

3. Determination of Moisture and Total Solids

3.1 Introduction

Moisture content is one of the most commonly measured properties of food materials. It is important to food scientists for a number of different reasons:

- *Legal and Labeling Requirements.* There are legal limits to the maximum or minimum amount of water that must be present in certain types of food.
- *Economic.* The cost of many foods depends on the amount of water they contain - water is an inexpensive ingredient, and manufacturers often try to incorporate as much as possible in a food, without exceeding some maximum legal requirement.
- *Microbial Stability.* The propensity of microorganisms to grow in foods depends on their water content. For this reason many foods are dried below some critical moisture content.
- *Food Quality.* The texture, taste, appearance and stability of foods depends on the amount of water they contain.
- *Food Processing Operations.* A knowledge of the moisture content is often necessary to predict the behavior of foods during processing, e.g. mixing, drying, flow through a pipe or packaging.

It is therefore important for food scientists to be able to reliably measure moisture contents. A number of analytical techniques have been developed for this purpose, which vary in their accuracy, cost, speed, sensitivity, specificity, ease of operation, etc. The choice of an analytical procedure for a particular application depends on the nature of the food being analyzed and the reason the information is needed.

3.2 Properties of Water in Foods

The moisture content of a food material is defined through the following equation:

$$\% \text{Moisture} = (m_w / m_{\text{sample}}) \times 100$$

Where m_w is the mass of the water and m_{sample} is the mass of the sample. The mass of water is related to the number of water molecules (n_w) by the following expression: $m_w = n_w M_w / N_A$, where M_w is the molecular weight of water (18.0 g per mole) and N_A is Avadagro's number (6.02×10^{23} molecules per mole). In principle, the moisture content of a food can therefore be determined accurately by measuring the number or mass of water molecules present in a known mass of sample. It is not possible to directly measure the number of water molecules present in a sample because of the huge number of molecules involved. A number of analytical techniques commonly used to determine the moisture content of foods are based on determinations of the mass of water present in a known mass of sample. Nevertheless, as we will see later, there are a number of practical problems associated with these techniques that make highly accurate determinations of moisture content difficult or that limit their use for certain applications. For these reasons, a number of other analytical methods have been developed to measure the moisture content of foods that do not rely on direct measurement of the mass of water in a food. Instead, these techniques are based on the fact that the water in a food can be distinguished from the other components in some measurable way.

An appreciation of the principles, advantages and limitations of the various analytical techniques developed to determine the moisture content of foods depends on an understanding of the molecular characteristics of water. A water molecule consists of an oxygen atom covalently bound to two hydrogen atoms (H_2O). Each of the hydrogen atoms has a small positive charge (δ^+), while the oxygen atom has two lone pairs of electrons that each has a small negative charge (δ^-). Consequently, water molecules are capable of forming relatively strong hydrogen bonds ($\text{O}-\text{H}^{\delta^+} \cdots \delta^- \text{O}$) with four neighboring water molecules. The strength and directionality of these hydrogen bonds are the origin of many of the unique physicochemical properties of water. The development of analytical techniques to determine the moisture content of foods depends on being able to distinguish water (the "analyte") from the other components in the food (the "matrix"). The characteristics of water that are most commonly used to achieve this are: its relatively low boiling point; its high polarity; its ability to undergo unique chemical reactions with certain reagents; its unique electromagnetic absorption spectra; and, its characteristic physical properties (density, compressibility, electrical conductivity and refractive index).

Despite having the same chemical formula (H_2O) the water molecules in a food may be present in a variety of different molecular environments depending on their interaction with the surrounding molecules. The water molecules in these different environments normally have different physicochemical properties:

- *Bulk water.* Bulk water is free from any other constituents, so that each water molecule is surrounded only by other water molecules. It therefore has physicochemical properties that are the same as those of pure water, e.g., melting point, boiling point, density, compressibility, heat of vaporization, electromagnetic absorption spectra.

