw materials and is reflected in the final product. This result confirm the need to quantify determination the iodine content in the plant raw materials which can be used as a dietary supplement in fortified food.

It should be noted that these results are the total iodine content in the range of values determined by other experimental methods.

Conclusions

In this paper, the use of the most common ways of mineralization by dry alkaline digestion allowed to study the content of iodine in dried seaweed in an aqueous solution iodide. For detecting iodine content in seaweed the method of galvanostatic coulometry has been developed. Basic characteristics of validation for this analytical methods allows to conclude on the statistic reliability of the results. The iodine content surveyed was 394-743 mg per 100 g of dry sample for Kombu. These values were obtained for samples of various series of products. This fact proves the necessity of the quantitative control of the iodine content in food additives used for the development of iodine-containing functional foods and nutraceuticals.

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Determination of ultrafiltration membranes shrinkage factor

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Abstract

Introduction. Actuality of the theme is caused by the absence of low-productive domestic ultrafiltration installations, which is explained by the insufficient number of experimental data necessary for the calculation of the processes and equipment for ultrafiltration processing of food raw materials.

Materials and methods. During the research, moderately hydrophilic semipermeable ultrafiltration membranes based on copolymers of acrylonitrile type PAN (PAN-50 and PAN-100 brands) were used.

For experimental research of the ultrafiltration process of high-polymeric poly-disperse system (skim milk) in a dead end mode semi-batch ultrafiltration laboratory installation with internal recycle was used.

Results and discussion. Initial productivity of ultrafiltration membranes depending on the ultrafiltration pressure is determined. Therefore, during the ultrafiltration pressure of 0.1 MPa, initial productivity of UF-50 PAN membranes equals 120...125 $dm^3/(m^2 \cdot h)$. In UF PAN-100 membrane it is slightly higher and amounts to 160...165 $dm^3/(m^2 \cdot h)$. By increasing the ultrafiltration pressure to 0.25 MPa, initial productivity of the studied membranes increases more than 3 times: 355...350 $dm^3/(m^2 \cdot h)$ and 535...540 $dm^3/(m^2 \cdot h)$ respectively. It is determined that productivity decrease of PAN-50 membrane during 2.5×60^2s constitutes 34,3%, PAN-100 membrane – 28.5%.

Experimental data concerning the shrinkage factor of the studied PAN type membranes, which equal 0,18...0,2 for PAN-50 membranes and 0,28...0,3 – for PAN-100 membranes, are obtained.

Conclusions. The shrinkage factor of PAN-type ultrafiltration membranes is specified. The results of the research demonstrate good selectivity of PAN-type membranes by milk protein, and expedience of their use for UF-processing of protein-carbohydrate raw milk.

Introduction

Membrane technology is now a modern tool for the implementation of priority directions of science, engineering and technology. Practical significance of membrane methods of raw materials processing is primarily associated with the solution of global problems facing the humanity in the twenty-first century. These issues include the creation of high-tech technologies, the production of organic foods, high-quality drinking water and the formation of a proper balance between the solution of social and environmental issues and preservation of the environment [1,2].

Membrane processes of substances and materials processing belong to the most advanced technologies of today. Analysis of the results of fundamental research shows that without the use of membrane science and membrane separation processes implementation of many critical technologies requires increased financial and time costs. Modern membrane processes are characterized by high selectivity, low energy consumption, simplicity of instrumentation formalization. They are the basis for the creation of non-waste technology, and are able to "build a bridge" between the industry and clean environment, because they cannot negatively impact the environment as they are reagentless [3-5].

In food industry, the use of membrane technology is especially important as it allows realize the purification and concentration of food biological fluids without temperature impact, to save native properties of food nutrients, to perform low-temperature sterilization of solutions, to clean drinking water, etc.

The introduction of membrane technology is relevant globally due to the simplicity of its operation, environmental friendliness and low-waste production. Insufficient development of theoretical propositions concerning the processes occurring in the ultrafiltration of food raw materials, the lack of objective experimental data concerning the characteristics, properties and operating conditions of modern UF membranes, imperfection of the existing industrial UF systems are among the factors hindering the introduction of membrane methods, in particular, ultrafiltration (UF), into the food industry both in Ukraine and throughout the world [6].

The dairy industry is an industry characterized by a high level of wastes, it is an object of wide application of ultrafiltration processes. Traditionally, UF is used for the isolation of proteins from protein-carbohydrate milk raw materials (PCMRM) - skim milk, buttermilk, milk whey, and concentration of milk for the increase of curds extraction and reduction of production costs [5,7].

Nevertheless, insufficient number of the researches of raw milk materials UV processing, low relative capacity of the membranes determined by the specific properties of macromolecular substances of dairy raw materials, lack of low-productive domestic ultrafiltration plants, which is explained by the insufficient number of experimental data required for calculating the process and UF-processing equipment, play an obviously moderating role in the further development of ultrafiltration methods of raw milk materials processing.

Therefore, the study of subjects related to the improvement of the process of protein-carbohydrate raw milk materials ultrafiltration and its equipment appearance is relevant and is of great scientific and practical interest.

Materials and methods

In the study moderately hydrophilic semipermeable ultrafiltration membranes based on PAN-type copolymers of acrylonitrile produced by the Institute of Physical Organic

Chemistry, National Academy of Sciences of the Republic of Belarus were used. Investigations were carried out on PAN-50 and PAN-100 membranes.

Protein-carbohydrate raw milk materials were produced at the company «MOLAGRO PLUS» Ltd in Lozova, Kharkiv region. Skim milk, used in the research, meets the requirements of current regulatory documents of Ukraine and international standards ISO 7208:2008 (IDF 22: 2008) и ISO 8968-1:2014 (IDF 20-1:2014) .

For experimental studies of PCMRM-ultrafiltration in dead-end mode and barbotage-mode, a semi-batch ultrafiltration laboratory equipment with internal recycle was used. The scheme of the laboratory equipment is shown in Fig. 1.

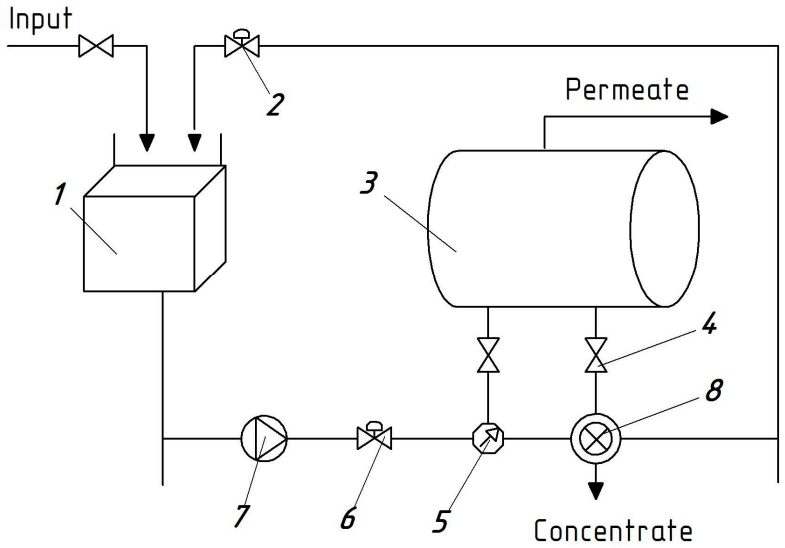

Fig. 1. Scheme of semi-batch ultrafiltration equipment:
1 – container with separated LHPS; 2, 6 – supply valves; 3 –ultrafiltration module; 4 –tap; 5 –manometer; 7 –peristaltic pump; 8 –refractometer.

Semi-batch ultrafiltration equipment consists of the following structural elements: a container with the separated liquid highly molecular poly-disperse system LHPS 1, ultrafiltration module 3, two supply valves 2 and 6. Supply valve 2 is intended for controlling the supply of UF-concentrate in the recycle from the ultrafiltration module to the container 1. Supply valve 6 is intended for regulating the supply of liquid high-molecular poly-disperse systems (LHPS) to ultrafiltration module using peristaltic pump 7. The pressure in the UV unit is controlled by the manometer 5. The construction provides an exhaust valve 4 for removing UF-concentrate after the end of ultrafiltration separation and refractometer 8 to control dry matters content in the concentrate.

Ultrafiltration system works in the following manner. LHPS is in the container 1, from which it moves to ultrafiltration module 3 by means of the pump 7. Formed UF-concentrate moves along the closed path «a container with separated LHPS-pump-ultrafiltration module» till the specified concentration factor values are achieved. The content of dry matters in the concentrate is controlled by means of refractometer 8. The formed in this case permeate is removed from the recycle. The advantage of the scheme is that peristaltic pump in the system maintains constant high level of pressure, controlled by manometer 5.

Shrinkage factor of semi-permeable membrane was calculated by means of the following dependence [8]:

$$K_y = 1 - \frac{G}{G_0}, \quad (1)$$

where K_y is the membrane shrinkage factor, ea;

G_0 is initial productivity of membrane (in the first 30 min. of the UF process), $dm^3/(m^2 \cdot h)$.

Results and discussion

It is known that the main characteristic of the semipermeable membranes is their performance. Herewith, the difference between the initial performance of membranes, namely performance of membranes in the initial period of operation, and actual performance, which is typical for membranes in their permanent operation, is distinguished. Usually, actual performance has smaller absolute values, which is the consequence of the porosity reduction in semipermeable membranes because of physical shrinkage. It is also the result of the membrane pores clogging by the shared LHPS particles.

At the first stage, initial performance of PAN type semi-permeable membranes was studied. The research was conducted using LHPS - skim milk at 20 °C and various values of ultrafiltration pressure. The results are shown in Table 1.

Table 1

Initial performance of ultrafiltration membranes

The amount of ultrafiltration pressure, MPa	Initial performance of UF-membranes $dm^3/(m^2 \cdot h)$				
	PAN-50	PAN-100	GR61PP	GR81PP	Ripor3
0,1	120…125	160…165	Unplumbed		
0,25	350…355	535…540	480…500	240…250	150…155

As Table 1 shows, initial performance of ultrafiltration membranes depends on the value of ultrafiltration pressure. Therefore, at ultrafiltration pressure of 0.1 MPa an initial performance of PAN-50 UF-membranes is 120...125 $dm^3/(m^2 \cdot h)$, of PAN-100 membranes it is slightly higher and ranges from 160 to 165 $dm^3/(m^2 \cdot h)$. With the increase of the ultrafiltration pressure to 0.25 MPa, initial performance of the studied membranes increases more than 3 times, respectively, and equals 350...355 $dm^3/(m^2 \cdot h)$, and 535...540 $dm^3/(m^2 \cdot h)$ accordingly.

The researched membranes exceed the control membrane GR81PP in terms of the initial performance: membrane PAN-50 is 42...46% more effective, and PAN-100 membrane is 116...123%. Initial performance of GR61PP membrane is 27...29% higher than the initial performance of the studied PAN-50 membrane, but it ranks 8...11% below this indicator to UF PAN-100 membrane. Regarding the control membrane Ripor 3, both studied UF-membranes have a much higher initial performance: for PAN-50, it is 129...133% and for PAN-100, it ranges from 248 to 256%.

Then, the dependence of the researched ultrafiltration membranes' performance on the duration of the ultrafiltration process was studied. The research was conducted with distilled water at temperature of 20 °C and various filtration pressure values: 0.1 MPa and 0.25 MPa. The results are shown in Fig. 2 and 3, respectively.

