4. Analysis of Ash and Minerals

4.1 Introduction

The *ash content* is a measure of the total amount of minerals present within a food, whereas the *mineral content* is a measure of the amount of specific inorganic components present within a food, such as Ca, Na, K and Cl. Determination of the ash and mineral content of foods is important for a number of reasons:

- *Nutritional labeling.* The concentration and type of minerals present must often be stipulated on the label of a food.
- *Quality.* The quality of many foods depends on the concentration and type of minerals they contain, including their taste, appearance, texture and stability.
- *Microbiological stability.* High mineral contents are sometimes used to retard the growth of certain microorganisms.
- *Nutrition.* Some minerals are essential to a healthy diet (*e.g.,* calcium, phosphorous, potassium and sodium) whereas others can be toxic (*e.g.,* lead, mercury, cadmium and aluminum).
- *Processing.* It is often important to know the mineral content of foods during processing because this affects the physicochemical properties of foods.

4.2. Determination of Ash Content

Ash is the inorganic residue remaining after the water and organic matter have been removed by heating in the presence of oxidizing agents, which provides a measure of the total amount of minerals within a food. Analytical techniques for providing information about the total mineral content are based on the fact that the minerals (the analyte) can be distinguished from all the other components (the matrix) within a food in some measurable way. The most widely used methods are based on the fact that minerals are not destroyed by heating, and that they have a low volatility compared to other food components. The three main types of analytical procedure used to determine the ash content of foods are based on this principle: *dry* ashing, *wet* ashing and *low temperature plasma dry* ashing. The method chosen for a particular analysis depends on the reason for carrying out the analysis, the type of food analyzed and the equipment available. Ashing may also be used as the first step in preparing samples for analysis of specific minerals, by atomic spectroscopy or the various traditional methods described below. Ash contents of fresh foods rarely exceed 5%, although some processed foods can have ash contents as high as 12%, *e.g.,* dried beef.

4.2.1. Sample Preparation

As with all food analysis procedures it is crucial to carefully select a sample whose composition represents that of the food being analyzed and to ensure that its composition does not change significantly prior to analysis. Typically, samples of 1-10g are used in the analysis of ash content. Solid foods are finely ground and then carefully mixed to facilitate the choice of a representative sample. Before carrying out an ash analysis, samples that are high in moisture are often dried to prevent spattering during ashing. High fat samples are usually defatted by solvent extraction, as this facilitates the release of the moisture and prevents spattering. Other possible problems include contamination of samples by minerals in grinders, glassware or crucibles which come into contact with the sample during the analysis. For the same reason, it is recommended to use deionized water when preparing samples.

4.2.2. Dry Ashing

Dry ashing procedures use a high temperature muffle furnace capable of maintaining temperatures of between 500 and 600 ^{o}C. Water and other volatile materials are vaporized and organic substances are burned in the presence of the oxygen in air to CO_2, H_2O and N_2. Most minerals are converted to oxides, sulfates, phosphates, chlorides or silicates. Although most minerals have fairly low volatility at these high temperatures, some are volatile and may be partially lost, *e.g.,* iron, lead and mercury. If an analysis is being carried out to determine the concentration of one of these substances then it is advisable to use an alternative ashing method that uses lower temperatures.

The food sample is weighed before and after ashing to determine the concentration of ash present. The ash content can be expressed on either a *dry* or *wet* basis:

$$\%\ \text{Ash (dry basis)} = \frac{M_{ASH}}{M_{DRY}} \times 100$$

$$\%\ \text{Ash (wet basis)} = \frac{M_{ASH}}{M_{WET}} \times 100$$

where M_{ASH} refers to the mass of the ashed sample, and M_{DRY} and M_{ASH} refer to the original masses of the dried and wet samples.