- *Capillary or trapped water*: Capillary water is held in narrow channels between certain food components because of capillary forces. Trapped water is held within spaces within a food that are surrounded by a physical barrier that prevents the water molecules from easily escaping, *e.g.*, an emulsion droplet or a biological cell. The majority of this type of water is involved in normal water-water bonding and so it has physicochemical properties similar to that of bulk water.
- *Physically bound water*: A significant fraction of the water molecules in many foods are not completely surrounded by other water molecules, but are in molecular contact with other food constituents, *e.g.* proteins, carbohydrates or minerals. The bonds between water molecules and these constituents are often significantly different from normal water-water bonds and so this type of water has different physicochemical properties than bulk water *e.g.*, melting point, boiling point, density, compressibility, heat of vaporization, electromagnetic absorption spectra.
- *Chemically bound water*: Some of the water molecules present in a food may be chemically bonded to other molecules as water of crystallization or as hydrates, *e.g.* $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$. These bonds are much stronger than the normal water-water bond and therefore chemically bound water has very different physicochemical properties to bulk water, *e.g.*, lower melting point, higher boiling point, higher density, lower compressibility, higher heat of vaporization, different electromagnetic absorption spectra.

Foods are heterogeneous materials that contain different proportions of chemically bound, physically bound, capillary, trapped or bulk water. In addition, foods may contain water that is present in different physical states: gas, liquid or solid. The fact that water molecules can exist in a number of different molecular environments, with different physicochemical properties, can be problematic for the food analyst trying to accurately determine the moisture content of foods. Many analytical procedures developed to measure moisture content are more sensitive to water in certain types of molecular environment than to water in other types of molecular environment. This means that the measured value of the moisture content of a particular food may depend on the experimental technique used to carry out the measurement. Sometimes food analysts are interested in determining the amounts of water in specific molecular environments (*e.g.*, physically bound water), rather than the total water content. For example, the rate of microbial growth in a food depends on the amount of bulk water present in a food, and not necessarily on the total amount of water present. There are analytical techniques available that can provide some information about the relative fractions of water in different molecular environments (*e.g.*, DSC, NMR, vapor pressure).

3.3. Sample preparation

Selection of a representative sample, and prevention of changes in the properties of the sample prior to analysis, are two major potential sources of error in any food analysis procedure. When determining the moisture content of a food it is important to prevent any loss or gain of water. For this reason, exposure of a sample to the atmosphere, and excessive temperature fluctuations, should be minimized. When samples are stored in containers it is common practice to fill the container to the top to prevent a large headspace, because this reduces changes in the sample due to equilibration with its environment. The most important techniques developed to measure the moisture content of foods are discussed below.

3.4. Evaporation methods

3.4.1. Principles

These methods rely on measuring the mass of water in a known mass of sample. The moisture content is determined by measuring the mass of a food before and after the water is removed by evaporation:

$$\% \text{Moisture} = \frac{M_{\text{INITIAL}} - M_{\text{DRIED}}}{M_{\text{INITIAL}}} \times 100$$



Here, M_{INITIAL} and M_{DRIED} are the mass of the sample before and after drying, respectively. The basic principle of this technique is that water has a lower boiling point than the other major components within foods, *e.g.*, lipids, proteins, carbohydrates and minerals. Sometimes a related parameter, known as the *total solids*, is reported as a measure of the moisture content. The total solids content is a measure of the amount of material remaining after all the water has been evaporated:

$$\% \text{Total Solids} = \frac{M_{\text{DRIED}}}{M_{\text{INITIAL}}} \times 100$$



Thus, $\% \text{Total Solids} = (100 - \% \text{Moisture})$. To obtain an accurate measurement of the moisture content or total solids of a food using evaporation methods it is necessary to remove all of the water molecules that were originally present in the food, without changing the mass of the food matrix. This is often extremely difficult to achieve in practice because the high temperatures or long times required to remove all of the water molecules would lead to changes in the mass of the food matrix, *e.g.*, due to volatilization or chemical changes of some components. For this reason, the drying conditions used in evaporation methods are usually standardized in terms of temperature and time so as to obtain results that are as accurate and reproducible as possible given the practical constraints. Using a standard method of sample preparation and analysis helps to minimize sample-to-sample variations within and between laboratories.

3.4.2. Evaporation Devices

The thermal energy used to evaporate the water from a food sample can be provided directly (*e.g.*, transfer of heat from an oven to a food) or indirectly (*e.g.*, conversion of electromagnetic radiation incident upon a food into heat due to absorption of energy by the water molecules).