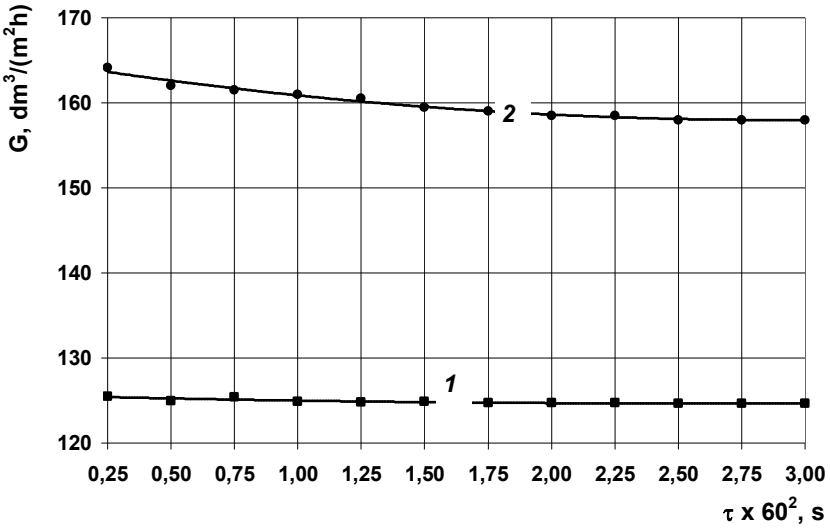

Fig. 2. Duration of the ultrafiltration process (t = 20 °C; P = 0,1 MPa) 1 – PAN-50; 2 – PAN-100.

According to the data in Fig. 2, the productivity of PAN-type ultrafiltration membranes at the filtration pressure of 0,1 MPa changes over time insignificantly. Thus, the productivity of PAN-50 UF-membrane in $0.3 \cdot 60^2$s decreases at 1,1% for PAN-100 membrane's productivity falls at 2.9%.

This can be explained by the fact that the membrane shrinkage at this value of filtration pressure is insignificant. Therefore, membranes' productivity does not reduce sufficiently. Furthermore, as follows from the plot in Fig. 2, after $2 \cdot 60^2$ s, the reduced productivity of UF-membranes slows significantly, its values are stabilized and remain practically constant. Further reduction of PAN type membranes' productivity due to shrinkage at pressure of 0.25 MPa may occur in insignificant limits over a prolonged period of their exploitation.

Use of the filtration pressure of 0.25 MPa (Fig. 3) during the ultrafiltration of distilled water alters regularity of changes in the membranes' productivity depending on the duration of ultrafiltration.

According to the data in the figure, the productivity of PAN-type membranes reduces over time more significantly than at pressure of 0,1 MPa and only in $(1,5\ldots2,0) \cdot 60^2$ s its value is stabilized.

Productivity decrease of the PAN-50 membrane during $2,5 \cdot 60^2$ s is 34.3% and that of PAN-100 membrane equals 28.5%.

Similar decrease in the initial productivity with subsequent stabilization of its values was also observed in the control GR type membrane [3]. The similar situation is observed due to the compression of the studied membranes' structure, which occurs under the elevated pressure filtration.

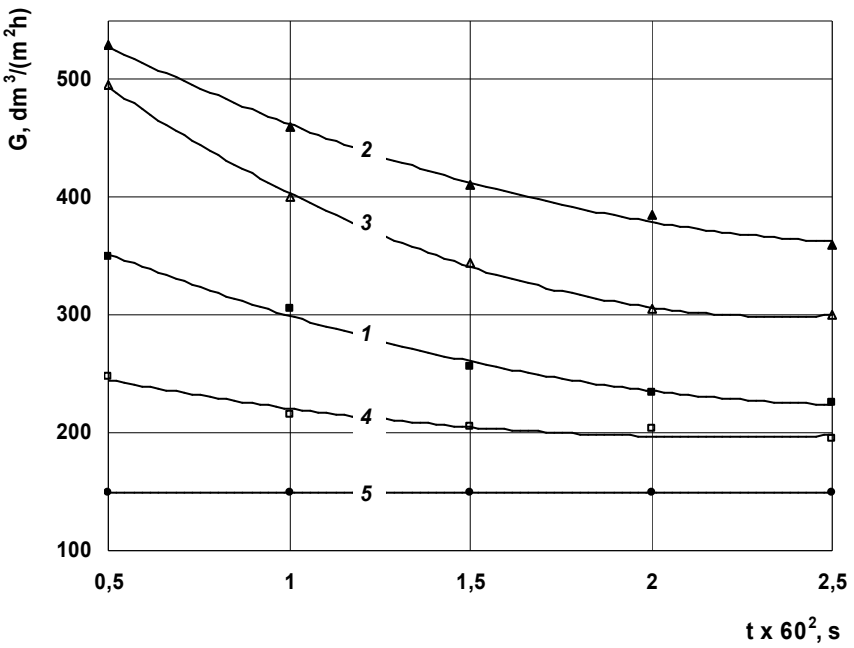

Fig. 3. The dependence of productivity of test and control UF-membranes on the duration of the ultrafiltration process
(filtered liquid – skim milk; t = 20 °C; P = 0,25 MPa)
1 – PAN-50; 2 – PAN-100; 3 – GR61PP; 4 – GR81PP; 5 – Ripor3

The control Ripor3 membrane (Fig. 2) does not visibly lose productivity; its value remains constant as noted in [4]. The membranes of this type have a greater total usable area of the microporous filtration layer of the substrate, which is caused by a large pore size (10 nm). At such values of pore diameter, even macroporous substrate shrinkage does not result in the reduction of the membrane's overall productivity. In this regard, further research considered only GR type UF-membranes as control ones.

It is known that instability of ultrafiltration membranes' productivity in the initial exploitation period is accounted by the indicator called shrinkage. On the basis of the obtained graphic dependences and their subsequent analysis and generalization experimental shrinkage factors of the studied PAN-type membranes were obtained. The received data are shown in Table 2.

Table 2

The shrinkage factor of test and control membranes

UF-membrane brand	**PAN-50**	**PAN-100**	**GR61PP**	**GR81PP**	**Ripor3**
The shrinkage factor	0,18…0,20	0,28…0,30	0,40…0,45	0,20…0,25	1,0

Conclusions

As we can see from Table. 2, the lowest shrinkage factor belongs to the studied PAN-50 UF-membrane. The shrinkage factor of ultrafiltration PAN-100 membrane is 1.5 larger than that of PAN-50 membrane, but it is 1,4 times smaller than GR61PP UF-membrane. It indicates a good selectivity of PAN type membranes and appropriateness of their use for UF-processing of protein-carbohydrate raw milk materials.

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Comparative analysis of beet cossettes extraction of different profiles on the industrial extractors

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Abstract

Introduction. The process extraction of sucrose conducted from the beet cossettes of different cross-sections. Quality and mechanical characteristics, sucrose loss in pulp, raw juice quality and energy cost depends on the profile shape beet cossettes.

Materials and methods. It were investigated the beet cossettes of triangle and grooved profiles obtained on centrifugal beet slicers using specially sharpened and set in a special way blades. Research was undertaken on two parallel lines. Installed in this lines extractors DC-12 have same construction, were working in the same process conditions.

Results and discussion. There was made a comparison in the study of major quality indicators of beet cossettes of grooved and triangular cross-sections and determined the sucrose content in the extracted pulp of the cross-sections. The average value of defect ratio of the triange profile pulp is 35 % less comparing to the grooved profile pulp. The average value of the Swedish factor for the triangle cossettes cross-sections is 42 % more than for the actual rate for the grooved cross-sections. Average value of sucrose content in the pulp for triangular profiles is 0.45 % by the weight of pulp and for grooved one - 0.50 %. So the cossettes with a triangular cross-section more than 10 % extracts better in industrial diffusion devices under the same process conditions. This can be explained by increased mechanical strength of triangular cossettes (greater resistance to bending moment) and fewer defect ratio. Increasing the mechanical strength of the cossettes and reducing the number of defect ratio leads to:

- counterwork to the cossettes layer compression by the fluid flow and increasing its porosity, that provides good cossettes washing with extractant;
- reducing dead zones;
- steady transition of the diffusion equipments by transport systems.

Conclusion. The triangular profile cossette being under the same process conditions has better quality characteristics and better extraction compared to grooved one.

Introduction

The extraction of sucrose from beet pulp is one of the most important processes of sugar production. It determines the loss of sucrose in spent beet cossettes (pulp), molasses, energy cost and raw juice quality. Cossettes obtained by cutting sugar beets in beet slicing machines. Cutting food and plant materials devoted to the work of scientists: M. A. Moore, G. C. Jones, Y. D. Yiljep, B. Denkena, M. J. O`Dogerty, P. F. Davis, O. Knaifl and other [1-13].

According to the studies of Terent'eva Y.A., Pushanka M.M., M.D. Khomenko, Kutsenko V.O. the rhomb-shaped (square) profile is considered to be rational among all pulp profiles (that can be get using knives of keningsfeld type), that are used for processing healthy beets and beet-roots of impaired quality Fig. 1.b.

The knives of keningsfeld type of 1011V models manufactured with profile angle of 75 ° and 8.25 mm increments have widely bacame popular in the CIS countries. When getting the rhomb-shaped cossette using these knives of keningsfeld type (each knive is offset by 0.5 step of the previous one, the lifting height of the knive above the control bar is equal to 2 heights of knife blades) the side of the rhomb cossette will be about 7 mm. These cossettes will be too rough, its length is 100 g (Silin number) and will be less than 5 m. Therefore, in most cases sugar factories using keningsfeld knives with a pitch 8,25 mm get cossettes of the grooved cross section (Pic. 1.a) with the side of 3.5 ... 5 mm (length 100 g - 8 ... 10 m).

At the european factories beets are cut in the beet slicing machines into cossettes with a square (rhomb-shaped) and grooved cross-section (V-shaped cross-section) [14]. This demonstrates that the rhomb-shaped and grooved cossette cross-section is the most common in the world.

It was recently suggested a method of producing a triangular (Pic. 1.C) and plane-comb (Pic. 1.d) profiles on existing types of beet slicing machines. It is implemented with knives of keningsfeld type and knives with flat cutting edge, that are alternating in knive chassis [15].