There are a number of different types of crucible available for ashing food samples, including quartz, Pyrex, porcelain, steel and platinum. Selection of an appropriate crucible depends on the sample being analyzed and the furnace temperature used. The most widely used crucibles are made from porcelain because it is relatively inexpensive to purchase, can be used up to high temperatures (< 1200^{o}C) and are easy to clean. Porcelain crucibles are resistent to acids but can be corroded by alkaline samples, and therefore different types of crucible should be used to analyze this type of sample. In addition, porcelain crucibles are prone to cracking if they experience rapid temperature changes. A number of dry ashing methods have been officially recognized for the determination of the ash content of various foods (AOAC Official Methods of Analysis). Typically, a sample is held at 500-600 ^{o}C for 24 hours.

- *Advantages:* Safe, few reagents are required, many samples can be analyzed simultaneously, not labor intensive, and ash can be analyzed for specific mineral content.
- *Disadvantages:* Long time required (12-24 hours), muffle furnaces are quite costly to run due to electrical costs, loss of volatile minerals at high temperatures, *e.g.,* Cu, Fe, Pb, Hg, Ni, Zn.

Recently, analytical instruments have been developed to dry ash samples based on microwave heating. These devices can be programmed to initially remove most of the moisture (using a relatively low heat) and then convert the sample to ash (using a relatively high heat). Microwave instruments greatly reduce the time required to carry out an ash analysis, with the analysis time often being less than an hour. The major disadvantage is that it is not possible to simultaneously analyze as many samples as in a muffle furnace.

4.2.3. Wet Ashing

Wet ashing is primarily used in the preparation of samples for subsequent analysis of specific minerals (see later). It breaks down and removes the organic matrix surrounding the minerals so that they are left in an aqueous solution. A dried ground food sample is usually weighed into a flask containing strong acids and oxidizing agents (*e.g.,* nitric, perchloric and/or sulfuric acids) and then heated. Heating is continued until the organic matter is completely digested, leaving only the mineral oxides in solution. The temperature and time used depends on the type of acids and oxidizing agents used. Typically, a digestion takes from 10 minutes to a few hours at temperatures of about 350^{o}C. The resulting solution can then be analyzed for specific minerals.

- *Advantages:* Little loss of volatile minerals occurs because of the lower temperatures used, more rapid than dry ashing.
- *Disadvantages* Labor intensive, requires a special fume-cupboard if perchloric acid is used because of its hazardous nature, low sample throughput.

4.2.4. Low Temperature Plasma Ashing

A sample is placed into a glass chamber which is evacuated using a vacuum pump. A small amount of oxygen is pumped into the chamber and broken down to nascent oxygen (O_2 $2O^{\cdot}$) by application of an electromagnetic radio frequency field. The organic matter in the sample is rapidly oxidized by the nascent oxygen and the moisture is evaporated because of the elevated temperatures. The relatively cool temperatures (< 150^{o}C) used in low-temperature plasma ashing cause less loss of volatile minerals than other methods.

- *Advantages:* Less chance of losing trace elements by volatilization
- *Disadvantages:* Relatively expensive equipment and small sample throughput.

4.2.5. Determination of Water Soluble and Insoluble Ash

As well as the total ash content, it is sometimes useful to determine the ratio of water soluble to water-insoluble ash as this gives a useful indication of the quality of certain foods, *e.g.,* the fruit content of preserves and jellies. Ash is diluted with distilled water then heated to nearly boiling, and the resulting solution is filtered. The amount of soluble ash is determined by drying the filtrate, and the insoluble ash is determined by rinsing, drying and ashing the filter paper.

4.2.6. Comparison of Ashing Methods

The conventional dry ashing procedure is simple to carry out, is not labor intensive, requires no expensive chemicals and can be used to analyze many samples simultaneously. Nevertheless, the procedure is time-consuming and volatile minerals may be lost at the high temperatures used. Microwave instruments are capable of speeding up the process of dry ashing. Wet ashing and low temperature plasma ashing are more rapid and cause less loss of volatile minerals because samples are heated to lower temperatures. Nevertheless, the wet ashing procedure requires the use of hazardous chemicals and is labor intensive, while the plasma method requires expensive equipment and has a low sample throughput.

