Atomic absorption spectroscopy: history and applications

1. 0 Introduction

Atomic Absorption Spectroscopy (AAS) relates to the study of the absorption of radiant energy commonly within the ultraviolet or possibly in the visible region of the electromagnetic spectrum by isolated atoms in the gaseous phase. Considering that, in Atomic Absorption Spectroscopy, the analyte is introduced to the optical beam of the instrument as free atoms, all the likely rotational and vibrational energy levels are degenerate (of the same energy). Contrary to the absorption spectra of polyatomic chemical species (ions or molecules) in which there is often a multiplicity of feasible transitions corresponding to several rotational and vibrational energy levels superimposed on distinct electronic energy levels, the spectra of free atoms are characterized by merely a reasonably very few sharp absorbances (line spectra) which are often correlated with changes in electronic energy levels. The multitude of possible different energy levels accessible to polyatomic species leads to almost a continuum of possible transitions. As a result the spectra of ions (molecules) are comprised of somewhat broad bands which are caused by the partial resolution of several individual transitions. Hence, one feature of atomic spectra is their simpleness compared to the spectra of polyatomic species.

2. 0 History of Atomic Spectroscopy

The historical past associated with atomic spectroscopy can be directly linked to the study of daylight. In 1802, the German researcher Wollaston documented the existence of black colored regions (lines) within the spectrum of natural light. These kind of regions began to be referred to as Fraunhofer lines in honour of the scientist who actually invested most of his illustrious career understanding them. It had been implied, as early as 1820, these particular Fraunhofer lines resulted from absorption processes that took place within the sun’s environment. Kirchoff and Bunsen established that the standard yellowish light produced by sodium compounds, when positioned in a flame, seemed to be similar to the black colored “ D” line in sun’s spectrum. Several scientific studies applying a very early spectrometer lead Kirchoff (1859) to report that virtually any substance which could emit light at a provided wavelength also can absorb light at that same exact wavelength. He was the very first researcher to discover that there’s a comparable relationship regarding the absorption spectrum as well as the emission spectrum of the very same element. Agricola in 1550 used the characteristic colors associated with fumes to “ control” the whole process of smelting of ores. Talbot (1826) and Wheatstone (1835) claimed the fact that colors associated with flame and spark induced emissions were typical of distinct substances.

The actual quantitative facets of atomic spectroscopy have been formulated merely within the past 60-70 years. The substitution of photoelectric devices pertaining to visual detection and also the advancement and commercialisation of equipment go back to the later part of 1930s. The creation of all these devices was made feasible not simply owing to continued advancement in the understanding of the principle makeup and behaviour of atoms but have also been reinforced by the growing realisation that the existence of minimal and trace quantities (low mg/kg) of specific elements can impact industrial processes substantially. Consequently, devices had been developed in response to technical and technological demands.

Contemporary atomic spectroscopy could very well be divided ideally into 3 connected techniques based on the processes employed to generate, to be able to detect as well as determine the free atoms of analyte. While atomic absorption spectrometry (AAS) calculates the amount of light absorbed by atoms of analyte, atomic emission and atomic fluorescence determine the amount of the radiation emitted by analyte atoms (although under distinct conditions) that have been promoted to increased energy levels (excited states). Atomic emission (AE) and atomic fluorescence (AF) vary basically in the procedures through which analyte atoms obtain the extra energy associated with their excited states; perhaps by means of collisional events (AE) or through the absorption of radiant energy (AF). Every one of these 3 spectroscopic techniques can certainly be classified as a trace technique (meaning both a higher level of sensitivity and also a high selectivity), can be pertinent to numerous elements, and yet relative to the other two, every individual technique presents specific benefits as well as drawbacks.

Ever since the arrival of commercial atomic absorption spectrometry devices around the early 1960s, this specific technique has quickly obtained wide acceptance to the point where surveys of equipment available in scientific labs have implied, constantly, that an AAS instrument is actually the 4th or 5th most popular instrument (exceeded only by a balance, a pH meter, an ultra violet – visible spectrophotometer and quite possibly an HPLC).