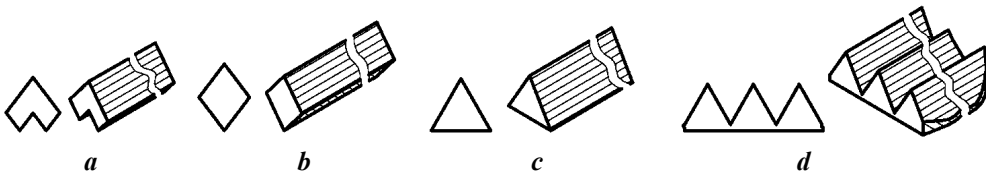
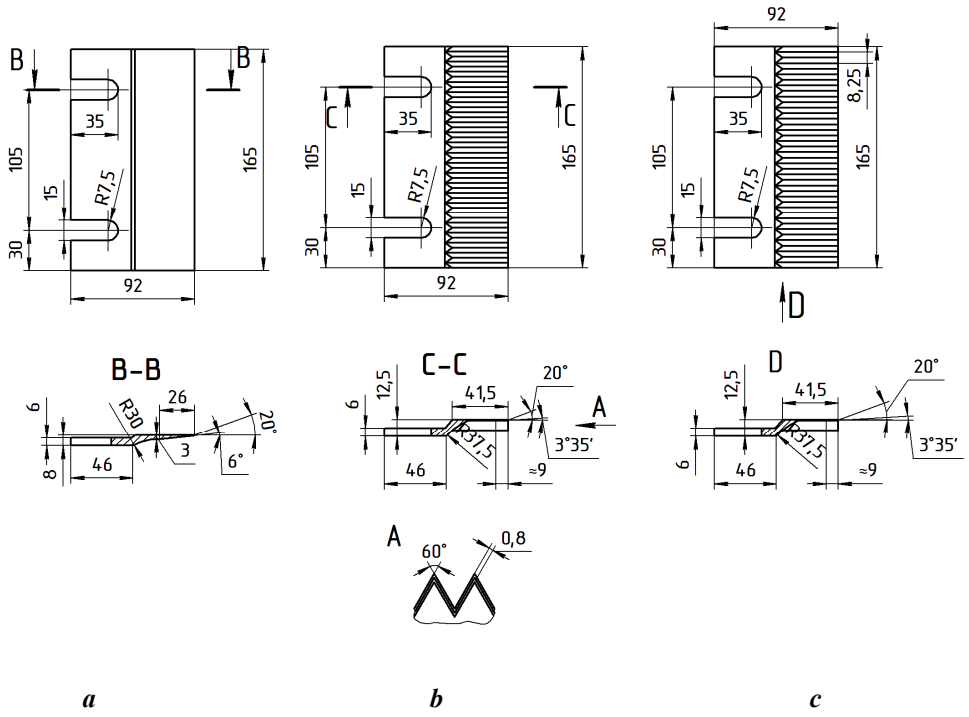


Fig. 1. Profiles beet chips:
a - cossettes of the grooved cross section (V-shaped cross-section);
b - square (rhomb-shaped) cross-section;
c - triangular cross-section cossettes;
d - plane-comb cross section cossettes.

Beet cossettes with a triangular profile compared to the rhomb-shaped cossettes with the same cross-sectional area has a larger perimeter (diffusion area), shorter internal diffusion and greater moment of resistance (greater substantiality for deflection and jam). Based on the above, the triangular cross-section of the cossette is more efficient compared to the others known today. To test the theoretical information in practice, the studies of industrial diffusion apparatus performance of perpetual action were undertaken on the triangular cross-section beet cossettes.

Materials and methods

Materials which was studied. In this work beet cossettes of triangle and grooved profiles were invastigated. Beet cossette was obtained from beets belonging to categories 1 and 2. Category 1 includes fresh, healthy, with normal turgor (water loss is less than 5%), frost-undamaged beet containing less than 1% of roots that blossomed (woody) and a small number (10%) of beet with strong mechanical damage, and those that have less than 3% green material and contamination (quantity of foreign material) to 10% and were collected in late September and early October.



a ***b*** ***c***

Fig. 2. Beet slicing knives:
a - special plane beet slicing knife;
b - a special knife of keningsfeld type with a vertical angle of 60 °;
c - knife of 1011V model manufactured with angle of 75 ° profile and step 8.25 mm.

Beets of 1 category are placed in piles of prolonged storage. 2 category includes frost-undamaged sugar beets, containing less than 5% slightly dried and up to 12% severely damaged roots, containing 3% of green material and those, that were collected in the period up to mid-September and after mid-October. Beets of 2 category are placed in piles of the medium term storage.

During experiments cossettes were obtained on centrifugal beet RBA-2-12 using specially sharpened and set in a special way blades for triangular cossettes (Fig. 1.a, b) and knives of keningsfeld type model 1011V that were manufactured with profile angle of 75 ° and step 8.25 mm (Fig. 1.C).

All knives were manufactured at the company LLC "Company" KORUND "and sharpened by grinding wheels of cubanite on sharpening line of beet slicing knives of the enterprise, consisting of semiautomatic machine-UZN-3 (knives trimming) UZN-1 (thinning) UZN-2 (facet formation).

Geometric characteristics of the blades.

1. Special plane blades:
   a. smooth cutting edge with stepped sharpening of the one side;
   b. thinning angle - 6 ° for length ≈26 mm;
   c. sharpening bevel angle - 20 °;
   d. the sharpness of the blade - 10 microns.
2. Special knives of keningsfeld type with a profile angle of 60 ° and knives model 1011V, with a profile angle of 75 ° and step 8.25 mm:
   a. winding cutting edge is smooth, with one-sided stepped sharpening;
   b. thinning angle ≈3 ° for the length ≈9 mm;
   c. sharpening bevel angle - 20 °;
   d. the sharpness of the blade - 10 microns.

Research procedures. Studies were undertaken in October 2014 at LLC «Novoorzhytskyy sugar beet plant» (centrifugal beet slicing machines RBA-2-12 that supplied extraction apparatus inclining type DC-12 with cossettes).

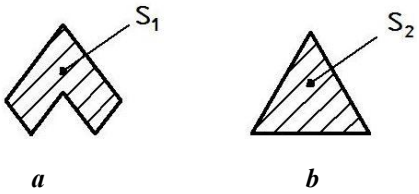


Fig. 3. Cossettes profiles:
a – grooved; b – triangular.

There worked during the studies in the beet processing department of sugar factory two parallel lines with efficiency of of 3000 tons sugar beets processing per day each. Installed in this lines extractors DC-12 have same design, worked in the same process conditions. Each extraction apparatus has been supplied with cossettes by the single centrifugal beet slicing machine.

During the research beet slicing machine RBA-2-12 was set with: each double-row frame of beet slicing machine №1 (that cuts chips for 1st extraction device) was set with knives of keningsfeld type with a vertical angle of 60 ° (the first row of each frame) and plane blades (second number of frames); each double-row frame of beet slicing machine №2 (that cuts chips for 2st extraction device) was set knives of keningsfeld type alternately performing A and B of 8.25 mm increments for grooved cossettes.

After starting the centrifugal beet slicing machines the cross-sectional area of grooved cossettes (Fig. 3.a) and triangular cossettes (Fig. 3.b) was set the same, changing the lift height of the blades. The moment of the expiration of cossettes cross-sectional area regulation was the reference time. Since then with intervals of 1 hour cossettes samples of grooved and triangular profiles (equal parts of each knife frames) were collected and

determined its quality indicators - Silin number (SN), the Swedish factor (SWN) and percentage of defects in cossettes (MC). There have been 3 series of 8 experiments.

After 2 hours from the countdown (extraction device will be completely filled with grooved and triangular profiles cossettes) at intervals of 30 min samples of pulp of grooved and triangular cossettes were selected. The collected samples were separated into groups:

Group №1 - beet cossettes with a triangular cross-section;

Group №2 - beet cossettes with grooved cross- section.

Then by the conventional methods the sucrose content in extracted cossettes of each group was determinated. There have been 3 series of 7 experiments.

Description of research methods. Qualitative characteristics of cossettes with various forms of cross-sections were found according to the typical methodes of determining the Silin number, Swedish factor and the defect ratio in cossettes.

Results and discussion

Comparison of major quality indicators of beet cossettes with grooved and triangular cross-sections, got on the industrial centrifugal beet slicing machines RBA-2-12 are shown in Fig. 4 ... 6.

As shown on Figures 4 ... 6 the cossettes quality increases within1 hour of work (Silin number, Swedish factor increasing and and defect ratio reduces).

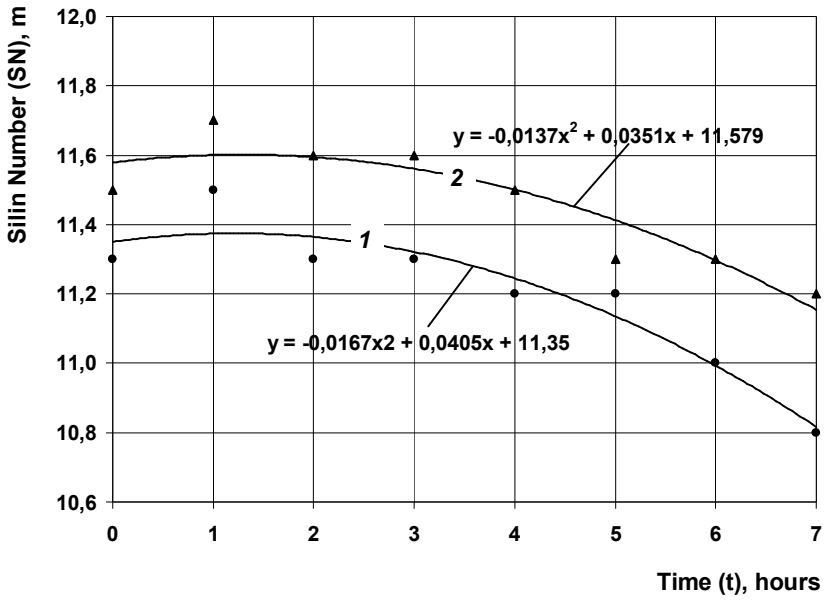


Fig. 4. Dependence of Silin number with grooved and triangular cossettes profiles of the working time of centrifugal beet slicer:
1 – grooved cossettes profiles; 2 – triangular cossettes profiles.

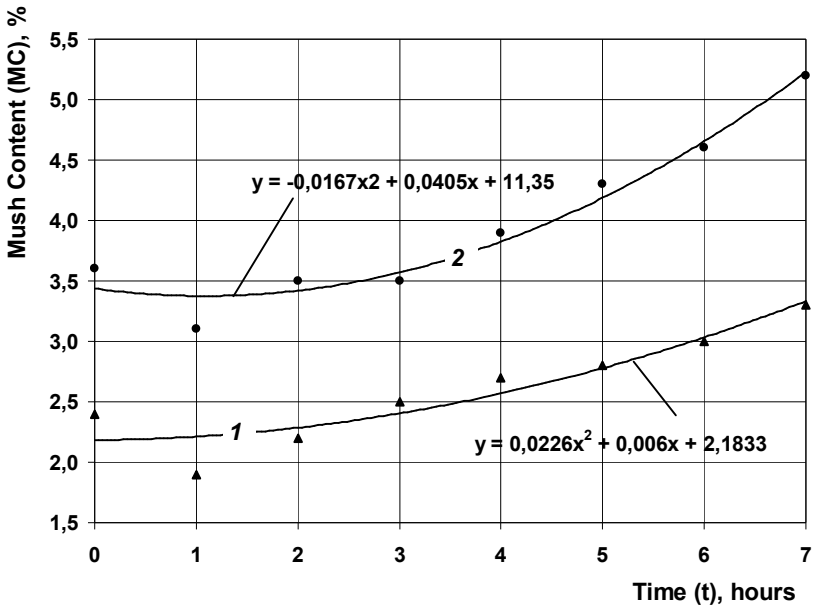


Fig. 5. Grooved and triangular cossettes profiles defect ratio dependence from working time of the centrifugal beet slicer:
1 – grooved cossettes profiles; 2 – triangular cossettes profiles.