4.3. Determination of Specific Mineral Content

Knowledge of the concentration and type of specific minerals present in food products is often important in the food industry. The major physicochemical characteristics of minerals that are used to distinguish them from the surrounding matrix are: their low volatility; their ability to react with specific chemical reagents to give measurable changes; and their unique electromagnetic spectra. The most effective means of determining the type and concentration of specific minerals in foods is to use atomic absorption or emission spectroscopy. Instruments based on this principle can be used to quantify the entire range of minerals in foods, often to concentrations as low as a few ppm. For these reasons they have largely replaced traditional methods of mineral analysis in institutions that can afford to purchase and maintain one, or that routinely analyze large numbers of samples. Institutions that do not have the resources or sample throughput to warrant purchasing an atomic spectroscopy instrument rely on more traditional methods that require chemicals and equipment commonly found in food laboratories. Many of the minerals of importance to food scientists can be measured using one of these traditional methods.

4.3.1. Sample preparation

Many of the analytical methods used to determine the specific mineral content of foods require that the minerals be dissolved in an aqueous solution. For this reason, it is often necessary to isolate the minerals from the organic matrix surrounding them prior to the analysis. This is usually carried out by ashing a sample using one of the methods described in the previous section. It is important that the ashing procedure does not alter the mineral concentration in the food due to volatilization. Another potential source of error in mineral analysis is the presence of contaminants in the water, reagents or glassware. For this reason, ultrapure water or reagents should be used, and/or a blank should be run at the same time as the sample being analyzed. A blank uses the same glassware and reagents as the sample being analyzed and therefore should contain the same concentration of any contaminants. The concentration of minerals in the blank is then subtracted from the value determined for the sample. Some substances can interfere with analysis of certain minerals, and should therefore be eliminated prior to the analysis or accounted for in the data interpretation. The principles of a number of the most important traditional methods for analyzing minerals are described below. Many more traditional methods can be found in the AOAC Official Methods of Analysis.

4.3.2. Gravimetric Analysis

The element to be analyzed is precipitated from solution by adding a reagent that reacts with it to form an insoluble complex with a known chemical formula. The precipitate is separated from the solution by filtration, rinsed, dried and weighed. The amount of mineral present in the original sample is determined from a knowledge of the chemical formula of the precipitate. For example, the amount of chloride in a solution can be determined by adding excess silver ions to form an insoluble silver chloride precipitate, because it is known that Cl is 24.74% of AgCl. Gravimetric procedures are only suitable for large food samples, which have relatively high concentrations of the mineral being analyzed. They are not suitable for analysis of trace elements because balances are not sensitive enough to accurately weigh the small amount of precipitate formed.

4.3.3. Colorimetric methods

These methods rely on a change in color of a reagent when it reacts with a specific mineral in solution which can be quantified by measuring the absorbance of the solution at a specific wavelength using a spectrophotometer. Colorimetric methods are used to determine the concentration of a wide

variety of different minerals. Vandate is often used as a colorimetric reagent because it changes color when it reacts with minerals. For example, the phosphorous content of a sample can be determined by adding a vandate-molybdate reagent to the sample. This forms a colored complex (yellow-orange) with the phosphorous which can be quantified by measuring the absorbance of the solution at 420nm, and comparing with a calibration curve. Different reagents are also available to colorimetrically determine the concentration of other minerals.

4.3.4. Titrations

EDTA complexiметric titration

EDTA is a chemical reagent that forms strong complexes with multivalent metallic ions. The disodium salt of EDTA is usually used because it is available in high purity: Na_2H_2Y. The complexes formed by metal ions and EDTA can be represented by the following equations:

$m^{2+} + H_2Y^{2-} \rightarrow mY^{2-} + 2H^+$

$m^{3+} + H_2Y^{2-} \rightarrow mY^{-} + 2H^+$

$m^{4+} + H_2Y^{2-} \rightarrow mY + 2H^+$

The calcium content of foods is often determined by this method. An ashed food sample is diluted in water and then made alkaline (pH 12.5 to 13). An indicator that can form a colored complex with EDTA is then added to the solution, and the solution is titrated with EDTA. The EDTA-indicator complex is chosen to be much weaker than the EDTA-mineral complex. Consequently, as long as multivalent ions remain in the solution the EDTA forms a strong complex with them and does not react with the indicator. However, once all the mineral ions have been complexed, any additional EDTA reacts with the indicator and forms a colored complex that is used to determine the end-point of the reaction. The calcium content of a food sample is determined by comparing the volume of EDTA required to titrate it to the end-point with a calibration curve prepared for a series of solutions of known calcium concentration. If there is a mixture of different multivalent metallic ions present in a food there could be some problems in determining the concentration of a specific type of ion. It is often possible to remove interfering ions by passing the solution containing the sample through an ion-exchange column prior to analysis.