Convection and forced draft ovens. Weighed samples are placed in an oven for a specified time and temperature (*e.g.* 3 hours at 100 °C) and their dried mass is determined, or they are dried until they reach constant mass. The thermal energy used to evaporate the water is applied directly to the sample *via* the shelf and air that surround it. There are often considerable temperature variations within convection ovens, and so precise measurements are carried out using *forced draft ovens* that circulate the air so as to achieve a more uniform temperature distribution within the oven. Samples that contain significant quantities of carbohydrates that might undergo chemical changes or volatile materials other than water should not be dried in a convection or forced draft oven. Many official methods of analysis are based on forced draft ovens.

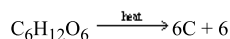
Vacuum oven. Weighed samples are placed under reduced pressure (typically 25-100 mm Hg) in a vacuum oven for a specified time and temperature and their dried mass is determined. The thermal energy used to evaporate the water is applied directly to the sample *via* the metallic shelf that it sits upon. There is an air inlet and outlet to carry the moisture lost from the sample out of the vacuum oven, which prevents the accumulation of moisture within the oven. The boiling point of water is reduced when it is placed under vacuum. Drying foods in a vacuum oven therefore has a number of advantages over conventional oven drying techniques. If the sample is heated at the same temperature, drying can be carried out much quicker. Alternatively, lower temperatures can be used to remove the moisture (*e.g.* 70°C instead of 100 °C), and so problems associated with degradation of heat labile substances can be reduced. A number of vacuum oven methods are officially recognized.

Microwave oven. Weighed samples are placed in a microwave oven for a specified time and power-level and their dried mass is weighed. Alternatively, weighed samples may be dried until they reach a constant final mass - analytical microwave ovens containing balances to continuously monitor the weight of a food during drying are commercially available. The water molecules in the food evaporate because they absorb microwave energy, which causes them to become thermally excited. The major advantage of microwave methods over other drying methods is that they are simple to use and rapid to carry out. Nevertheless, care must be taken to standardize the drying procedure and ensure that the microwave energy is applied evenly across the sample. A number of microwave oven drying methods are officially recognized.

Infrared lamp drying. The sample to be analyzed is placed under an infrared lamp and its mass is recorded as a function of time. The water molecules in the food evaporate because they absorb infrared energy, which causes them to become thermally excited. One of the major advantages of infrared drying methods is that moisture contents can be determined rapidly using inexpensive equipment, *e.g.*, 10-25 minutes. This is because the IR energy penetrates into the sample, rather than having to be conducted and convected inwards from the surface of the sample. To obtain reproducible measurements it is important to control the distance between the sample and the IR lamp and the dimensions of the sample. IR drying methods are not officially recognized for moisture content determinations because it is difficult to standardize the procedure. Even so, it is widely used in industry because of its speed and ease of use.

3.4.3. Practical Considerations

- Sample dimensions.** The rate and extent of moisture removal depends on the size and shape of the sample, and how finely it is ground. The greater the surface area of material exposed to the environment, the faster the rate of moisture removal.
- Clumping and surface crust formation.** Some samples tend to clump together or form a semi-permeable surface crust during the drying procedure. This can lead to erroneous and irreproducible results because the loss of moisture is restricted by the clumps or crust. For this reason samples are often mixed with dried sand to prevent clumping and surface crust formation.
- Elevation of boiling point.** Under normal laboratory conditions pure water boils at 100 °C. Nevertheless, if solutes are present in a sample the boiling point of water is elevated. This is because the partial vapor pressure of water is decreased and therefore a higher temperature has to be reached before the vapor pressure of the system equals the atmospheric pressure. Consequently, the rate of moisture loss from the sample is slower than expected. The boiling point of water containing solutes (T_b) is given by the expression, $T_b = T_0 + 0.51m$, where T_0 is the boiling point of pure water and m is the molality of solute in solution (mol/kg of solvent).
- Water type.** The ease at which water is removed from a food by evaporation depends on its interaction with the other components present. Free water is most easily removed from foods by evaporation, whereas more severe conditions are needed to remove chemically or physically bound water. Nevertheless, these more extreme conditions can cause problems due to degradation of other ingredients which interfere with the analysis (see below).
- Decomposition of other food components.** If the temperature of drying is too high, or the drying is carried out for too long, there may be decomposition of some of the heat-sensitive components in the food. This will cause a change in the mass of the food matrix and lead to errors in the moisture content determination. It is therefore normally necessary to use a compromise time and temperature, which are sufficient to remove most of the moisture, but not too long to cause significant thermal decomposition of the food matrix. One example of decomposition that interferes with moisture content determinations is that of carbohydrates.