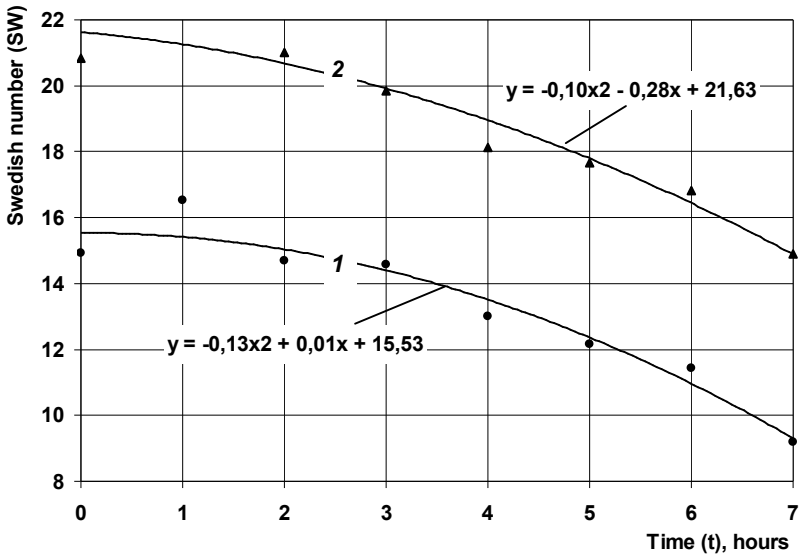


Fig. 6. Grooved and triangular cossettes profiles Swedish number dependence from working time of the centrifugal beet slicer:
1 – grooved cossettes profiles; 2 – triangular cossettes profiles.

Quality improvement during the one hour of work for both profiles is attributable that knives on the initial stage are lapped by beets, they lose scorings and rigidity of incisal surface becomes lower, as a consequence they give best quality of shavings after a while after start of work. In the further work increasing defect ratio, decreasing of Swedish factor and Silin number can be explained that knives are becoming dull and damaged by extraneous contaminants.

The average value of the Silin number beet cossettes of triangle cross-section is 3 % more than when working with grooved profile. The average value for the triangle cossettes is 11.5 m, for the grooved cossettes is 11.2 m according to 3 series of research results.

The average number of the defect ratio of the triangle cossettes profile is 35 % less than in the grooved profile cossettes. The average number for the triangle cossettes is 2.6 %, for the grooved cossettes is 4.0 %, according to 3 series of research results.

The average value of the Swedish number for the triangle cossettes cross-sections is 42 % more than for the actual rate for the grooved cross-sections. The average number of the triangle cossettes is 18.9, for the grooved cossettes is 13.3, according to 3 series of research results.

As cross-sections of the triangle and grooved cossettes profiles have nearly equal square (it's arranged with original setting of the knive's lifting height), so their average values of the Silin number are differed by 3 %. Obviously, the Silin number characterizes the degree of the sugar beet breakage (the cossettes cross-section area) and fractional characterizes the rate of defect ratio in the cossettes, that doesn't have any influence on the Silin number's value. It can be illustrated by estimation of the given rate using by formula [16]:

$$SN = \frac{0.1 \cdot \phi}{S \cdot \rho}$$

where: □ – coefficient, considering the percentage of high-quality cossettes (at 3% MC → □ = 0.97, where 5% MC → □ = 0.95);

S - cross-sectional area of one pulp, m^2;

ρ - the average density of sugar beet material, kg / m^3 (ρ = 1060 kg / m^3).

Table 1

Silin number dependence of the defect ratio for cossettes with averaged cross-sectional area of 9.15 mm^2

Index	Value			
Defect ratio (MC), %	1	3	5	7
Silin number (SN), m	10,2	10	9,8	9,6

As the Table 1 shows the 7 times defect ratio increasing results the Silina number decreasing for only 6%.

Significantly lower rates of cossettes defect ratio of triangular cross-section compared to grooved one can be explained by the fact that while cutting the triangular chips (unlike grooved one) vertical displacement of roots, which occurs during the beet transition from

one blade frame to another does not affect the quality of received cossettes. It means, when cutting on the roots of sugar beet contacting with special knives of keningsfeld type (they are set in the first row of double-row blade frame) winding cuts are formed, and after contacting with special plane blades (set in the second row of double-row blade frame) - straight cuts are formed. Thus, special knives of keningsfeld type always form cossettes on a flat surface of the beet-root cut, providing ideal conditions for the formation of the right shaped cossettes with a minimum of defect ratio, and plane blades cut formed winding print and make the beet surface plane. I.e., while transiting of the beet-roots between frames (distance between two knife frames) beets have plane surface cut, that's why their vertical displacement does not affect the quality of the pulp.

High cossettes rates of Swedish factor with a triangular profile compared to grooved one can be explained by a significantly lower defect ratio of triangular pulp and 28 % higher the average point of resistance (arithmetical value when calculating the moment of resistance for the basis and the top of figure) with relative to the x-axis in Fig. 7. Then with the cross-section area of 9.16 mm^2 the average resistance point relative to the x-axis ($W_{X\,aver.}$) will be will be 4.6 mm^3 for the triangular cross-section, for grooved one - 3.6 mm^3. It means, when standing out the knife frames, when hitting the beet slicer cover, transportation to the extraction device and by transport systems of extraction installations beet pulp of triangular shape will be less grounded, compressed and will have a better filtration capacity compared to the grooved one.

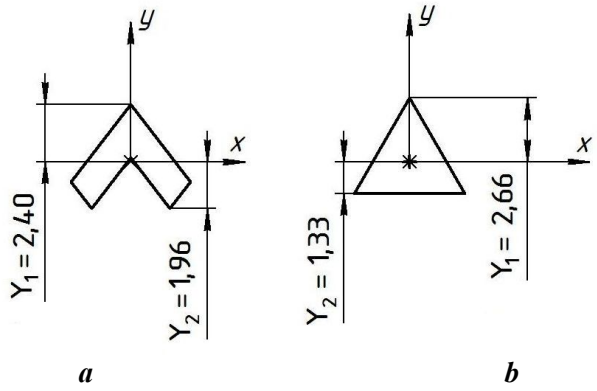


Fig. 7. Scheme to determine resistance profiles of cossettes:
a – grooved; b – triangle.

The sucrose content in extracted cossettes of different profiles. According to the research average value of sucrose content in the pulp for triangular profiles is 0.45 % by the weight of pulp and for grooved one - 0.50 %. So the cossettes with a triangular cross-section more than 10 % extracts better in industrial extraction devices under the same process conditions. This can be explained by increased mechanical strength of triangular cossettes (greater resistance to bending moment) and fewer defect ratio. Increasing the mechanical strength of the cossettes and reducing the number of defect ratio leads to:

– counterwork to the cossettes layer compression by the fluid flow and increasing its porosity, that provides good cossettes washing with extractant;

– reducing dead zones;

steady transition of the extraction equipments by transport systems.

Conclusions

As the result in the studies it is revealing the main inherent specifications and sucrose content in extracted pulp of triangular and grooved profiles obtained in industrial centrifugal beet slicing machines. Results indicate that triangular profile cossettes being under the same process conditions has better mechanical (28 % more the average bending moment of resistance), quality characteristics, less defect ratio (35 %) and better extraction (more than 10 % lower sucrose content in the pulp) compared to grooved one - the most common today.

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Анотації

Безпека харчових продуктів

Неруйнівне виявлення фальсифікації харчових продуктів як засіб забезпечення здоров'я і безпеки людства

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Вступ. Метою даного огляду є критичний розгляд основних понять неруйнівного виявлення фальсифікації і підробки продуктів харчування, які в цілому викликають величезні щорічні фінансові збитки у всьому світі і є однією з основних причин захворювань людства.

Матеріали та методи. Література, зазначена в даному огляді, була отримана в результаті пошуку бібліографічної інформації в CAB abstracts, AGRICOLA, SciFinder Scholar, Modern Language Association (MLA), American Psychological Association (APA), OECD/EEA database щодо інструментів, які використовуються для екологічної політики й управління природними ресурсами, та Web of Science.

Результати та обговорення. Фальсифікація харчових продуктів означає умисне, облудне додавання сторонніх, нестандартних або дешевих інгредієнтів у продукти, розбавлення чи видалення деяких цінних інгредієнтів з метою збільшення прибутків. У сучасних умовах виробники прагнуть збільшити випуск своєї продукції найчастіше шляхом виготовлення та продажу неякісних і фальсифікованих продуктів.

Неруйнівне виявлення фальсифікації харчових продуктів передбачає аналіз зразка і його істотних ознак без зміни фізичних і хімічних властивостей.

Підвищення якості та безпеки харчових продуктів шляхом розробки наукових методів виявлення фальсифікації є головною умовою для підтримки здоров'я споживачів. Точна об'єктивна оцінка якості і виявлення фальсифікації харчових продуктів вважається найважливішою метою харчової промисловості. У зв'язку з удосконаленням технології фальсифікації продуктів важливо бути в курсі сучасних, найбільш точних методів контролю їх фальсифікації. З цією метою у статті розглянуто основні поняття виявлення фальсифікації продуктів харчування, принципи пристроїв і можливі практичні застосування сучасних методів неруйнівного виявлення фальсифікації продуктів харчування. Здійснено порівняльний аналіз переваг і недоліків інструментальних методів, що застосовуються в харчових технологіях.

Кожен з розглянутих методів обговорюється з точки зору можливих різних консистенцій продуктів - газів (вільного простору навколо продукту), вільно текучих рідин (соків), каламутних і в'язких рідин (меду та рослинних олій) та інтактних продуктів (фруктів і овочів).

Висновки. Результати, висвітлені в огляді, рекомендується використовувати під час контролю якості та безпеки харчових продуктів.

Ключові слова: *харчовий продукт, фальсифікація, безпека, якість, неруйнівний, автентифікація*.

Перспективи використання методу клиновидної дегідратації для оцінки фізико-хімічних властивостей багатокомпонентних водних розчинів

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Вступ. Актуальність теми зумовлена активізацією досліджень явищ у краплі у зв'язку з розвитком біотехнологій та практичним застосуванням для оцінки якості рідких продуктів.

Матеріали та методи. Досліджено модельний розчин сироватки крові, одержаний на основі електрохімічно активованих розчинів. Вивчення фацій у процесі їх висихання проведено за допомогою біологічного мікроскопа, обладнаного цифровим фотооб'єктивом.

Результати та обговорення. Аналіз фацій модельних розчинів показав, що вони відповідають типовій картині фацій білково-сольового розчину – вздовж краю розміщений білковий валик, а посередині - білково-сольова область. Виявлено, що фації на основі електрохімічно активованої води – католіту, аноліту та їхньої суміші – відрізняються структурними елементами білково-сольової області. Зокрема, у ній виявлено значну кількість правильних кристалів солі з дендритними відгалуженнями. Крім того, фації відрізняються характером утворених «клітин» у білково-сольовій області. Показано, що структурні особливості перенасиченого розчину впливають на процес росту кристалів. Розчинені в активованій воді солі кристалізуються з утворенням правильних кристалів на відміну від анізотропних мікрокристалів, які утворюються під час висихання розчину на звичайній воді. Оскільки pH та окисно-відновний потенціал суміші католіту й аноліту практично не відрізняється від показників дистильованої води, то на структуроутворення фацій і ширину білкового валика визначальний вплив мають метастабільні властивості отриманої води, а саме нескомпенсованість гідратованих зарядів – вільних протонів та електронів. Показано, що час формування білкового валика залежить від наявності іонів гідроксилу та гідроксонію у рідині для приготування модельного розчину: зі збільшенням вмісту іонів гідроксилу час формування зменшується, а зі збільшенням вмісту іонів гідроксонію – збільшується порівняно з неактивованою дистильованою водою.

Висновки. Використання методу клиновидної дегідратації із застосуванням можливостей сучасної комп'ютерної техніки дозволяє отримати набір показників для ідентифікації різних рідин і зміни їхніх властивостей внаслідок дії зовнішніх впливів.