3. 0 Principles

3. 1 Energy Transitions in Atoms

Atomic absorption spectra usually are generated in the event that ground state atoms absorb energy originating from a radiation source. Atomic emission spectra tend to be generated if excited neutral atoms discharge energy upon coming back to the ground state or simply a reduced energy state. Absorption of a photon associated with the radiation will cause an exterior shell electron to jump to a greater energy level, switching the particular atom in to an excited state. The excited atom will certainly drop back again to a reduced energy state, liberating a photon during this process. Atoms absorb or discharge radiation of distinct wavelengths considering that the permitted energy levels of electrons in atoms are generally fixed (not arbitrary). The energy change of a typical transition involving 2 energy levels is proportional to your frequency of the absorbed radiation:

Eeˆ’Eg = hÎ½

where:

Ee = energy in excited state

Eg = energy in ground state

h = Planck’s constant

Î½ = frequency of the radiation

Rearranging, we have:

Î½ = (Ee ˆ’ Eg)/h

or, since Î½ = c/Î»

Î» = hc/(Ee ˆ’ Eg)

where:

c = speed of light

Î» = wavelength of the absorbed or emitted light

The aforementioned relationships demonstrate that for any given electronic transition, the radiation of any distinct wavelength will be possibly absorbed or emitted. Every single element contains a distinctive set of permitted transitions and for that reason a distinctive spectrum.

Pertaining to absorption, transitions include principally the excitation of electrons in the ground state, therefore the amount of transitions is fairly minimal. Emission, alternatively, takes place in the event that electrons in a number of excited states drop to reduced energy levels which includes, yet not restricted to, the ground state. That is why the emission spectrum possesses far more lines compared to the absorption spectrum. Whenever a transition is via as well as to the ground state, it’s classified as a resonance transition. Additionally, the ensuing spectral line is termed as a resonance line.

3. 2 Atomization

Atomic spectroscopy necessitates that atoms belonging to the element of interest remain in the atomic state (i. e not coupled with other components within a compound) not to mention that they must be properly segregated in space. In foodstuffs, pretty much all the components exist as compounds or perhaps complexes and, as a result, should be transformed into neutral atoms (atomized) prior to atomic absorption can be accomplished. Atomization necessitates isolating particles in to individual compounds (by vaporization) and then breaking these compounds in to atoms. Most commonly it is attained simply by exposing the analyte to excessive heat using a flame or perhaps plasma even though alternative strategies can be utilized. A solution comprising the analyte is normally placed in the flame or plasma in the form of fine mist. The actual solvent immediately evaporates, leaving behind solid particles within the analyte which vaporizes as well as decomposes to atoms which may absorb radiation. This phenomenon is essentially the atomic absorption. This mechanism is displayed schematically in the figure adjacent to this description.

4. 0 Instrumentation

The typical design of the atomic absorption spectrometer is remarkably uncomplicated and not distinct from the more well-known spectrophotometers utilized for liquid phase studies. It is made up of:

A light source that produces the spectrum of the element of interest. Ordinarily a hollow cathode lamp (HCL) and also the electrode-less discharge lamp (EDL) are employed as light sources

An atom reservoir (which serves as an absorption cell) through which free atoms of your analyte are usually produced – ordinarily a flame. Commonly a nebulizer-burner system as well as an electrothermal furnace function as an atom reservoir.

A monochromator, (a piece of equipment to resolve the transmitted light in to it's component wavelengths) which has an adjustable exit slit to choose the wavelength complimenting to your resonant line. Generally an ultraviolet-visible (UV-Vis) grating monochromator is utilized.

A detector (a photomultiplier tube (PMT) or maybe a solid-state detector (SSD) having ancillary electronics to determine the radiation intensity and also to amplify the ensuing signal.

Flame photometers have one crucial disadvantage – the flame is a luminous source of radiation. The instrument must recognise the contribution from the flame and disregard it. The power of the beam transmitted to the detector (P) will likely be equivalent to the power of the beam incident on the sample (Po) excluding the power of the beam absorbed (PA) by the sample including a contribution from the luminosity of the flame (PF).

P = Po- PA + PF

Practically all Atomic Absorption spectrometers function using a radiation source that is modulated (chopped mechanically and / or electrically at a fixed frequency). The net impact would be that the detector will get a modulated signal from your emission source including a constant signal from the flame. The continual signal from your luminous flame will then be subtracted electronically (filtered out by the instrument) through the modulated signal which began from the lamp. This modulated radiation from your lamp is symbolised in the following figure as a dotted line (as opposed to the solid line for the lamp radiation in Figure).

5. 0 Applications in Food Analysis

Atomic Absorption Spectroscopy (AAS) can be described as a fairly straightforward and uncomplicated technique and has been one of the most widespread form of atomic spectroscopy in food analysis for several years. It is actually primarily employed for the determination of trace metals within a sample as well as for vitamin level determinations in feeds.

