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A review: Water and methods employed for moisture determination in food

Georgeta Sofia Popescu[1]*, Florina Radu[1], Ariana B. Velciov[1*], Luminița Pîrvulescu[2], Antoanela Cozma[3], Mihaela Maria Stănciugelu[4], Daniela-Florentina Marcu[5], Nicoleta G. Hădărugă[1]

[1]Faculty of Food Engineering, [2]Faculty of Management and Rural Tourism, [3]Faculty of Agriculture - University of Life Sciences"King Mihai I" from Timişoara; 300645 Timişoara, Calea Aradului No. 119, Romania
[4] Faculty of Sciences, "Lucian Blaga" University of Sibiu, 5-7 Ion Ratiu Street, Sibiu, 550012, Romania
[5] "1 Decembrie 1918" University of Alba Iulia, Str. Unirii nr. 15-17, 510009 – Alba Iulia, Romania

Abstract

Water is the ubiquitous substance in nature (in all existing materials on the earth and every living creature) and is an essential substance for life. Water plays an essential role in the physical and chemical functions of living organisms,

The water content is important for the processing and handling of the following product categories: food, pharmaceutical, cosmetic, personal care, household products, etc. Also, water has an important role in various industries such as in the various branches of the food industry, the pulp and paper industry, the pharmaceutical industry, etc.

The water content of certain materials can be very difficult to determine due to the complexity of the water molecule and its strong intermolecular bonding capabilities. Most of the time, the measuring water content is better defined by measuring moisture content.

Keywords: moisture content, direct method, refractometry

1.Introduction

Water is one of the most widespread substances on planet Earth, forming one of its shells, the hydrosphere. Three quarters of the earth's surface is covered with water. Water is the ubiquitous compound present in nature. Water is found in all existing materials on earth and is the fundamental basis for sustaining the life of all living beings, without water there would be no life. And in the atmosphere there is water, in the form of vapors in a small amount**.**.The high polarity of water molecules gives water high reactivity [1].

The quality of the products is directly influenced by water both by its quantitative content and by its state/ in the products. Water is found both in a free state and in a bounding state in food and non-food products [1,2,3,4].

The most used and important analytical method used in the processing and testing of food products is the determination of moisture [5,6,7,8].

The terms "moisture content" and "water content" have been used interchangeably in the literature to denote the amount of water present in food products and other substances. The special chemical reactivity and abundance of water cause moisture and moisture determination a major concern (interest) for many industries (such as food, paper, and plastics) where acceptable moisture levels vary between materials and, in some cases, small amounts of moisture can negatively affect product quality [1,9-11].

There are numerous methods of analysis used in laboratory determinations that differ from each other in applicability and value.

Corresponding authors: E-mail: sofiapopescu@usab-tm.ro

One of the fundamental methods used in food analysis and control is the determination of moisture (water) content.

This method provides information about food regarding its nutritional value, its perishability, information about food capability to be technologically processed, etc. Both moisture and dry matter are rated for all foods (dry matter is reciprocity of moisture). In general, the term "moisture" supposes the summation of all volatile substances that are removed simultaneously under the same conditions as water [1,5,8,9,11,12]. Although there are materials in the scientific literature for the determination of moisture (water determination), each category of food and non-food products presents certain distinctive features - although not essential - regarding the work procedure.

According to the nature of the evaluated compound, these methods have been described directly (water quantity assessment) or indirectly (measurement of dry matter after the removal of water). It is commonly thought that the indirect methods are faster, and yet they sometimes display a higher degree of inaccuracy [10]. The direct techniques involve a more laborious process, but are more exact (not taking into consideration the systematic error due to the addition of the other volatile substances to water.

This paper provides information on the properties of water, the importance of water (in food, nutrition and, food processing) as well as a presentation of the refracometric methods used for water determination.

2. Water. Water Properties.

Water is one of the most widespread substances on planet Earth, forming one of its shells, the hydrosphere. Water is the ubiquitous substance in nature (in all existing materials on the earth and every living creature) and is an essential substance for life. Water can exist in nature in three forms of aggregation: gaseous, liquid and solid. Water is the basic constituent of living organisms. Under normal conditions of temperature and pressure, water is an odourless, tasteless and colourless liquid. Water is an absolutely indispensable substance for life, regardless of its form, being one of the most universal solvents. From a chemical point of view, water is a compound of hydrogen and oxygen, having the crude chemical formula H_2O [13].

The water molecule is formed by strong covalent bonds that hold together the oxygen atom and two hydrogen atoms.