Ключові слова: *дегідратація, фація, аноліт, католіт, оцінка.*

Харчові технології

Вплив способу зберігання на фізико-хімічні характеристики вина Вранац

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Вступ. Вино Вранац виробляється з винограду сорту Вранац, що є найбільш важливим для виробництва червоних вин у Македонії. Вранац є місцевим сортом Чорногорії, вирощується у всіх виноградниках регіону Вардар, хоча в інших виноградниках поширений начно менше.

Матеріали та методи. Вивчались два зразки вина Вранац у резервуарі з винограду одного сорту – Вранац, винарня Стобі, розташована у винному регіоні Тіквеш. Вино Вранац, вироблене з врожаю 2011 року, відрізняється методом зберігання після його ферментації. Один зразок зберігається в резервуарі, тоді як інший, з урожаю винограду того ж року, був переміщений і зберігався в дубовій бочці об'ємом 5000 літрів.

Результати та обговорення. В даному дослідженні були вивчені фізико-хімічні властивості вина, що зберігалось в різних умовах (в резервуарі і в бочці). Концентрація іонів водню pH у зразках вина, що зберігались в резервуарі і бочці, знаходиться в межах від 3,33 до 3,42, що, по суті, є допустимим рівнем pH для червоних вин. Стосовно кислот у цілому, загальна кислотність вища в тому зразку вина, що зберігався в бочці. Вміст летючих кислот має більше значення у зразку вина з бочки. Вміст яблучної кислоти складає 0 мг на літр в зразку вина з бочки, що свідчить про повне перетворення яблучної кислоти в молочну. Вміст лимонної кислоти вищий у зразку з резервуара (0,38). Вміст оцтової кислоти вищий у зразку з бочки (0,48). Вищий вміст цукрів у загальному (5,1 г на літр) і зменшення (0,95 г на літр) спостерігався в зразку з бочки. Кількість алкоголю в протестованих зразках варіюється від 14,53 до 14,75 градусів, що відповідає вимогам Міжнародної організації винограду і вина.

Що стосується наявності SO_2, з одного боку, підвищений вміст SO_2 призводить до пригнічення активності небажаних мікроорганізмів (що є бажаним), а з іншого - підвищений вміст SO_2 створює потенційні проблеми для людей з астмою. Слід зазначити, що, згідно з вимогами Міжнародної організації винограду і вина, максимальний вміст SO_2 не повинен перевищувати 350 мг на літр, тоді як в протестованих зразках вміст SO_2 в три рази менший.

Висновки. Метод зберігання вина Вранац з регіону Тіквеш, що зберігалось у резервуарі і бочці, впливає на фізико-хімічні властивості протестованих зразків вина.

Ключові слова: *вино, Вранац, зберігання, Македонія.*

Вплив обробки двох видів риб з південних вод Ірану на їх склад і енергетичну цінність

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Вступ. Мета - дослідження впливу різних способів приготування (жаріння, варіння і випікання) на хімічний і мінеральний склад зразків риб *Scomberoides commersonnianus* і *Spyraena jello*.

Матеріали та методи. Свіжі Scom beroides lysan (*Scomberoides commersonnianus*) і Sphyraenidae (*Spyraena jello*) були відібрані на ринку Бехбехан в Ірані. Під час транспортування в лабораторію харчової хімії Бехбеханского технологічного університету їх зразки знаходилися в пластиковому контейнері. Для дослідження біохімічного складу риби були використані методи AOAC.

Результати та обговорення. Вміст білку і ліпідів був вищим у запеченої та смаженої риби *S.commersonnianus* (74.29% і 20.20%), риби *S. jello* (88.12% і 17.77%) відповідно. Зольність у зразках риби *S.commersonnianus* коливається від 9,80% до 15,34%, а *S. jello* - від 5,83% до 7,68%.

При порівнянні вмісту поживних речовин у варених філе двох риб було виявлено, що риба *S. jello* показала кращі результати. Низький вміст жиру у вареному і запеченому *S. jello* в основному пов'язаний з поглинанням води, яка використовується під час приготування карі. Таке ж поглинання води відбувалося і за умови жаріння *S. jello*. Як і очікувалося, вміст білку в цілому високий. Це пов'язано з тим, що риба є гарним джерелом білка. Вищий рівень вмісту білка спостерігається в смаженій рибі. Результат обумовлений тим, що м'ясо риби втратило вологу. Ще одним доказом цього є той факт, що *S. jello*, приготована в карі паровим способом, мала нижчий вміст білка, але за вищого вмісту вологи. Це може бути пов'язано з поглинанням води під час приготування, що викликає розрідження м'язової тканини в аналізованих зразках. Хімічний склад сирого філе обох видів риб аналогічний попереднім звітам з дослідження риби. Безпосередній склад білків, жирів і золи *S. commersonnianus* і *S. jello* відрізнявся в усіх способах приготування їжі. Варто відмітити, що жодної істотної відмінності у вмісті жиру у відвареному, запеченому і сирому філе риби не спостерігалося. ($P > 0,05$). Підвищений вміст золи відмічений в усіх приготованих філе *S. commersonnianus* у порівнянні із сирим філе риби. Відповідно, збільшення вмісту золи, білка і жиру за умови приготування філе *Scomberoides commersonnianus* пояснюється зниженням вологості.

Висновок. Найвищий вміст білка, низька жирність і калорійність були виявлені у вареній рибі, тому варіння є кращим способом приготування їжі для здорового харчування.

Ключові слова: *риба, Scomberoides lysan, Sphyraenidae, приготування, здоров'я.*

Вплив упаковки і умов зберігання на збереження аскорбінової кислоти в листі гуньби

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Вступ. Дане дослідження визначило важливість упаковки і умов зберігання на збереження аскорбінової кислоти в листі гуньби.

Матеріали та методи. Листя гуньби з коренями і без коренів вагою 100 грам було зібрано й упаковано в перфоровані і неперфоровані пакети розміром 30х25 см (750 $см^2$) чотирьох різних типів, а саме: ПЕВД-100, ПЕВД-200, ПП (поліпропілен)-100 и ПП-200. Для перфорації були зроблені отвори діаметром 0,59 см, площа яких становила 1,87 $см^2$. Ці екземпляри зберігались за кімнатної температури (від 14 до 35 ºС, вологість 50-60%) і низькій температурі (0-5%, вологість 80-90%) до припустимої норми. Зразки були проаналізовані за однакові інтервали часу на вміст аскорбінової кислоти, на основі методу 2,6 діхлорофенол ідофенола.

Результати та обговорення. Свіже листя гуньби мало 51,4 мг аскорбінової кислоти на 100 грам ваги. За низької температури в неперфорованих пакетах зразки гуньби мали термін придатності 6 днів і середнє значення зберігання аскорбінової кислоти 80,95%. Упаковка зразків з коренями зменшила строк придатності до 4 днів і зберегла 66,05% аскорбінової кислоти. Перфорація в пакувальному матеріалі також зменшила період зберігання до 4 днів в зразках гуньби як без коренів, так і з ними.

Зразки гуньби без коренів і з коренями, які зберігались за кімнатної температури в неперфорованих пакетах показали максимальний строк зберігання 2 дні і середнє значення зберігання аскорбінової кислоти 69,99% і 56,47% відповідно. Поступове зменшення середнього значення зберігання аскорбінової кислоти спостерігалось як за низької, так і за кімнатної температури за наявності коренів і перфорації в пакувальному матеріалі. Також зниження вмісту аскорбінової кислоти спостерігалось із збільшенням днів зберігання як за низької, так і за кімнатної температури. Гнучкий пакувальний матеріал (ПЕВД і ПП щільністю 100 і 200) не показав жодної значної різниці в зберіганні аскорбінової кислоти. Серед взаємодії між перфорацією, наявністю коренів, температурою, днями зберігання і пакувальним матеріалом, взаємодія між днями зберігання є значною разом з перфорацією (0,023), наявністю коренів (0,053) і температурою (0,00).

Висновки. Зразки гуньби, що зберігались без коренів в неперфорованому матеріалі, відображають найвище зберігання аскорбінової кислоти за низьких температур.

Ключові слова: *гуньба, листя, пакування, аскорбінова кислота.*

Застосування інфрачервоної спектроскопії у кількісному аналізі нових харчових емульгаторів

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Вступ. Актуальним є спектроскопічне дослідження синтезованих авторами у м'яких умовах нових емульгаторів з метою визначення в них моно- і діацилгліцеринів жирних кислот і доведення збереження есенціальних біологічно активних компонентів, гальмування процесів термоокиснення.

Матеріали та методи. Для дослідження синтезовано емульгатори ацилгліцеринної природи переестерифікацією рафінованої соняшникової олії у бінарному розчиннику в м'яких умовах (35...40 °С). Якісне і кількісне вивчення цих емульгаторів здійснено із застосуванням інфрачервоної спектроскопії на Фур'є-спектрометрі Perkin-Elmer Spectrum One FTIR Spectrometer методом роздавленої краплі.

Результати та обговорення. Вивчено інфрачервоні спектри нових емульгаторів ацилгліцеринної природи і зроблено аналіз характеристичних смуг поглинання, віднесених до відповідних типів валентних і деформаційних коливань триацилгліцеринів (1110 $см^{-1}$, 1173 $см^{-1}$, 1244 $см^{-1}$ - ν(C=O) естерів; 1377 $см^{-1}$ и 1416 $см^{-1}$ - δ_s(C–H) у групах $–CH_3$ и $–CH_2–$; 1736 $см^{-1}$ - ν(C=O) естерів; 2855 $см^{-1}$ і 2927 $см^{-1}$ - ν(C–H) у групах $–CH_2–$; 3009 $см^{-1}$ - ν_{as}(C–H) у групах –CH=CH– у цис-формі), гідроксильних груп моно-, діацигліцеринів жирних кислот (3435 $см^{-1}$), первинних спиртів (1061 $см^{-1}$).

Доведено наявність у складі нових емульгаторів моно-, діацигліцеринів жирних кислот і встановлено, що завдяки м'яким умовам їх одержання, вони не містять транс-ізомерів і в них збережені ненасичені кислоти у нативній формі.

На підставі визначених спектральних характеристик (пікової інтенсивності, ширини смуги поглинання, площі *S*, обмеженої кривою і горизонтальною нульовою лінією) побудовано градуювальний графік залежності величини *S* від масової частки моно-, діацигліцеринів у модельних композиціях Е471 з рафінованою соняшниковою олією. За допомогою отриманого рівняння прямої визначено сумарний вміст моно-, діацилгліцеринів карбонових кислот 52,6±0,2% у зразках емульгаторів ацилгліцеринної природи, синтезованих у бінарній системі гексан:ізопропанол із співвідношенням об'ємних часток розчинників 0,4:0,6. Співвідношення прийнято як раціональне для одержання нових харчових емульгаторів із вмістом моно-, діацилгліцеринів 54±1,2%.

Висновки. Пропонується застосовувати методу ІЧ-спектроскопії у кількісному аналізі моно-, діацигліцеринів жирних кислот в емульгаторах ряду ацилгліцеринів Е471.

Ключові слова: *емульгатор, ацилгліцерин, моноацилгліцерин, діацилгліцерин, спектроскопія, поглинання.*

Біологічно активоване зерно пшениці як функціональний компонент батончика глазурованого

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Вступ. Біологічно активоване зерно пшениці містить значну кількість вітамінів групи В, вітаміну Е, мінеральних речовин, харчових волокон і є перспективною сировиною для створення оздоровчих харчових продуктів.