Redox reactions

Many analytical procedures are based on coupled reduction-oxidation (redox) reactions.→ Reduction is the gain of electrons by atoms or molecules, whereas oxidation is the removal of electrons from atoms or molecules. Any molecular species that gains electrons during the course of a reaction is said to be *reduced*, whereas any molecular species that loses electrons is said to be *oxidized*, whether or not oxygen is involved. Electrons cannot be created or destroyed in ordinary chemical reactions and so any oxidation reaction is accompanied by a reduction reaction. These coupled reactions are called *redox* reactions:

$X^n \rightarrow X^{n+1} + e^-$
(Oxidation reaction → loss of electrons)

$Y^m + e^- \rightarrow Y^{m-1}$
(Reduction reaction → gain of electrons)

$X^n + Y^m \rightarrow X^{n+1} + Y^{m-1}$ (Coupled reaction→ transfer of electrons)

Analysts often design a coupled reaction system so that one of the half-reactions leads to a measurable change in the system that can be conveniently used as an end-point, *e.g.,* a color change. Thus one of the coupled reactions usually involves the mineral being analyzed (*e.g.,* X = analyte), whereas the other involves an indicator (*e.g.,* Y = indicator).

For example, permanganate ion (MnO_4^-) is a deep purple color (oxidized form), while the mangenous ion (Mn^{2+}) is a pale pink color (reduced form). Thus permanganate titrations can be used as an indicator of many redox reactions:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_20$
(Reduction reaction)

(Deep Purple)(Pale Pink)

The calcium or iron content of foods can be determined by titration with a solution of potassium permanganate, the end point corresponding to the first change of the solution from pale pink to purple. The calcium or iron content is determined from the volume of permanganate solution of known molarity that is required to reach the end-point. For iron the reaction is:

$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$
(Oxidation reaction)

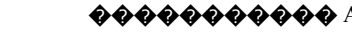
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_20$
(Reduction reaction)

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_20$ (Coupled reaction)

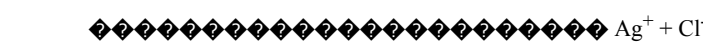
Potassium permanganate is titrated into the aqueous solution of ashed food. While there is Fe^{2+} remaining in the food the MnO_4^- is converted to Mn^{2+} that leads to a pale pink solution. Once all of the Fe^{2+} has been converted to Fe^{3+} then the MnO_4^- remains in solution and leads to the formation of a purple color, which is the end-point.

Precipitation titrations

When at least one product of a titration reaction is an insoluble precipitate, it is referred to as a *precipitation* titration. A titrimetric method commonly used in the food industry is the *Mohr* method for chloride analysis. Silver nitrate is titrated into an aqueous solution containing the sample to be analyzed and a chromate indicator.

 $AgNO_3 + NaCl \rightarrow AgCl(s) + NaNO_3$

The interaction between silver and chloride is much stronger than that between silver and chromate. The silver ion therefore reacts with the chloride ion to form AgCl, until all of the chloride ion is exhausted. Any further addition of silver nitrate leads to the formation of silver chromate, which is an insoluble orange colored solid.

 $Ag^+ + Cl^- \rightarrow AgCl$ (colorless) - until all Cl^- is complexed

 $2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4$ (orange) - after all Cl^- is complexed

The end point of the reaction is the first hint of an orange color. The volume of silver nitrate solution (of known molarity) required to reach the endpoint is determined, and thus the concentration of chloride in solution can be calculated.