The water that is released by this reaction is not the water we are trying to measure and would lead to an overestimation of the true moisture content. On the other hand, a number of chemical reactions that occur at elevated temperatures lead to water absorption, *e.g.*, sucrose hydrolysis (sucrose + H₂O $\xrightarrow{\text{heat}}$ fructose + glucose), and therefore lead to an

underestimation of the true moisture content. Foods that are particularly susceptible to thermal decomposition should be analyzed using alternative methods, *e.g.* chemical or physical.

6. *Volatilization of other food components.* It is often assumed that the weight loss of a food upon heating is entirely due to evaporation of the water. In practice, foods often contain other volatile constituents that can also be lost during heating, *e.g.*, flavors or odors. For most foods, these volatiles only make up a very small proportion and can therefore be ignored. For foods that do contain significant amounts of volatile components (*e.g.* spices and herbs) it is necessary to use alternative methods to determine their moisture content, *e.g.*, distillation, chemical or physical methods.
7. *High moisture samples.* Food samples that have high moisture contents are usually dried in two stages to prevent "spattering" of the sample, and accumulation of moisture in the oven. Spattering is the process whereby some of the water jumps out of the food sample during drying, carrying other food constituents with it. For example, most of the moisture in milk is removed by heating on a steam bath prior to completing the drying in an oven.
8. *Temperature and power level variations.* Most evaporation methods stipulate a definite temperature or power level to dry the sample so as to standardize the procedure and obtain reproducible results. In practice, there are often significant variations in temperatures or power levels within an evaporation instrument, and so the efficiency of the drying procedure depends on the precise location of the sample within the instrument. It is therefore important to carefully design and operate analytical instruments so as to minimize these temperature or power level variations.
9. *Sample pans.* It is important to use appropriate pans to contain samples, and to handle them correctly, when carrying out a moisture content analysis. Typically aluminum pans are used because they are relatively cheap and have a high thermal conductivity. These pans usually have lids to prevent spattering of the sample, which would lead to weight loss and therefore erroneous results. Pans should be handled with tongs because fingerprints can contribute to the mass of a sample. Pans should be dried in an oven and stored in a desiccator prior to use to ensure that no residual moisture is attached to them.

3.4.4. Advantages and Disadvantages

- ◆ *Advantages:* Precise; Relatively cheap; Easy to use; Officially sanctioned for many applications; Many samples can be analyzed simultaneously
- ◆ *Disadvantages:* Destructive; Unsuitable for some types of food; Time consuming

3.5. Distillation Methods

3.5.1. Principles

Distillation methods are based on *direct* measurement of the amount of water removed from a food sample by evaporation: %Moisture = $100 (M_{\text{WATER}}/M_{\text{INITIAL}})$. In contrast, evaporation methods are based on *indirect* measurement of the amount of water removed from a food sample by evaporation: %Moisture = $100 (M_{\text{INITIAL}} - M_{\text{DRIED}})/M_{\text{INITIAL}}$. Basically, distillation methods involve heating a weighed food sample (M_{INITIAL}) in the presence of an organic solvent that is immiscible with water. The water in the sample evaporates and is collected in a graduated glass tube where its mass is determined (M_{WATER}).

3.5.2. Dean and Stark Method

Distillation methods are best illustrated by examining a specific example: the Dean and Stark method. A known weight of food is placed in a flask with an organic solvent such as xylene or toluene. The organic solvent must be insoluble with water; have a higher boiling point than water; be less dense than water; and be safe to use. The flask containing the sample and the organic solvent is attached to a condenser by a side arm and the mixture is heated. The water in the sample evaporates and moves up into the condenser where it is cooled and converted back into liquid water, which then trickles into the graduated tube. When no more water is collected in the graduated tube, distillation is stopped and the volume of water is read from the tube.