Матеріали та методи. Досліджено зерно пшениці сортів Поліська, Миронівська 137, Безоста та зразки батончика на основі біологічно активованого

зерна пшениці. Вітамін С визначали титрометричним методом, вміст поліфенолів – спектрофотометричним аналізом.

Результати і обговорення. Найперспективнішим сортом пшениці за фізичними властивостями є Поліська. Зерно цього сорту є вирівняним за розмірами, його об'ємна маса – 788 г/л; енергія та здатність проростання зерна складають, відповідно, 97,2% та 98,8%; життєздатність зародка – 100%.

У процесі тривалого інтенсивного зволожування та подальшого пророщування зерна пшениці за температури 16˚С вміст водорозчинних вітамінів зростає на 8-66%. Кількість вітаміну С збільшується більш як у два рази. Вміст токоферолів зростає у десять разів.

З урахуванням принципів оздоровчого харчування розроблено рецептуру та розраховано норми витрат сировини для виготовлення 1 т батончика глазурованого на основі біологічно активованого зерна пшениці. Рецептура батончика не містить цукру, тому такий продукт може бути включений до харчового раціону людей, які страждають на порушення обміну речовин. Запропонований режим термічного оброблення основної сировини забезпечує мікробіологічну стійкість продукту. Енергетична цінність батончика складає 190,3 ккал; співвідношення основних енергогенних речовин – 11…13 % (білки): 21…23% (жири): 66% (вуглеводи). Ступінь забезпечення добової потреби в окремих мінеральних речовинах за рахунок споживання 100 г батончика від 13,1 до 53,6 %.

Кількість мікроорганізмів зразків, які зберігались у герметичних умовах протягом 10 діб, не перевищує встановлені стандартні норми.

Висновки. Рекомендується використання біологічно активованого зерна пшениці в технології оздоровчих харчових продуктів, зокрема батончика глазурованого.

Ключові слова: *БАД, пшениця, цукерка, батончик, здоров'я.*

Визначення вмісту йоду в сушених сланях ламінарії методом гальваностатичної кулонометрії

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Вступ. Розробка експрес-методик кількісного визначення загального вмісту йоду в сушених водоростях важлива для використання останніх як самостійно, так і у вигляді функціональних інгредієнтів в розроблюваних дієтичних продуктах харчування для профілактики йододефіцитних станів.

Матеріали та методи. Загальний вміст йоду в зразках сушених сланей ламінарії, відомих як комерційний продукт Kombu, визначено методом кулонометричного титрування в гальваностатичному режимі з потенціометричною індикацією точки кінця титрування у водних розчинах, отриманих шляхом мінералізації вихідної сировини.

Результати і обговорення. Йодовмісні сполуки (як органічного, так і неорганічного походження), які містяться в досліджуваних зразках, шляхом сухої лужної мінералізації були переведені у водний розчин у формі йодидів. Зазначена процедура проведена за оптимальних температурних умов в межах 420-480ºС, що забезпечує максимальний вихід продукту.

Стандартні водні розчини йодиду натрію в діапазоні концентрацій 15-300 мг/100 г розчину використані для валідації методики визначення концентрації йодидів методом гальваностатичної кулонометрії з електрогенерованим титрантом бромом. Стехіометрія реакції зазначеного титранту з йодидом у співвідношенні 1:1 підтверджена вивченням залежності необхідного для генерації брому кількості електрики від концентрації йодиду в розчині.

Отримані основні показники валідаційної оцінки, такі як специфічність, лінійність, аналітична область методики, правильність і відтворюваність, дозволили зробити висновок про можливість застосування гальваностатичної кулонометрії для визначення загального вмісту йодиду в досліджуваних розчинах.

Загальний вміст йоду в зразках Kombu, визначений за запропонованою методикою, склали величини 394, 476, 587 та 743 мг на 100г сухої речовини в залежності від серії партії виробника.

Висновки. Розроблена методика визначення загального вмісту йоду рекомендована як статистично обгрунтований експрес-метод для вирішення завдань, пов'язаних з кількісним визначенням даного елемента в харчових добавках на прикладі сушених морських водоростей.

Ключові слова: *йод, кулонометрія, титрометрія, ламінарія, водорость.*

Процеси і обладнання харчових виробництв

Визначення коефіцієнта ущільнення структури ультрафільтраційних мембран

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Вступ. Актуальність теми обумовлена відсутністю ультрафільтраційних установок малої продуктивності з використанням мембран типу ПАН, що пояснюється недостатньою кількістю експериментальних даних, необхідних для розрахунків процесів і устаткування ультрафільтраційної переробки харчової сировини.

Матеріали й методи. Досліджували помірно гідрофільні напівпроникні ультрафільтраційні мембрани на основі співполімерів акрилонітрилу типу ПАН марок ПАН-50 і ПАН-100. Для проведення експериментальних досліджень з вивчення процесу ультрафільтрації рідкої високомолекулярної полідисперсної системи (знежиреного молока) у тупиковому режимі, застосовували ультрафільтраційну лабораторну установку періодичної дії з внутрішнім рециклом.

Результати. Встановлена початкова продуктивність ультрафільтраційних мембран залежно від величини тиску ультрафільтрації. Так, за тиску ультрафільтрації 0,1 МПа початкова продуктивність Уф-Мембран ПАН-50 складає 120…125 дм^3/(м^2·год), в Уф-Мембран ПАН-100 трохи вище і складає 160…165 дм^3/(м^2·год). Зі збільшенням тиску ультрафільтрації до 0,25 МПа початкова продуктивність дослідних мембран збільшується більш ніж у 3 рази й складає, відповідно, 350…355 дм^3/(м^2·год) і 535…540 дм^3/(м^2·год). Зниження продуктивності мембрани ПАН-50 протягом 2,5·60^2 с складає 34,3 %, а мембрани ПАН-100 – 28,5 %.

Отримані експериментальні дані про коефіцієнти ущільнення структури досліджених мембран типу ПАН, які складають для мембран марки ПАН-50 – 0,18…0,2; для мембран марки ПАН-100 – 0,28…0,3.

Висновки. Встановлені коефіцієнти ущільнення ультрафільтраційних мембран типу ПАН. Результати досліджень свідчать про належну селективність мембран типу ПАН по молочному білку й доцільність їх застосування для ультрафільтраційної обробки білково-вуглеводної молочної сироватки.

Ключові слова: *мембрани, ультрафільтрація, пористість, ущільнення, концентрат, пермеат.*

Порівняльний аналіз знецукрення бурякової стружки різних профілів на промислових екстракторах

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Вступ. Досліджено процес екстрагування сахарози з бурякової стружки різних поперечних перерізів. Від профілю стружки залежать її якість, механічні характеристики, втрати сахарози в жомі, якість екстракту й енергетичні витрати.

Матеріали та методи. Досліджували бурякову стружку трикутного та жолобчатого профілів, отриману на відцентрових бурякорізках з використанням типових й спеціальних ножів. Дослідження проводили на двох паралельних виробничих лініях з екстракторами DC-12 за однакових технологічних режимів.

Результати. Проведено порівняння основних якісних характеристик бурякової стружки трикутного і жолобчатого профілів та визначено вміст сахарози в висолодженій стружці даних поперечних перерізів. Середнє значення відсотка браку в стружці трикутного профілю на 35 % менше, ніж у стружці жолобчатого профілю. Середнє значення шведського фактора для трикутного поперечного перерізу стружки на 42 % більше від даного показника для жолобчатого перерізу. Середнє значення вмісту сахарози в жомі для трикутного профілю становить 0,45 % до маси жому, а для жолобчатого – 0,50 %. Тобто зі стружки з трикутним поперечним перерізом більш, ніж на 10 % краще вилучається сахароза в промислових екстракторах за однакових технологічних умов.

Це пояснюється підвищеною механічною міцністю трикутної стружки (більшим моментом опору згину) та меншою кількістю браку. Підвищення механічної міцності стружки та зменшення кількості браку призводить до:

– протидії стисненню шару стружки потоком рідини та збільшення його пористості, що забезпечує належне омивання стружки екстрагентом;

– зменшення застійних зон в апараті;

– більш рівномірного переміщення сокостружкової суміші транспортними системами промислових екстракторів.

Висновки. Стружка трикутного профілю має кращі якісні характеристики, та краще висолоджується порівняно з жолобчатою за однакових технологічних умов.

Ключові слова: *буряк, стружка, різання, екстрагування.*

Аннотации

Безопасность пищевых продуктов

Неразрушающее выявление фальсификации пищевых продуктов как средство обеспечения здоровья и безопасности человечества

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Введение. Целью данного обзора является критическое рассмотрение основных понятий неразрушающего выявления фальсификации и подделки продуктов питания, которые в целом вызывают огромные ежегодные финансовые убытки во всем мире и являются одной из основных причин заболеваний человечества.

Материалы и методы. Литература, указанная в данном обзоре, была получена в результате поиска библиографической информации в CAB abstracts, AGRICOLA, SciFinder Scholar, Modern Language Association (MLA), American Psychological Association (APA), OECD / EEA database по инструментам, которые используются для экологической политики и управления природными ресурсами, и Web of Science.

Результаты и обсуждение. Фальсификация пищевых продуктов означает преднамеренное, обманное добавление посторонних, нестандартных или дешевых ингредиентов в продукты, разбавление или удаление некоторых ценных ингредиентов с целью увеличения прибыли. В современных условиях производители стремятся увеличить выпуск своей продукции зачастую путем изготовления и продажи некачественных и фальсифицированных продуктов.

Неразрушающее выявление фальсификации пищевых продуктов предполагает анализ образца и его существенных признаков без изменения физических и химических свойств.

Повышение качества и безопасности пищевых продуктов путем разработки научных методов обнаружения фальсификации является главным условием для поддержания здоровья потребителей. Точная объективная оценка качества и выявление фальсификации пищевых продуктов представляется важнейшей целью пищевой промышленности. В связи с совершенствованием технологии фальсификации продуктов важно быть в курсе современных, самых точных методов контроля их фальсификации. С этой целью рассматриваются основные понятия выявления фальсификации продуктов питания, принципы устройств и возможные практические применения современных методов неразрушающего выявления фальсификации продуктов питания; сравнительный анализ преимуществ и недостатков инструментальных методов, используемых в пищевых технологиях.

Каждый из рассмотренных методов обсуждается с точки зрения возможных различных консистенций продуктов – газов (свободного пространства вокруг продукта), свободно текущих жидкостей (соков), мутных и вязких жидкостей (меда и растительных масел) и интактных продуктов (фруктов и овощей).

Выводы. Результаты, освещенные в обзоре, рекомендуется использовать при контроле качества и безопасности пищевых продуктов.

Ключевые слова: *пищевой продукт, фальсификация, безопасность, качество, неразрушающий, аутентификация.*

Перспективы использования метода клиновидной дегидратации для оценки физико-химических свойств многокомпонентных водных растворов

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Введение. Актуальность работы обусловлена интенсификацией исследований явлений в капле в связи с развитием биотехнологий и практическим применением для оценивания качества жидких продуктов.

Материалы и методы. Исследован модельный раствор сыворотки крови, полученный на основе электрохимически активированных растворов. Изучение фаций в процессе их высыхания выполнено при помощи биологического микроскопа, оборудованного цифровым фотообъективом.