5. 1 Trace Metal Determinations in Foods

Atomic Absorption Spectroscopy finds its applications extensively in the determination of trace metal concentrations in foodstuffs, Two conditions need to be rigidly met for a trace element analysis to be of any value whatsoever. The analytical sample, that is in fact introduced to the instrument (usually under 1 mL) has to be (i) homogeneous and (ii) a miniature replica of the bulk material that has been sampled.

Food materials satisfy the first condition i. e. they are heterogeneous with regards to both particle size as well as analyte concentrations, in addition it varies significantly from one food to a different food when it comes to bulk composition. However, For biological materials, especially for foods, generally speaking, the issue of acquiring a sample that is a accurate miniature replica of the bulk material is particularly severe and may be likely to make contribution considerably to the total uncertainty linked to the final result.

The evaluation of foodstuff, as well as biological items in most cases, with regard to trace elements presents specific analytical difficulties which aren't experienced with several other sample types. A variety of elements of consideration tend to be present at amounts which range from very low to sub ~g/kg at one particular extreme while some other analyte components can be found at amounts in excess of 100 mg/kg. Considering that an analyte trace element might be found in a variety of chemical forms (several oxidation states, coupled with diverse anions bound to organic ligands or even proteins), the organic component of the analyte may result in significant matrix interferences through the detection process. Usually, to decrease these kinds of interferences the laboratory test sample is pretreated to transform all these variations associated with the analyte to a well-known cationic form whereas destroying the organic components of the sample (that are oxidised to Carbon dioxide as well as H20). In most cases, these kind of digestion treatments are complicated, time intensive, error prone, and restricted by the dimensions of sample which is often treated. The pre-analysis digestion acts to solubilise the sample(s) to improve homogeneity, and also to decrease probable interferences.

Two generalised digestion procedures are popular; (i) samples can be " dry ashed" in a furnace at 500 to 600~ and the ash solubilised in an acid solution or (2) the sample can be " wet" digested with a combination of heat, strong acids, and/or oxidising agents. Often, a triacid mixture consisting of concentrated nitric acid, with lesser amounts of 57% (v/v) perchloric and sulphuric acids (40: 4: 1) is used to digest plant material, however, the proportions of reagents, the sample size (2 g or less) and the volume of the final digest must be rigidly controlled to avoid analyte loss via precipitation (e. g., $CaSO_4$ and/or $PbSO_4$). These digestion reagents are highly corrosive. Moreover, the concentration, by evaporation, of perchloric acid digests can volatile perchlorate salts from the mixture. These salts can accumulate on the walls of the fume hood venting system with explosive results. More recently, efforts have been directed to automating the digestion process and to shortening the time required for sample pre-treatment by optimising procedures using microwave digesters. However, digestion procedures which are effective for one food matrix may not be effective with a different food.

5. 1. 1 Heavy Metals

5. 1. 1. 1 Cadmium and Lead

Making use of this approach, Pb and Cd in foodstuffs could be determined. It may well be applied to many other elements as well. The determination of Pb and Cd in foods necessitates initial destruction of organic matter present in the sample. This can be done employing a dry-ashing or even a wet digestion procedure. Pb and Cd by nature, are volatile components. Thus, a good ashing aid like magnesium nitrate or sulfuric acid is often introduced when utilizing a dry-ashing procedure.

Pertaining to wet digestion, numerous processes are explained in literature. A good number of of these techniques commonly involve an H_2SO_4 / H_2O_2 digestion. Cd and Pb exist in very low levels in foods. For that reason, it is almost always important to concentrate these elements prior to analyzing them through atomic absorption. This is accomplished by chelation as well as extraction directly into an organic solvent or through the use of an ion exchange column.

5. 1. 1. 2 Lead: Analysis of Food Coloring Dyes

Analysis of lead metal concentration in organic food coloring dyes can be carried out making use of atomic absorption spectroscopy. Water soluble dyes, in many cases are analyzed effortlessly by very simple dilution using deionized H2O. Water insoluble dyes are generally digested with nitric acid, HClO4, followed by chelation, and are then extracted into xylene.

5. 1. 1. 3 Lead and Copper: Analysis of Meat Products

Atomic Absorption Spectroscopy works extremely well in determining the concetration of Pb and Cu in animal meats as well as meat products. Only dry ashing method is commonly employed to the meat samples. Following ashing, the particular samples will be blended in acid as well as diluted. This technique offers the subsequent benefits: 1) usually requires minimal operator attention 2) Virtually no sample losses resulting from splattering, volatilization or perhaps retention on crucibles.