3.5.3. Practical Considerations

There are a number of practical factors that can lead to erroneous results: (i) emulsions can sometimes form between the water and the solvent which are difficult to separate; (ii) water droplets can adhere to the inside of the glassware, (iii) decomposition of thermally labile samples can occur at the elevated temperatures used.

3.5.4. Advantages and Disadvantages

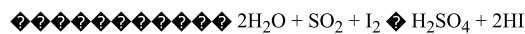
- ◆ *Advantages:* Suitable for application to foods with low moisture contents; Suitable for application to foods containing volatile oils, such as herbs or spices, since the oils remain dissolved in the organic solvent, and therefore do not interfere with the measurement of the water; Equipment is relatively cheap, easy to setup and operate; Distillation methods have been officially sanctioned for a number of food applications.
- ◆ *Disadvantages:* Destructive; Relatively time-consuming; Involves the use of flammable solvents; Not applicable to some types of foods.

3.6. Chemical Reaction Methods

Reactions between water and certain chemical reagents can be used as a basis for determining the concentration of moisture in foods. In these methods a chemical reagent is added to the food that reacts specifically with water to produce a measurable change in the properties of the system, *e.g.*, mass, volume, pressure, pH, color, conductivity. Measurable changes in the system are correlated to the moisture content using calibration curves. To make accurate measurements it is important that the chemical reagent reacts with all of the water molecules present, but not with any of the other components in the food matrix. Two methods that are commonly used in the food industry are the *Karl-Fisher titration* and *gas production* methods. Chemical reaction methods do not usually involve the application of heat and so they are suitable for foods that contain thermally labile substances that would change the mass of the food matrix on heating (*e.g.*, food containing high sugar concentrations) or foods that contain volatile components that might be lost by heating (*e.g.*, spices and herbs).

3.6.1. Karl-Fisher method

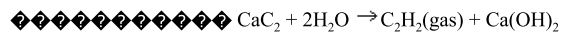
The Karl-Fisher titration is often used for determining the moisture content of foods that have low water contents (*e.g.* dried fruits and vegetables, confectionary, coffee, oils and fats). It is based on the following reaction:



This reaction was originally used because HI is colorless, whereas I₂ is a dark reddish brown color, hence there is a measurable change in color when water reacts with the added chemical reagents. Sulfur dioxide and iodine are gaseous and would normally be lost from solution. For this reason, the above reaction has been modified by adding solvents (*e.g.*, C₅H₅N) that keep the S₂O and I₂ in solution, although the basic principles of the method are the same. The food to be analyzed is placed in a beaker containing solvent and is then titrated with *Karl Fisher reagent* (a solution that contains iodine). While any water remains in the sample the iodine reacts with it and the solution remains colorless (HI), but once all the water has been used up any additional iodine is observed as a dark red brown color (I₂). The volume of iodine solution required to titrate the water is measured and can be related to the moisture content using a pre-prepared calibration curve. The precision of the technique can be improved by using electrical methods to follow the end-point of the reaction, rather than observing a color change. Relatively inexpensive commercial instruments have been developed which are based on the Karl-Fisher titration, and some of these are fully automated to make them less labor intensive.

3.6.2. Gas production methods

Commercial instruments are also available that utilize specific reactions between chemical reagents and water that lead to the production of a gas. For example, when a food sample is mixed with powdered calcium carbide the amount of acetylene gas produced is related to the moisture content.



The amount of gas produced can be measured in a number of different ways, including (i) the volume of gas produced, (ii) the decrease in the mass of the sample after the gas is released, and (iii) the increase in pressure of a closed vessel containing the reactants.

3.7 Physical Methods

A number of analytical methods have been developed to determine the moisture content of foods that are based on the fact that water has appreciably different bulk physical characteristics than the food matrix, *e.g.* density, electrical conductivity or refractive index. These methods are usually only suitable for analysis of foods in which the composition of the food matrix does not change significantly, but the ratio of water-to-food matrix changes. For example, the water content of oil-in-water emulsions can be determined by measuring their density or electrical conductivity because the density and electrical conductivity of water are significantly higher than those of oil. If the composition of the food matrix changes as well as the water content, then it may not be possible to accurately determine the moisture content of the food because more than one food composition may give the same value for the physical property being measured. In these cases, it may be possible to use a combination of two or more physical methods to determine the composition of the food, *e.g.*, density measurements in combination with electrical conductivity measurements.