4.3.5. Ion-Selective Electrodes

The mineral content of many foods can be determined using ion-selective electrodes (ISE). These devices work on the same principle as pH meters, but the composition of the glass electrode is different so that it is sensitive to specific types of ion (rather than H^+). Special glass electrodes are commercially available to determine the concentration of K^+, Na^+, NH_4^+, Li^+, Ca^{2+} and Rb^+ in aqueous solution. Two electrodes are dipped into an aqueous solution containing the dissolved mineral: a reference electrode and a ion-selective electrode. The voltage across the electrodes depends on the concentration of the mineral in solution and is measured at extremely low current to prevent alterations in ion concentration. The concentration of a specific mineral is determined from a calibration curve of voltage versus the logarithm of concentration. The major advantages of this method are its simplicity, speed and ease of use. The technique has been used to determine the salt concentration of butter, cheese and meat, the calcium concentration of milk and the CO_2 concentration of soft drinks. In principle, an ion selective electrode is only sensitive to one type of ion, however, there is often interference from other types of ions. This problem can often be reduced by adjusting pH, complexing or precipitating the interfering ions.

Finally, it should be noted that the ISE technique is only sensitive to the concentration of *free* ions present in a solution. If the ions are complexed with other components, such as chelating agents or biopolymers, then they will not be detected. The ISE technique is therefore particularly useful for quantifying the binding of minerals to food components. If one wants to determine the total concentration of a specific ion in a food (rather than the free concentration), then one needs to ensure that ion binding does not occur, *e.g.,* by ashing the food.

4.3.6 Atomic Spectroscopy

The determination of mineral type and concentration by atomic spectroscopy is more sensitive, specific, and quicker than traditional wet chemistry methods. For this reason it has largely replaced traditional methods in laboratories that can afford it or that routinely analyze for minerals.

Principles of Atomic Spectroscopy

The primary cause of absorption and emission of radiation in atomic spectroscopy is *electronic transitions* of outer shell electrons. Photons with the energy associated with this type of transition are found in the UV-visible part of the electromagnetic spectrum. In this respect atomic spectroscopy is similar to UV-visible spectroscopy, however, the samples used in atomic spectroscopy are individual atoms in a gaseous state, whereas those used in UV-visible spectroscopy are molecules dissolved in liquids. This has important consequences for the nature of the spectra produced. In atomic spectroscopy the peaks are narrow and well defined, but in UV-visible spectroscopy they are broad and overlap with one another. The are two major reasons for this. Firstly, because absorption or emission is from atoms, rather than molecules, there are no vibrational or rotational transitions superimposed on the electronic transitions. Secondly, because the atoms are in a gaseous state they are well separated from each other and do not interact with neighboring molecules.

The energy change associated with a transition between two energy levels is related to the wavelength of the absorbed radiation: $\Delta E = hc/\lambda$, where, h = Planks constant, c = the speed of light and λ = the wavelength. Thus for a given transition between two energy states radiation of a discrete wavelength is either absorbed or emitted. Each element has a unique electronic structure and therefore it has a unique set of energy levels. Consequently, it absorbs or emits radiation at specific wavelengths. Each spectrum is therefore like a "fingerprint" that can be used to identify a particular element. In addition, because the absorption and emission of radiation occurs at different wavelengths for different types of atom, one element can be distinguished from others by making measurements at a wavelength where it absorbs or emits radiation, but the other elements do not.

Absorption occurs primarily when electrons in the ground state are promoted to various excited states. Emission occurs when electrons in an excited state fall back to a lower energy level. Atoms can exist in a number of different excited states, and can fall back to one of many different lower energy states (not necessarily the ground state). Thus there are many more lines in an emission spectra than there are in an absorption spectra.