In the three-dimensional/spatial representation, oxygen is in the center of a tetrahedron, forming with the two hydrogen atoms a bond angle of 105^0 in liquid water and a greater angle of 109^o 6' in ice [13,14] .

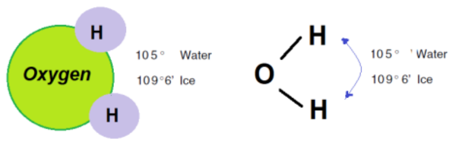

Figure 1. Bond angle in water and ice between hydrogen and oxygen atoms

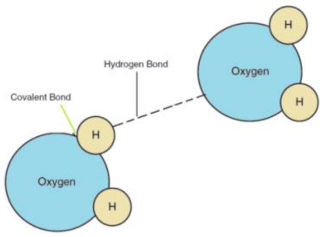

Figure 2. Covalent and hydrogen bonds in water molecules and ice

Water is found in the gaseous state in the form of monomolecular water vapor. In the liquid state, water is largely found in the form of dihydrol where/in which two water molecules are linked by the forces of the hydrogen bond. Water molecules are bound by hydrogen bond forces in the liquid water state. In the solid state, the degree of molecular association with water is different, existing in several solid forms as ices [1].

Water plays an essential role in the physical and chemical functions of living organisms, being a component of various tissues. Water is a universal solvent, dissolves the nutrients that the body receives through food and solubilizes mineral substances, making possible their action in the body. This compund transports nutrients into the cells, where they are metabolized; favors a series of enzymatic reactions in the cell; participate in the tertiary and quaternary structure of proteins [13,15].

A large amount of food products is processed by the human body in the process of substance exchange. The nature of the substances which make up in the composition of the food products is very different, as is their proportion.

Food products can be classified according to the preponderance of a certain group of chemical substances [5], as follows: foods with a predominance of protein compounds (eggs, milk and dairy products, meat, fish and their processing products), foods with a predominance preponderance of lipids content (dietary fats), with foods with a predominance of carbohydrate compounds (cereals and derivatives, legumes, vegetables and fruits, sugar and sweets, sugar products).

Between oxygen and each hydrogen atom are polar bonds, which have a partial ionic character of 40% [14]. Consequently, the electrons in the outer shell are distributed unequally between the oxygen and hydrogen atoms, each hydrogen atom attracting them more weakly than the oxygen atom. Therefore, each hydrogen atom is slightly positively charged and each oxygen atom is slightly negatively charged. Thus these atoms are capable of forming hydrogen bonds.

A hydrogen bond is a weak bond that forms between polar compounds in such a way that a hydrogen atom of one molecule is attracted to an electronegative atom of another molecule (Figure 2). The hydrogen bond is a weak bond compared to other types of chemical bonds (eg covalent or ionic bonds), but it is very important because it usually occurs in large numbers and therefore has a significant cumulative effect on the properties of the substance in which is found. Hydrogen bonds are not only formed between water molecules, between hydrogen and oxygen, but are common bonds that form between hydrogen and another electronegative atom in many other types of molecules that are important in foods, such as carbohydrates, starches, fats, pectins and proteins [13, 14].

Due to the V-shaped spatial structure, each water molecule can form up to four hydrogen bonds with its nearest neighbors. The oxygen atom can form two hydrogen bonds, and each hydrogen atom can form a single hydrogen bond, resulting in a three-dimensional lattice in ice.

The ice has a dynamic structure, and hydrogen bonds are continuously broken and renewed between different water molecules.Also, liquid water contains hydrogen bonds that are continuously breaking and reforming creating a diversity of ordered (continuously changing) structures [14].

3. Water in food system

For the human body, water is indispensable (vital), fulfilling various roles such as: solvent and transport medium (allows the absorption of soluble substances and the elimination of some metabolic products); participates in numerous biochemical reactions; role in thermoregulation; role of lubricant (eg. synovial fluid); protection role (eg. tears) etc [15, 16, 17].

Some foods consist almost exclusively of a single substance but generally contain the five major groups of chemicals: water, minerals, carbohydrates, lipids and proteides. Also, the composition of food products includes vitamins, pigments, acids, enzymes, tanning, essential oils, glucosides, alkaloids, hormones, phytoncides, etc. It should be tahen into consideration that not all foods have significant nutritional potential, instead they have taste, aromatic or other properties that favorably influence the feeding process [16,17,18].