Результаты и обсуждение. Анализ фракций модельных растворов показал, что они соответствуют типичной картине фаций белково-солевых растворов – вдоль края находится белковый валик, а в середине - белково-солевая область. Обнаружено, что фации на основе электрохимически активированной воды – католита, анолита и их смеси – отличаются структурными элементами белково-солевой области. В частности в ней обнаружено большое количество правильных кристаллов соли с дендритными отростками. Кроме того, фации отличаются характером образованных «клеток» в белково-солевой области. Показано, что структурные особенности перенасыщенного раствора влияют на процесс роста кристаллов. Растворенные в активированной воде соли кристаллизируются с образованием правильных кристаллов в отличии от анизотропных микрокристаллов, которые образуются во время высыхания раствора на обычной воде. Поскольку pH и оксислительно-восстановительный потенциал смеси католита и анолита практически не отличаются от показателей дистиллированной воды, то на структурообразование фаций и ширину белкового валика определяющее влияние оказывают метастабильные свойства полученной воды, а именно нескомпенсированность гидратированных зарядов – свободных протонов и электронов. Показано, что время формирования белкового валика зависит от наличия ионов гидроксила и гидроксония в жидкости для приготовления модельного раствора: с увеличением содержания ионов гидроксила время формирования уменьшается, а с увеличением содержания ионов гидроксония – увеличивается по сравнению с неактивированной дистиллированной водой.

Выводы. Использование метода клиновидной дегидратации с использованием возможностей современной компьютерной техники позволяет получить набор показателей для идентификации различных жидкостей и изменения их свойств под действием внешних факторов.

Ключевые слова: *дегидратация, фация, анолит, католит, оценка.*

Пищевые технологии

Влияние способа хранения на физико-химические характеристики вина Вранац

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Введение. Вино Вранац производится из винограда сорта Вранац, который является наиболее важным для производства красных вин в Македонии. Вранац является местным сортом в Черногории, выращивается во всех виноградниках региона Вардар, однако имеет меньшее распространение в других виноградниках.

Материалы и методы. Было изучено два образца вина Вранац с законченной ферментацией в резервуаре из винограда одного сорта – Вранац (винодельня Стоби, расположенная в винном регионе Тиквеш). Вино Вранац изготовлено из урожая 2011 г. и отличается методом сохранения вина после его ферментации. Один образец сохраняется в резервуаре, тогда как второй, из урожая винограда того же года, был перемещен и сохранялся в дубовой бочке объемом 5000 литров.

Результаты и обсуждение. Концентрация ионов водорода pH в образцах вина, которое сохранялось в резервуаре и бочке, находится в пределах от 3,33 до 3,42, что является допустимым уровнем pH для красных вин. Что касается кислоты в целом, общая кислотность выше в том образце вина, которое сохранялось в бочке. Содержание летучих кислот имеет высшее значение в образце вина, которое хранилось в бочке. Содержание яблочной кислоты составляет 0 мг на литр в образце вина, которое хранилось в бочке, что свидетельствует о полном превращении яблочной кислоты в молочную кислоту. Содержание лимонной кислоты выше в образце из резервуара (0,38). Содержание уксусной кислоты выше в образце из бочки (0,48).

Высшее содержание сахаров в общем (5,1 г на литр) и уменьшение (0,95 г на литр) наблюдалось в образце из бочки. Количество алкоголя в протестированных образцах варьируется от 14,53 до 14,75 градусов, что соответствует требованиям Международной организации винограда и вина.

Что касается наличия SO_2, то, с одной стороны, повышенное присутствие SO_2 приводит к подавлению активности нежелательных микроорганизмов (что является желаемым), а с другой - повышенное содержание SO_2 подразумевает потенциальные проблемы со здоровьем для людей с астмой, что подтверждено научными исследованиями. Максимальное общее содержание SO_2 согласно требованиям Международной организации винограда и вина составляет 350 мг на литр, тогда как в протестированных образцах значение SO_2 в три раза меньше.

Выводы. Метод хранения вина Вранац из региона Тиквеш (которое хранилось в резервуаре и в бочке) влияет на физико-химические свойства протестированных образцов вина.

Ключевые слова: вино, Вранац, хранение, Македония.

Влияние обработки двух видов рыб из южных вод Ирана на их состав и энергетическую ценность

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Введение. Цель – исследование влияния различных способов приготовления (жарки, варки и выпекания) на химический и минеральный состав образцов рыб *Scomberoides commersonnianus* и *Spyraena jello*.

Материалы и методы. Свежий Scom beroides lysan (*Scomberoides commersonnianus*) и Sphyraenidae (*Spyraena jello*) были отобраны на рынке Бехбехан в Иране. При транспортировке в лабораторию пищевой химии Бехбеханского технологического университета образцы содержали в пластиковом контейнере. Для исследования биохимического состава рыбы были использованы методы AOAC.

Результаты и обсуждение. Содержание белка и липидов были выше у запеченной и жареной рыбы *S.commersonnianus* (74.29% и 20.20%), рыбы *S. jello* (88.12% и 17.77%) соответственно. Зольность в образцах рыбы *S.commersonnianus* колеблется от 9,80% до 15,34%, а *S. jello* - от 5,83% до 7,68%.

При сравнении содержания питательных веществ в вареных филе двух рыб оказалось, что рыба *S. jello* показала результаты лучше. Низкое содержание жира в вареном и запеченом *S. jello*, в основном, связано с поглощением воды, которая используется при подготовке карри. Такое же поглощение воды происходило и при жарке *S. jello*. Содержание белка в целом высокое, как и ожидалось, и связано с тем, что рыба является хорошим источником белка. Установлено, что более высокое содержание белка в жареной рыбе. Результат обусловлен тем, что мясо рыбы потеряло влагу. Еще одним доказательством этого является тот факт, что *S. jello*, приготовленная в карри и на пару, имела более низкое содержание белка, но при более высоком содержании влаги. Это может быть связано с поглощением воды во время приготовления, что вызывает разжижение мышечной ткани в анализированных образцах.

Химический состав сырого филе обоих видов рыб аналогичен предыдущим отчетам по исследованию рыбы. Непосредственный состав белков, жиров и золы *S. commersonnianus* и *S. jello* отличался во всех способах приготовления пищи. Стоит отметить, что существенного различия в содержании жира в отварном, запеченном и сыром филе рыбы не наблюдалось ($P > 0,05$). Повышенное содержание золы отмечено во всех приготовленных филе *S. commersonnianus* по сравнению с сырым филе рыбы. Соответственно, увеличение золы, белка и жира при приготовлении филе *Scomberoides commersonnianus* объясняется снижением влажности.

Вывод. Самый высокий уровень содержания белка, низкая жирность и калорийность были обнаружены в вареной рыбе, поэтому варка является лучшим способом приготовления пищи для здорового питания.

Ключевые слова: *рыба, Scomberoides lysan, Sphyraenidae, приготовление, здоровье.*

Влияние упаковки и условий хранения на сохранение аскорбиновой кислоты в листьях пажитника

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Введение. Настоящее исследование определило важность влияния упаковки и условий хранения на сохранение аскорбиновой кислоты в листьях пажитника.

Материалы и методы. Листья пажитника с корнями и без корней весом 100 грамм были собраны и упакованы в перфорированные и неперфорированные пакеты размером 30х25 см (750 $см^2$) четырех разных типов, а именно, ПЭВД-100, ПЭВД-200, ПП (полипропилен)-100 и ПП-200. Для перфораций были сделаны отверстия диаметром 0,59 см, которые покрывали площадь 1,87 $см^2$. Эти экземпляры сохранялись при комнатной температуре (от 14 до 35 ºС, влажность 50-60%) и низкой температуре (0-5%, влажность 80-90%) до допустимой нормы. Образцы были проанализированы за одинаковые интервалы времени на содержание аскорбиновой кислоты с использованием метода 2,6 дихлорофенол индофенола.

Результаты и обсуждение. Свежие листья пажитника содержали 51,4 мг аскорбиновой кислоты на 100 г веса. При низкой температуре в неперфорированных пакетах, образцы пажитника имели срок годности 6 дней и среднее значение сохранения аскорбиновой кислоты 80,95%. Упаковка образцов с корнями уменьшила срок годности до 4 дней и сохранила 66,05% аскорбиновой кислоты. Перфорация в упаковочном материале также уменьшила период сохранения до 4 дней в образцах пажитника как без корней, так и с корнями.

Образцы пажитника без корней и с корнями, которые сохранялись при комнатной температуре в неперфорированных пакетах показали максимальный срок годности 2 дня и среднее значение сохранения аскорбиновой кислоты 69,99% и 56,47% соответственно. Постепенное снижение среднего значения сохранения аскорбиновой кислоты наблюдалось как при низкой, так и при комнатной температуре с наличием корней и перфорацией в упаковочном материале. Также снижение сохранности аскорбиновой кислоты наблюдалось при увеличении дней хранения как при низкой, так и при комнатной температуре.

Гибкий упаковочный материал (ПЭВД и ПП плотностью 100 и 200), не показал значительной разницы в сохранения аскорбиновой кислоты. Среди взаимодействия между перфорацией, наличием корней, температурой, днями хранения и упаковочным материалом взаимосвязь межу днями хранения является значительной вместе с перфорацией (0,023), наличием корней (0,053) и температурой (0,000).

Выводы. Образцы пажитника, которые хранились без корней в неперфорированном материале, отображают наивысшую сохранность аскорбиновой кислоты при низких температурах.

Ключевые слова: *пажитник, лист, пакование, аскорбиновая кислота.*

Применение инфракрасной спектроскопии в количественном анализе новых пищевых эмульгаторов

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Введение. Актуальным является спектроскопическое исследование синтезированных авторами в мягких условиях новых эмульгаторов с целью определения в них содержания моно- и диацилглицеров жирных кислот и доказательства сохранения эссенциальных биологически активных компонентов, замедления процессов термоокисления.

Материалы и методы. Для исследования синтезированы эмульгаторы ацилглицеринной природы переэстерификацией рафинированного подсолнечного масла в бинарном растворителе в мягких условиях (35...40 °С). Качественное и количественное изучение этих эмульгаторов выполнено с использованием инфракрасной спектроскопии на Фурье-спектрометре Perkin-Elmer Spectrum One FTIR Spectrometer методом раздавленной капли.

Результаты и обсуждение. Изучено инфракрасные спектры новых эмульгаторов ацилглицеринной природы и сделан анализ характеристических полос поглощения, отнесенных к соответствующим типам валентных и деформационных колебаний триацилглицеринов (1110 $см^{-1}$, 1173 $см^{-1}$, 1244 $см^{-1}$ - ν(C=O) эстеров; 1377 $см^{-1}$ и 1416 $см^{-1}$ - δ_s(C–H) в группах $–CH_3$ и $–CH_2–$; 1736 $см^{-1}$ - ν(C=O) эстеров; 2855 $см^{-1}$ и 2927 $см^{-1}$ – ν(C–H) в группах $–CH_2–$; 3009 $см^{-1}$ - ν_{as}(C–H) в группах –CH=CH– в *цис*-форме), гидроксильных групп моно-, диациглицеринов жирных кислот (3435 $см^{-1}$), первичных спиртов (1061 $см^{-1}$).

Доказано присутствие в составе новых эмульгаторов моно-, диациглицеринов жирных кислот и установлено, что благодаря мягким условиям их получения они не содержат *транс*-изомеров и в них сохранены ненасыщенные кислоты в нативной форме.