Atomic spectroscopy is used to provide information about the type and concentration of minerals in foods. The type of minerals is determined by measuring the position of the peaks in the emission or absorption spectra. The concentration of mineral components is determined by measuring the intensity of a spectral line known to correspond to the particular element of interest. The reduction in intensity of an electromagnetic wave that travels through a sample is used to determine the absorbance: $A = -\log(I/I_o)$. The Beer-Lambert law can then be used to relate the absorbance to the concentration of atoms in the sample: $A = a.b.c$, where A is absorbance, a is extinction cofficient, b is sample pathlength and c is concentration of absorbing species. In practice, there are often deviations from the above equation and so it is often necessary to prepare a calibration curve using a series of standards of known concentration prepared using the same reagents as used to prepare the sample. It is also important to run a blank to take into account any impurities in the reagents that might interfere with the analysis.

Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) is an analytical method that is based on the absorption of UV-visible radiation by free atoms in the gaseous state. The food sample to be analyzed is normally ashed and then dissolved in an aqueous solution. This solution is placed in the instrument where it is heated to vaporize and atomize the minerals. A beam of radiation is passed through the atomized sample, and the absorption of radiation is measured at specific wavelengths corresponding to the mineral of interest. Information about the type and concentration of minerals present is obtained by measuring the location and intensity of the peaks in the absorption spectra.

Instrumentation

The radiation source. The most commonly used source of radiation in AAS is the hollow cathode lamp. This is a hollow tube filled with argon or neon, and a cathode filament made of the metallic form of the element to be analyzed. When a voltage is applied across the electrodes, the lamp emits radiation characteristic of the metal in the cathode *i.e*., if the cathode is made of sodium, a sodium emission spectrum is produced. When this radiation passes through a sample containing sodium atoms it will be absorbed because it contains radiation of *exactly* the right wavelength to promote transition from one energy level to another. Thus a different lamp is needed for each type of element analyzed.

Chopper. The radiation arriving at the detector comes from two different sources: (i) radiation emitted by the filament of the lamp (which is partially absorbed by the sample); (ii) radiation that is emitted by the atoms in the sample that have been excited to higher energy levels by absorption of energy from the atomizer. To quantify the concentration of minerals in a sample using AAS it is necessary to measure the reduction in amplitude of the beam of radiation that has passed through the sample, rather than the radiation emitted by the excited sample. This can be done using a mechanical device, called a chopper, in conjunction with an electronic device that distinguishes between direct and alternating currents. The chopper is a spinning disk with a series of slits which is placed between the radiation source and the sample. The radiation from the light source is therefore continuously being switched on and off at a specific frequency, *i.e.,* it is an alternating current. On the other hand, the radiation emitted from the excited atoms in the sample is constant *i.e.,* it is direct current. The overall detected radiation is therefore the sum of a varying component and a constant component. Electronic devices are available which can separate alternating and constant current. These devices are used in AAS instruments to isolate the signal generated by the light from that emitted by the atoms in the sample.

Atomizer. Atomizers are used to convert the sample to be analyzed into individual atoms. The atomization process is achieved by exposing the sample to high temperatures, and involves three stages: (i) removal of water associated with molecules, (ii) conversion of molecules into a gas, and (iii) atomization of molecules. At higher temperatures the atoms may become ionized, which is undesirable because the atomic spectra of ionized atoms is different from that of non-ionized ones. Consequently, it is important to use a high enough temperature to atomize the molecules, but not so high that the atoms are ionized. Two types of atomizer are commonly used in atomic absorption instruments: flame and electrothermal atomization.

- Flame-atomizers consist of a nebulizer and a burner. The nebulizer converts the solution into a fine mist or aerosol. The sample is forced through a tiny hole into a chamber through which the oxidant and fuel are flowing. The oxidant and fuel carry the sample into the flame. The burner is usually 5 -10 centimeters long so as to give a long pathlength for the radiation to travel along. The characteristics of the flame can be altered by varying the relative proportions and types of oxidant and fuel used in the flame. Air-acetelyne and Nitrogen oxide-acetylene are the most commonly used mixtures of oxidant and fuel. Thus flames with different temperatures can be produced. This is important because the energy required to cause atomization, but not ionization, varies from substance to substance. Instrument manufactures provide guidelines with their instruments about the type of flame to use for specific elements.
- In electrothermal AAS the sample is placed in a small graphite cup which is electrically heated to a temperature (typically 2,000 - 3,000 ^{o}C) high enough to produce volatilization and atomization. The cup is positioned so that the radiation beam passes through the atomized sample. The advantage of electrothermal atomizers is that smaller samples are required and detection limits are lower. Major disadvantages are that they are more expensive to purchase, have a lower sample throughput, are more difficult to operate and have a lower precision than flame-atomizers.