Among the natural substances in food, water is the most dynamic element, being found depending on the product - in the limits of 0.05 - 95%. Water together with minerals, carbohydrates and proteins is a favorable environment for the development of microorganisms and therefore the reason of foods reach in water are easily altered. Their stability is inversely proportional to the water content and therefore, the less water they contain, the more their stability increases [16,19].

The water used in the manufacture of food products must have the same quality conditions as the drinking water. As a technological agent, water does not influence the water content of the product, but facilitates its production. For example, pasta is made from griffin flour with a moisture content of 14%. For them, a dough with a humidity of 30% must be obtained, which is kneaded, dried and from which pasta with a final humidity of 11-13% is obtained [3,15,16,20-22]. All foreign substances in the water, once penetrated into the food, remain there even if during the technological process the water is removed from the product. Water directly influences the quality of products both in quantity and condition. In food products, water is found in the free state (free water) and in the connected state (bond water).

Having the role of dissolving other chemicals in its mass, water is a nutrient necessary for the activity of bacterial enzymes.

Therefore, the content in water of food is monitoredit and specified in standards, as an essential element according to which the conditions and shelf life of food are established.

Also,the water content influences the consumer's perception of some characteristics of the products (eg. freshness) [4,14,19-23].

Water from food products can be found in two forms: free water and bound water. Nevertheless, water can be classified into at least three forms [1,4,7,17,22,24]:

- ***free water existing*** in the intergranular spaces and in the pores of the material. This water serves as a medium of dispersion for hydrophilic macromolecules (e.g. proteins, gums, and phenolic substances) to form molecular or colloidal solutions, and as a solvent for crystalline compounds.
- ***hygroscopic water*** is water that is adsorbed as a very thin, mono- or polymolecular layer on the internal or external surfaces of solid components (such as starch, pectins, cellulose and proteins) by molecular forces or by capillary condensation. Water molecules of this type and the absorbing macromolecules are strongly associated through absorption forces that are attributed to the formation of hydrogen bonds or to Van der Waals forces.
- "***bound water***" is water that is in chemical combination as water of hydration, Carbohydrates (e.g. dextrose, maltose, lactose) form stable monohydrates, and salts (e.g. potassium tartrate) also form hydrates.

Free water is in the form of cell juice or micro drops and is presented as a real solution. It can be extracted from the product by pressing or drying. Hygroscopic water is also a free water retained by absorption in the microcapillation or on the surface of the product. All enzymatic processes, some enzymatic reactions, the development of microorganisms, can take place only in the presence of free water [14,16, 17,23].

There is a permanent exchange between the water in the product and the water in the atmosphere until the equilibrium humidity is reached.

Food water is bound in different forms, depending on the nature of the way of binding, differing: physically bound water, physico-chemical and chemical.

Physically bound water is specific to porous materials and is retained by mechanical forces by hygroscopic materials by surface and capillary forces [16,24].

Water retained in the microcapillary (radius <10-5 cm) is called hygroscopic water and that in macrocapillary (radius> 10-5 cm) is also called free or surface moisture.

Capillary water represents 70% of the total moisture content of food products re and due to the weak connection with the product it is easily removed by evaporation [17,19,25-28].

Physically and chemically bound water is a more stable form of water binding, being present in most foods, without being closely related to the material. This type of connection is made by adsorbent bonding and by osmotic or structural bonding.

The adsorbent bond is specific to surface phenomen, has a medium intensity and is quite difficult to reverse. The osmotic connection is made when the covering of the cells comes into direct contact with water, for example by immersion. It is a weaker and more reversible intensity.

Chemically bound water is characterized by ionic or molecular bonds being determined in strictly stoichiometric quantities. Water retention is done in the form of water of crystallization or constitution. Constitution water is an integral part of the molecule of chemicals itself [14,21]. The chemical binding of water in biological environments is the strongest and can not be eliminated by classical dehydration processes, but only by calcination. Food water can change from one form to another: in the manufacture of cheese, for example, free milk water passes into bound water [14,18,21-24,29]. Bound water is the form of water that remains unchanged when food is subjected to a certain heat treatment. Concentration of bound water varies from one food to another. Products that have a high water content are easily perishable, provide favourable conditions for the development of pathogenic microorganisms and therefore their long-term storage requires special conditions at low temperatures. This category includes meat and fish, which are easily attacked by putrefactive bacteria, fruits and vegetables that are attacked by mold. A decrease in the water content of some products below the normal value, causes a decrease in the value of those products, for example fruits and vegetables [16,17,23].

4. Moisture determination methods

One of the essential methods used in food control is moisture determination (water content determination).