5. 1. 1. 4 Copper, Iron: Analysis of Alcoholic Beverages

Alcoholic beverage manufacturers need to have stringent quality control programs which usually symbolize good manufacturing practices. Atomic absorption spectroscopy serves the above mentioned objective by enabling the determination of Copper and Iron concentrations in spirits, gin, whiskey, rum, vermouth and other alike beverages which might be relevant to many other elements as well. Analysis by atomic absorption is precise, quick with no special sample preparation. The samples tend to be aspirated instantly and standards are usually made-up in alcohol to fit the content with the specific sample.

5. 1. 1. 5 Analysis of Wine

Using this approach, several metals in wine samples are determined by Atomic Absorption Spectroscopy. The wine sample is diluted and analyzed using aqueous standards for the determination of Sodium and Potassium ion concentrations. Specific heavy metals for instance copper and zinc could possibly be determined by direct aspiration vs standards made up of identical quantities of alcohol. Heavy metals might be determined through the use of an evaporation/ashing method to prepare the samples. Metals present in low concentrations can be concentrated by using an organic solvent extraction.

5. 1. 1. 6 Analysis of Beer

AAS can additionally be used for the determination of Na, K, Ca, Mg, Pb, Ni, Cu, Fe and Zn in beer. Most of these elements can easily be determined straightaway within beer. Nonetheless, elements found in higher levels should be diluted and also analyzed at wavelengths of relatively lower sensitivity. Elements like Pb, Ni and Fe exist in extremely low levels in beer. Solvent extraction could be used to concentrate these elements.

Practically all beers should be decarbonated through shaking or simply by swiftly transferring via one beaker to a different one repeatedly. The foam generated needs to be permitted to collapse back to the actual liquid prior to sampling further more. With regards to canned and bottled beers, 1-2 drops of octyl alcohol is added to regulate foam as appropriate.

In the event that solvent extraction is needed to concentrate the components of great interest, 25 mL of each and every standard solution and also beer sample is pipetted in to standalone darkened 100-mL flasks which in turn are usually equilibrated inside a water bath at 25 °C for half an hour, 2. 5 milliliters APDC (1%) solution is added in, blended and 15 milliliters MIBK is added. The flasks usually are shaked intensely for five min’s and even centrifuged to split up the layers. With regard to aqueous samples, alcohol can be included to the actual standards to ensure that content is similar to the samples. Pertaining to organic extraction, it is ascertained that the standards are made-up in organic solvents.

5. 1. 1. 7 Analysis of Whole Kernel Corn

AAS finds its applications in the determination of heavy metals in corn that includes Zn, Pb, Mn, Cu and Cr. Proper care is taken to make sure that all the organic matter is destroyed without any subsequent loss in trace metals when determining the heavy metal content level in corn samples. As there are merely little amounts of lead, Cd and C, and taking into consideration these particular elements exist in our environmental surroundings, contamination of samples through exterior sources is definitely problem to deal with. A sample that is at least 15 grams is actually weighed and subsequently a wet digestion is carried out with a combination of nitric acid and perchlorate. The resultant digest will then be refluxed with hydrochloric acid, diluted to volume and analyzed via atomic absorption.

5. 1. 1. 8 Analysis of Fish and Seafood

An acid digestion procedure is used for sample determination of many elements in fish and seafood tissue including K, Na, Zn, Cu, Cr, Cd, Fe, Ni and Pb. A weighed sample is placed in a digestion vessel, acid is added and the mixture is heated for several hours. The samples are digested with HNO_3 and $HClO_4$ or HNO_3 and H_2SO_4 depending on the technique and heating vessel used. After the digestion, the samples are diluted to a specific volume and analyzed directly or chelated and extracted into an organic solvent if the element of interest is present in low concentration.

The main advantage of this method is that it eliminates elemental loss by volatilization because the digestion takes place at a low temperature. The main disadvantages of a wet digestion procedure are that it is subject to reagent contamination and requires operator attention.

Dry ashing is a method that can be used for the determination of several elements in fish and seafood samples including Pb, Cd, Cu, Zn, Cr, Mn, Co, Na and K. It has been reported that the major drawback to dry ashing is loss of metal due to volatilization. However, if the temperature in the muffle furnace is held at 450-500 °C, loss from volatilization is minimal.