На основе вычисленных спектральных характеристик (пиковой интенсивности, ширины полосы поглощения, площади *S*, ограниченной кривой и горизонтальной нулевой линией) построен градуировочный график зависимости величины *S* от массовой доли моно-, диациглицеринов в модельных композициях Е471 с рафинированным подсолнечным маслом. С помощью полученного уравнения прямой определено наибольшее суммарное содержание моно-, диацилглицеринов карбоновых кислот 52,6±0,2% в образцах эмульгаторов ацилглицеринной природы, синтезированных в бинарной системе гексан:изопропанол с соотношением объемных долей растворителей 0,4:0,6. Это соотношение принято как рациональное для получения новых пищевых эмульгаторов с содержанием моно-, диацилглицеринов 54±1,2%.

Выводы. Предложено применение метода ИК-спектроскопии в количественном анализе моно-, диациглицеринов жирных кислот в эмульгаторах ряда ацилглицеринов Е471.

Ключевые слова: *эмульгатор, ацилглицерин, моноацилглицерин, диацилглицерины, спектроскопия, поглощение.*

Биологически активированное зерно пшеницы как функциональный компонент батончика глазированного

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Введение. Биологически активированное зерно пшеницы содержит значительное количество витаминов группы В, витамина Е, минеральных веществ, пищевых волокон и является перспективным сырьем для создания оздоровительных пищевых продуктов.

Материалы и методы. Исследовано зерно пшеницы сортов Полесская, Мироновская 137, Безостая и образцы батончика на основе биологически активированного зерна пшеницы.

Витамин С определяли титрометрическим методом, содержание полифенолов - спектрофотометрическим анализом.

Результаты и обсуждение. Наиболее перспективным сортом пшеницы по физическим свойствам является Полесская. Зерно этого сорта выровнено по размерам, его объемная масса - 788 г/л; энергия и способность прорастания зерна составляют, соответственно, 97,2% и 98,8%; жизнеспособность зародыша – 100 %.

В процессе длительного интенсивного увлажнения и дальнейшего проращивания зерна пшеницы при температуре 16˚С содержание водорастворимых витаминов возрастает на 8 – 66%. Количество витамина С увеличивается более чем в два раза. Содержание токоферолов возрастает в десять раз.

С учетом принципов оздоровительного питания разработана рецептура и рассчитаны нормы расхода сырья для изготовления 1 т батончика глазированного на основе биологически активированного зерна пшеницы. Рецептура батончика не содержит сахара, поэтому такой продукт может быть включен в пищевой рацион людей, страдающих нарушениями обмена веществ. Предложенный режим термической обработки основного сырья обеспечивает микробиологическую устойчивость продукта. Энергетическая ценность батончика составляет 190,3 ккал; соотношение основных энергогенных веществ - 11 ... 13% (белки): 21 ... 23% (жиры): 66% (углеводы). Степень обеспечения суточной потребности в отдельных минеральных веществах за счет потребления 100 г батончика составляет от 13,1 до 53,6%.

Количество микроорганизмов образцов, которые хранились в герметичных условиях в течение 10 суток, не превышает установленные стандартные нормы.

Выводы. Рекомендуется использование биологически активированного зерна пшеницы в технологии оздоровительных пищевых продуктов, в частности батончика глазированного**.**

Ключевые слова: *БАД, пшеница, конфета, батончик, здоровье.*

Определение содержания йода в сушеных слоевищах ламинарии методом гальваностатической кулонометрии

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Введение. Разработка экспресс-методик количественного определения общего содержания йода в сушеных водорослях важна для использования последних как самостоятельно, так и в виде функциональных ингредиентов в разрабатываемых диетических продуктах питания для профилактики йоддефицитных состояний.

Материалы и методы. Общее содержание йода в образцах сушеных слоевищ ламинарии, известных как коммерческий продукт Kombu, определено методом кулонометрического титрования в гальваностатическом режиме с потенциометрической индикацией точки конца титрования в водных растворах, полученных путем минерализации исходного сырья.

Результаты и обсуждение. Содержащиеся в исследуемых образцах йодсодержащие соединения (как органической так и неорганической природы) путем сухой щелочной минерализации были переведены в водный раствор в форме йодидов. Указанная процедура была проведена при оптимальном температурном режиме в пределах 420-480ºС, обеспечивающем максимальный выход продукта.

Стандартные водные растворы йодида натрия в диапазоне концентраций 15-300 мг/100 г раствора использованы для валидации методики определения концентрации йодидов методом гальваностатической кулонометрии с электрогенерированным титрантом бромом. Стехиометрия реакции указанного титранта с йодидом в соотношении 1:1 подтверждена изучением зависимости необходимого для генерации брома количества электричества от концентрации иодида в растворе.

Полученные основные показатели валидационной оценки, такие как специфичность, линейность, аналитическая область методики, правильность и воспроизводимость, позволили сделать вывод о возможности применения гальваностатической кулонометрии для определения общего содержания йодида в исследуемых растворах.

Общее содержание йода в образцах Kombu, определенное по предложенной методике, составили величины от 394, 476, 587 и 743 мг в 100г сухого вещества в зависимости от серии партии производителя.

Выводы. Разработанная методика гальваностатической кулонометрии для определения общего содержания йода рекомендована как статистически обоснованный экспресс-метод для решения задач, связанных с количественным определением данного элемента в пищевых добавках на примере сушеных морских водорослей.

Ключевые слова: *йод, кулонометрия, титрометрия, ламинария, водоросль.*

Процессы и оборудование пищевых производств

Определение коэффициента уплотнения структуры ультрафильтрационных мембран

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Введение. Актуальность темы обусловлена отсутствием ультрафильтрационных установок малой производительности с использованием мембран типа ПАН, что объясняется недостаточным количеством экспериментальных данных, необходимых

для расчета процессов и оборудования ультрафильтрационной переработки пищевого сырья с использованием данных мембран.

Материалы и методы. При проведении исследований использовали умеренно гидрофильные полупроницаемые ультрафильтрационные мембраны на основе сополимеров акрилонитрила типа ПАН марок ПАН-50 и ПАН-100. Для проведения экспериментальных исследований по изучению процесса ультрафильтрации жидкой высокомолекулярной полидисперсной системы (обезжиренного молока) в тупиковом режиме, применяли ультрафильтрационную лабораторную установку периодического действия с внутренним рециклом.

Результаты. Установлена начальная производительность ультрафильтрационных мембран в зависимости от величины давления ультрафильтрации. Так, при давлении ультрафильтрации 0,1 МПа начальная производительность УФ-мембран ПАН-50 составляет 120…125 $дм^3/(м^2 \cdot ч)$, у УФ-мембран ПАН-100 несколько выше и составляет 160…165 $дм^3/(м^2 \cdot ч)$. При увеличении давления ультрафильтрации до 0,25 МПа начальная производительность исследуемых мембран увеличивается более чем в 3 раза и составляет соответственно 350…355 $дм^3/(м^2 \cdot ч)$ и 535…540 $дм^3/(м^2 \cdot ч)$. Определено, что снижение производительности мембраны ПАН-50 в течении $2,5 \cdot 60^2$ с составляет 34,3 %, а мембрана ПАН-100 – 28,5 %.

Получены экспериментальные данные о коэффициентах уплотнения структуры исследуемых мембран типа ПАН, которые составляют для мембран марки ПАН-50 – 0,18…0,2; для мембран марки ПАН-100 – 0,28…0,3.

Выводы. Результаты исследований свидетельствуют о соответствующей селективности мембран типа ПАН по молочному белку и целесообразности их применения для ультрафильтрационной обработки белково-углеводного молочного сырья.

Ключевые слова: *мембраны, ультрафильтрация, поритость, уплотнение, концентрат, пермеат.*

Сравнительный анализ обессахаривания свекловичной стружки различных профилей на промышленных экстракторах

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Введение. Исследован процесс экстрагирования сахарозы из свекловичной стружки различных поперечных сечений. От профиля стружки зависят ее качество, механические характеристики, потери сахарозы в жоме, качество диффузионного сока и энергетические затраты.

Материалы и методы. Исследовали свекловичную стружку треугольного и желобчатого поперечных сечений, полученную на центробежных свеклорезках с использованием типовых и специальных ножей. Исследования проводились на двух параллельных производственных линиях с экстракторами DC-12 при одинаковых технологических режимах.

Результаты. В работе проведено сравнение основных качественных характеристик свекловичной стружки треугольного и желобчатого профилей, а также определено содержание сахарозы в обессахаренной стружке данных поперечных сечений. Среднее значение процента брака в стружке треугольного профиля на 35 %

меньше, чем в стружке желобчатого профиля. Среднее значение шведского фактора для треугольных поперечных сечений стружки на 42 % больше данного показателя для желобчатых сечений. Среднее значение содержания сахарозы в жоме для треугольных профилей составляет 0,45 % к массе жома, а для желобчатых - 0,50 %. То есть стружка с треугольным поперечным сечением более, чем на 10% лучше обессахаривается в промышленных экстракторах при одинаковых технологических условиях. Это объясняется повышенной механической прочностью треугольной стружки (большим моментом сопротивлению на изгиб) и меньшим количеством брака. Повышение механической прочности стружки и уменьшение количества брака приводит к:

– противодействию сжатия слоя стружки потоком жидкости и увеличение его пористости, что обеспечивает хорошее обтекание стружки экстрагентом;

– уменьшению застойных зон в аппарате;

– более равномерному перемещению сокостружечной смеси транспортными системами промышленных экстракторов.

Выводы. Стружка треугольного поперечного сечения имеет лучшие качественные характеристики и лучше обессахаривается по сравнению с желобчатой при одинаковых технологических условиях.

Ключевые слова: свекла, стружка, резание, экстрагирование.

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Мови статей – англійська, українська, російська
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   Popovici C., Gitin L., Alexe P. (2013), Characterization of walnut (Juglans regia L.) green husk extract obtained by supercritical carbon dioxide fluid extraction, *Journal of Food and Packaging Science, Technique and Technologies,* 2(2), pp. 104-108.

2. Посилання на книгу:

Автори (рік), Назва книги (курсивом), Видавництво, Місто.

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Приклад:

2. Wen-Ching Yang (2003), *Handbook of fluidization and fluid-particle systems*, Marcel Dekker, New York.

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Приклади:

1. (2013), *Svitovi naukovometrychni bazy*, availableat:http://www1.nas.gov.ua/publications/q_a /Pages/scopus.aspx
2. Cheung T. (2011), *World's 50 most delicious drinks [Text]*, available at: http://travel.cnn.com/explorations/drink/worlds-50-most-delicious-drinks-883542

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УДК 663/664

Ukrainian Food Journal публікує оригінальні наукові статті, короткі повідомлення, оглядові статті, новини та огляди літератури.

Тематика публікацій в Ukrainian Food Journal:

Харчова інженерія	Процеси та обладнання
Харчова хімія	Нанотехнології
Мікробіологія	Економіка та управління
Фізичні властивості харчових продуктів	Автоматизація процесів
	Упаковка для харчових продуктів
Якість та безпека харчових продуктів	Здоров'я

Періодичність виходу журналу 4 номери на рік.

Результати досліджень, представлені в журналі, повинні бути новими, мати чіткий зв'язок з харчовою наукою і представляти інтерес для міжнародного наукового співтовариства.

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Рецензія рукопису статті. Матеріали, представлені для публікування в «Ukrainian Food Journal», проходять «Подвійне сліпе рецензування» двома вченими, призначеними редакційною колегією: один є членом редколегії і один незалежний учений.

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