Moisture determination is a method that provides information on its nutritional value, perishability, value of its digestive use, as well as information on its technological efficiency [2,6,17]. The determination of water in various products can be done by physical or chemical methods, and by direct or indirect methods.

The water content (respectively dry substances – obtained by difference) is an indicator of quality, especially for products where the correction of humidity to optimal values is possible and necessary (eg. cereals, cheeses, meat preparations, sugary products, etc.) [3, 16].

A flawless technique for the assessment of humidity levels should have the following qualities: (1) speed, (2) applicability to the widest range of materials, (3) can be carried out without requiring a technical background, by anyone who receives only a brief training, (4) utilizes readily obtainable equipment with reduced initial investment and low cost per test, (5) shows correctness and reasonable precision, and (6) involves no operational risks [1,11,12,22].

The water content is an indicator of foods quality, representing a criterion of stability. In standards or in other quality norms related to foodstuffs, the water content is specified as a percentage, in the form of moisture (direct expression), as the maximum limit (max.%) or by the total amount of dry matter in the product (indirect expression), also as a percentage, as the minimum limit (% min.).

Analytical methods of humidity (moisture) determination can be classified in two ways (see table 1) [1,10-12,22]. One of the classification manner is based on analytical principles, and accordingly, there are methods based on sample drying (drying methods), methods based on distillation (distillation methods), physical and chemical methods. Another way of classifying the methods depends on the procedures in direct and indirect methods (procedures).

Tabel 1. Classification of analytical methods for moisture determination by procedure type and major principles [1,10]

	Procedures type	Principle type	Method
1.	Direct methods	Drying method	• Gravimetric methods ▪ oven drying ▪ vacuum drying ▪ freeze-drying ▪ chemical desiccation
		Distillation Method	Azeotropic distillation
		Chemical Methods	Karl Fischer titration Generation of Acetylene Heat on mixing with H_2SO_4
		Physical Methods	Gas chromatography Refractometer
2.	Indirect methods	Physical Methods	Infrared Absorption Near Infrared Reflectance Nuclear Magnetic Resonance Neutron Scattering Electrical Microwave absorption Dielectric capacitance Conductivity

In direct methods, the removal of water from solid food samples is normally done by drying, distillation, etc., and its amount is measured by weighing, titration, etc. [1,8,10]. In contrast, in indirect methods, wet solid properties are measured and water (moisture) is not removed from the sample [1,10,28-30]. The properties of the wet solid depend on the amount of water or the number of hydrogen atoms. In the case of indirect methods for the determination of water, it is necessary to calibrate against standard moisture values that have been accurately determined using one or more direct methods. Therefore, the direct measurement values used for calibration determine the accuracy of indirect methods [30,34].

The assessment of humidity by direct methods is done with precision (obtaining precise and even absolute values) [1,10,19,30]. Unfortunately, these methods require a long time (they are slow) and are mainly manual.In contrast to these, indirect methods usually are fast, do not destroy the investigated material and offer the possibility of continuous determination through automation.

5. Physical methods. Refractometry

Quantitative methods are divided into three large groups: gravimetric, volumetric and physico-chemical methods. Physico-chemical methods are those methods of analysis whose determinations are based on highlighting some physico-chemical properties specific to the substance being analyzed, which allow quantitative evaluation [5,31-33].

Physicochemical methods are called indirect methods of analysis, according to the classifications in the scientific literature/analytical chemistry. Thus, refractometry is an indirect method of analysis, being a physico-chemical method.Using physical methods, a parameter is determined, a property that is obtained through certain mathematical relationships according to the classifications in the scientific literature, analytical chemistry. Through physical methods, a parameter is determined, a property that is obtained through certain mathematical relationships according to the classifications in the scientific literature, analytical chemistry,

The refractometry is an optical method that is based on the phenomena of refraction or total reflection of a beam of light radiation at the boundary of separation between two media with different refractive indices [32-34].

This technique measures how light is refracted as it passes through a certain substance. The ratio of the speed of light in a vacuum to its speed in another substance is defined as the refractive index of the substance. The refractive index is a constant quantity for a pure substance under standard conditions of temperature and pressure. Refractive index is defined as the ratio between the sine of the angle of the light ray (incident) concerning the vertical (i) and the sine of the angle of refraction (r) [32-35].

$$RI = \frac{\sin i}{\sin r}$$

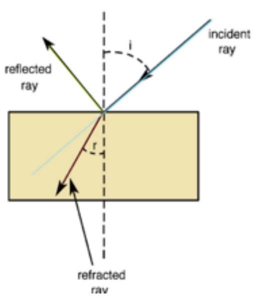

Figure 3. Concepts of refractometry (Reflection and refraction)

The refractive index ((RI)) is a dimensionless constant specific to each substance. Its value depends on the quantity, size and physical structure of the dissolved particles.