The dry-ashing method is less time-consuming than wet digestion methods. When levels of Pb and Cd are too low to be determined directly, solvent extraction can be used to concentrate these elements

5. 1. 1. 9 Analysis of Fruit Juice

Making use of this specific strategy, AAS can determine the concentration of calcium, magnesium, manganeese, iron, potassium, sodium, selenium and zinc in fruit juices. Dry ashing or wet oxidation can be employed; nevertheless these strategies tend to be time intensive. The juice sample may be hydrolyzed with a strong acid, allowing the preparation of several samples at once; the sample is then filtered after which it is analyzed by atomic absorption. To determine elements like Pb which are found in lower concentrations, chelation and solvent extraction may be used to concentrate the component of interest.

5. 1. 1. 10 Analysis of Milk

This technique details the determination of Calcium, Magnesium, Potassium, Sodium and Copper elements in milk by means of AAS. Making use of this process, typically the milk proteins which includes casein usually are precipitated through the use of trichloroaceticacid (TCA). The samples are then filtered and the resultant filtrate is analyzed by atomic absorption.

5. 1. 1. 11 Analysis of Evaporated Milk: Lead

AAS may also be used for the determination of Pb in evaporated milk. In this methodology, the milk sample is dry ashed after which it is extracted as the ammonium pyrrolidine dithiocarbamate (APDC) into butyl acetate and is then determined by atomic absorption making use of the 283. 3 nm wavelength

5. 1. 1. 12 Analysis of Baking Powder: Aluminum

The presence of aluminum metal in baking powder can be detected as well as determined by atomic absorption technique. The methodology is as follows, 1 g of sample is accurately weighed into a 250 mL Kjeldahl flask, and 2. 0 mL sulphuric acid is then added, followed by the addition 3 mL of 30% hydrogen peroxide. This leads to a vigorous reaction between the sample and the reagents. Once the vigorous reaction subsides, heat is applied using a Bunsen flame till the sample begins to char. 1 mL of additional increments of hydrogen peroxide is added and heated until the solution no longer chars; This is followed by another round of heating till fumes of SO3 emerge. The sample is then cooled and 50 mL water is added and one Pyrex glass chip and boiled for 3-5 min. The sampe is further cooled and filtered through Whatman No. 2 fast paper into a 100-mL volumetric flask rinsing thoroughly with H2O. The filtrate is diluted to volume. A reagent blank of 2. 0 mL sulphuric acid and 30% hydrogen peroxide is prepared. The standards are also prepared and the aluminum concentration is determined using the conditions listed on the “ Standard Conditions” pages.

5. 1. 1. 13 Analysis of Edible Oils

- Char-Ashing Technique

This method can be used to determine Cu, Fe, Mg, Mn, Na and K in glyceride oil, copper hydrogenated edible oils, salad oils, soybean oil and vegetable oils. It may also be applicable to other elements. The disadvantage of the char-ashing technique is that it is tedious and lengthy since the oil sample must first be completely carbonized on a hot plate before it is ashed in a muffle furnace. The entire process takes about 2 days. The advantage of this method is that it gives accurate results for several elements and it allows analysis for trace metals at a much lower level than direct aspiration. Digestion of oil samples using sulfuric acid has also been reported.

- Direct Solvent Method

Analysis by direct aspiration of fats and oils diluted with various organic solvents has found widespread use as a rapid method for the determination of trace metals in various oil samples. This method is applicable to the determination of Cu, Fe, Mn, Na, Mg, Ca, K and Rh and may be applicable to other elements. Using this method, oil samples are dissolved in various organic solvents or mixtures of solvents including MIBK, acetone, ethanol, isoamyl acetate/methyl alcohol and then read directly by atomic absorption. The main advantage of this method is that it is very rapid and little sample preparation is needed. The main disadvantages are that the samples are diluted and so some metals will be present in low concentrations and it is sometimes difficult to find oil standards that matrix match the samples being analyzed.

5. 1. 1. 14 Analysis of Tea and Instant Tea: Copper, Nickel

AAS could be used for the determination of Cu and Ni in tea. Copper and nickel salts are usually put in place to act as a protectant and eradicant to protect the crop from blister blight. It is a fungus disorder which has an effect on tea. A definitive technique to determine both of these elements is essential for good quality control purposes.

The 2 samples are generally wet-ashed utilizing a blend of HNO_3 and $HClO_4$. Instant teas decompose quickly and hence digestion with nitric acid alone would suffice. The principal benefit of wet ashing is the fact that it minimizes elemental loss given that the digestion occurs at a reduced temperature. Even so, it’s susceptible to reagent contamination and necessitates operator attention. Samples can even be dry-ashed. The standard solutions ought to be matrix matched to prevent interferences from Sodium or Potassium.