3.8 Spectroscopic Methods

Spectroscopic methods utilize the interaction of electromagnetic radiation with materials to obtain information about their composition, *e.g.*, X-rays, UV-visible, NMR, microwaves and IR. The spectroscopic methods developed to measure the moisture content of foods are based on the fact that water absorbs electromagnetic radiation at characteristic wavelengths that are different from the other components in the food matrix. The most widely used physical methods are based on measurements of the absorption of microwave or infrared energy by foods. Microwave and infrared radiation are absorbed by materials due to their

ability to promote the vibration and/or rotation of molecules. The analysis is carried out at a wavelength where the water molecules absorb radiation, but none of the other components in the food matrix do. A measurement of the absorption of radiation at this wavelength can then be used to determine the moisture content: the higher the moisture content, the greater the absorption. Instruments based on this principle are commercially available and can be used to determine the moisture content in a few minutes or less. It is important not to confuse infrared and microwave *absorption* methods with infrared lamp and microwave *evaporation* methods. The former use low energy waves that cause no physical or chemical changes in the food, whereas the latter use high-energy waves to evaporate the water. The major advantage of these methods is that they are capable of rapidly determining the moisture content of a food with little or no sample preparation and are therefore particularly useful for quality control purposes or rapid measurements of many samples.

3.9 Methods to Determine Water in Different Molecular Environments

The overall water content of a food is sometimes not a very reliable indication of the quality of a food because the water molecules may exist in different environments within foods, *e.g.*, "bound" or "free". Here "bound water" refers to water that is physically or chemically bound to other food components, whereas "free water" refers to bulk, capillary or entrapped water. For example, the microbial stability or physicochemical properties of a food are often determined by the amount of free water present, rather than by the total amount of water present. For this reason, it is often useful for food scientists to be able to determine the amount of water in different molecular environments within a food. A variety of analytical methods are available that can provide this type of information.

3.9.1. Vapor pressure methods

A physical parameter that is closely related to the amount of free water present in a food is the water activity:

$$a_w = \frac{P}{P_0}$$

where, P is the partial pressure of the water above the food and P_0 is the vapor pressure of pure water at the same temperature.

Bound water is much less volatile than free water, and therefore the water activity gives a good indication of the amount of free water present. A variety of methods are available for measuring the water activity of a sample based on its vapor pressure. Usually, the sample to be analyzed is placed in a closed container and allowed to come into equilibrium with its environment. The water content in the headspace above the sample is then measured and compared to that of pure water under the same conditions.

3.9.2. Thermogravimetric methods

Thermogravimetric techniques can be used to continuously measure the mass of a sample as it is heated at a controlled rate. The temperature at which water evaporates depends on its molecular environment: free water normally evaporates at a lower temperature than bound water. Thus by measuring the change in the mass of a sample as it loses water during heating it is often possible to obtain an indication of the amounts of water present in different molecular environments.

3.9.3. Calorimetric methods

Calorimetric techniques such as differential scanning calorimetry (DSC) and differential thermal analysis (DTA) can be used to measure changes in the heat absorbed or released by a material as its temperature is varied at a controlled rate. The melting point of water depends on its molecular environment: free water normally melts at a higher temperature than bound water. Thus by measuring the enthalpy change of a sample with temperature it is possible to obtain an indication of the amounts of water present in different molecular environments.

Spectroscopic methods

The electromagnetic spectrum of water molecules often depends on their molecular environment, and so some spectroscopy techniques can be used to measure the amounts of water in different environments. One of the most widely used of these techniques is nuclear magnetic resonance (NMR). NMR can distinguish molecules within materials based on their molecular mobility, *i.e.*, the distance they move in a given time. The molecular mobility of free water is appreciably higher than that of bound water and so NMR can be used to provide an indication of the concentrations of water in "free" and "bound" states.



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