The refractive index can be used to describe the nature of the food (such as syrup, oil, honey, or other liquid).

With the help of this method, the concentration of a solution can be determined and thus the percentage of dry substance or water can be established [32]. The determinations are made with the help of devices called refractometers, the most used being the Abbé refractometer.

Some refractometers are designed to only provide results as refractive indices. There are certain refractometers (especially portable units) that are quick to use and are equipped with calibrated scales to read the percentage solids, the percentage sugars (carbohydrates), and the like, depending on the products they are intended for. Measuring instruments (refractometers) are supplied with the necessary tables to convert values and adjust for temperature differences.

The refractive index is strongly influenced by temperature, so the determinations must be made at a well-regulated, constant temperature. For this purpose, the refractometers are usually coupled with an ultra-thermostated bath. Differential Refractometry, which does not require temperature control, can be used because this type of instrument records the difference between the sample and the reference.Some of the advantages of this refractometric method to determine the moisture in food products are listed/shown in table 2.

In refractometry, it is essential that the temperature be kept constant because both the refractive index and the density or specific gravity are sensitive to temperature [1].

The refractometric analysis is used to determine the concentration of a substance in a solution according to the refractive index. The refractometric method is applied to determine the concentrations of solutions in the sugar industry, canned vegetables, sugar products, glucose, etc.; determine the soluble dry substance and sugar concentration if sugars predominate in the soluble extract of a food product and non-sugar is constant. Refractometry is also used to determine the refractive index of fats, respectively to determine the fat content of a food product [1,34].

Table 2. Avantaje si dezavantaje ale metodei refractometrice de analiză

Advantages	Disadvantages
• It is a quick method (Determination takes only 5-10 minutes)	• It is sensitive to temperature
• It requires simple and cheap tools (instrumentation) and I has a low level of maintenance	• It requires the uniformity of the type of samples
• Refractometers are easy to operate -they do not require much skill to operate)	
• It has simple and reasonable accuracy	• Some assays require preparation of the tissue (ie meat) slurry
• It's a great method for fruit, milk, and high-carb foods	

Moisture in liquid sugar and condensed milk products can be determined using a Brix hydrometer (for sugar content), or a refractometer. The refractometric method is fast and accurate if performed correctly and no crystalline solids are evident, (AOAC, for solids in syrups). Refractometry is valuable in determining soluble solids in fruit and fruit products [34-37]. This method has been used for meat moisture analysis [1,38].

Refractometers are used in the laboratory or as portable units (hand-held units). as well as in a liquid processing line, where refractometers can be installed to monitor the °Brix (grad Brix; ^{0}B) of products such as carbonated soft drinks, dissolved solids in orange juice, and the percentage of solids in milk [1,33,35,39].

Applications of refracometric method in food industries

Refractometry methods are used to assess the ripeness of fruits, vegetables, cane and sugar beets before harvest - determining the maturity index of the fruit. This technique measures the sugar (glucydic) content of the fruit in degrees Brix (^{0}B, ^{0}Brix).

The Degree Brix of a liquid is equal to one (10 Brix =1% Brix) if the liquid has the same refractive index as a solution of 1 g of sucrose in 100 g of sucrose water solution [35]. It is used especially for grapes from vineyards. This procedure is mainly used for grapes in the vineyards to find out the ripening time (the maturity of the grapes) to be picked and used to obtain wine.

This methods are used to determine the alcohol content of wine and beer during the fermentation procces. Special refractometers are required which are equipped with calibrated scales to give the alcohol content directly [32,34].

This method can be used to checked quality of honey. (requires tables with the correlation between refractometric indices and water content, found in the literature [34, 39].

For honey there are also special types of refractometers which directly offer the amount of water in honey. This type of refractometer is preferred by bee keepers.

The water content of the honey should be low, because this ensures a better and longer shelf life for the product. In order to avoid honey fermentation, it is necessary that its water content be low. A high water content (over 20%) in honey can favor honey fermentation [33-35].

Refractometry method is used to monitor and control the quality of yoghurt, jam, fruit extract, syrup, coffee extract, chocolate, milk, baby food etc.[35]. For different types of oils and fats, the refractive index is an indicator of product purity. The purity of the product is evaluated by comparing the values read/recorded (on the refractometer) with those of the standard [35,38].

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human or animal subjects (if exist) respect the specific regulation and standards.

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