Wavelength selector. A wavelength selector is positioned in the optical path between the flame (or furnace) and the detector. It's purpose is to isolate the spectral line of interest from the rest of the radiation coming from the sample, so that only the radiation of the desired wavelength reaches the detector. Wavelength selectors are typically, monochromatic gratings or filters.

Detector/Readout. The detector is a photomultiplier tube that converts electromagnetic energy reaching it into an electrical signal. Most modern instruments have a computer to display the signal output and store the spectra.

Atomic Emission Spectroscopy

Atomic emission spectroscopy (AES) is different from AAS, because it utilizes the emission of radiation by a sample, rather than the absorption. For this reason samples usually have to be heated to a higher temperature so that a greater proportion of the atoms are in an excited state (although care must be taken to ensure that ionization does not occur because the spectra from ionized atoms is different from that of non-ionized atoms). There are a number of ways that the energy can be supplied to a sample, including heat, light, electricity and radio waves.

Instrumentation

In AES the sample itself acts as the source of the detected radiation, and therefore there is no need to have a separate radiation source or a chopper. The sample is heated to a temperature where it is atomized and a significant proportion of the atoms is in an excited state. Atomic emissions are produced when the electrons in an excited state fall back to lower energy levels. Since the allowed energy levels for each atom are different, they each have characteristic emission spectrum from which they can be identified. Since a food usually contains a wide variety of different minerals, each with a characteristics emission spectrum, the overall spectrum produced contains many absorption peaks. The emitted radiation is therefore passed through a wavelength selector to isolate specific peaks in the spectra corresponding to the atom of interest, and the intensity of the peak is measured using a detector and displayed on a read-out device.

Atomization-Excitation Source. The purpose of the atomization-excitation source is to atomize the sample, and to excite the atoms so that they emit a significant amount of detectable radiation. The two most commonly used forms of atomization-excitation sources in food analysis are Flame and Inductively Coupled Plasma (ICP) devices.

- In flame-AES a nebulizer-burner system is used to atomize the minerals in the sample and excite a large proportion of them to higher energy levels.
- In ICP-AES a special device is used that heats the sample to very high temperatures (6,000 to 10,000 K) in the presence of argon ions. The minerals in the sample are not ionized at these temperatures because of the high concentration of argon ions ($Ar \rightleftharpoons Ar^{+} + e^{-}$) leads to the release of electrons that push the equilibrium towards the non-ionized form of the mineral ($M^{+} + e^{-} \rightleftharpoons M$).

Wavelength selectors. Wavelength selectors are used to isolate particular spectral lines, which are characteristic of the material being studied, from all the other spectral lines. A number of different types of wavelength selector are available including filters and gratings. A filter can only be used to

measure the intensity at a particular fixed wavelength, whereas a grating can be used to measure the intensity at many different wavelengths. A filter can therefore only be used to analyze for one type of mineral, whereas a grating can be used to measure many different types of minerals.

Practical considerations

Prior to making atomic spectroscopy measurements a food sample is usually ashed. The resulting ash is dissolved in a suitable solvent, such as water or dilute HCl, before injecting it into the instrument. Sometimes it is possible to analyze a sample without ashing it first. For example, vegetables oils can be analyzed by dissolving them in acetone or ethanol and injecting them directly into the instrument.

Concentrations of mineral elements in foods are often at the trace level and so it is important to use very pure reagents when preparing samples for analysis. Similarly, one should ensure that glassware in very clean and dry, so that it contains no contaminating elements. It is also important to ensure there are no interfering substances in the sample whose presence would lead to erroneous results. An interfering substance could be something that absorbs at the same wavelength as the mineral being analyzed, or something that binds to the mineral and prevents it from being efficiently atomized. There are various techniques available for removing the effects of these interfering substances.

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