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State-of-the-Art and Trends in Atomic Absorption Spectrometry

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1. Introduction

Atomic Absorption Spectrometry, or AAS, is an analytical technique commonly used for the quantitative and qualitative determination of elements in samples such as aqueous solutions, waters, sea-waters, metals and alloys, glass, drugs, food, environmental samples, industrial wastes, biological samples among others.

This technique is based on measuring the amount of electromagnetic energy of a particular wavelength (ultraviolet or visible region), which is absorbed as it passes through a cloud of atoms of a particular chemical element (the analyte) coming from samples and standards. An appropriate mathematical treatment allows relating the amount of absorbed energy to the number of absorbed atoms by providing a measurement of the element concentration in the sample. This technique is established, relatively quickly, economically affordable and allows to determine more than 60 chemical elements from a huge type of samples. It is used by most of research laboratories and industry quality control around the world.

The aim of this text is to present concisely this powerful technique providing basic information about fundamental concepts, instrumentation and application. Relevant and effective techniques will be shown including flame atomization, hydride generation, cold vapor and electrothermic atomization or graphite furnace. Fundamental and theoretical details will not be presented on mechanical components, electronic, software and data processing. They are deeply discussed in specific literature.

2. A brief history

Isaac Newton made important discoveries about solar radiation in the 17th Century. He used a glass prism to break up white light into its constituent spectral colors. He studied the separation of white light in details and, from that discovery, he created the reflecting telescope, the Newtonian telescope. He, then, published his corpuscular theory of light by contraposition of Huygens' undulatory theory.

Two-hundred years after, Wollaston observed dark lines in the solar spectrum known as Fraunhofer lines, after being extensively studied by this German physicist. In 1832, Brewster

concluded that the Fraunhofer lines were produced due to the presence of atomic vapors in the solar atmosphere that absorbed part of radiation emitted by Sun.

From 1859 to 1861, Robert Bunsen and Gustav Kirchhoff demonstrated that each chemical element had a characteristic color or spectrum when heated to incandescence (Na yellow; K violet). Heating several elements during a flame test, they identified characteristic spectra of these elements and established a relation between emission spectrum and absorption spectrum. This explains the black lines in the solar spectrum: atoms in the solar corona absorbing part of energy emitted by Sun (continuous spectrum), originating the black lines observed. This also permits to identify absorbing atoms normally present in the corona, comparing the black lines to elements' emission spectrum produced in the laboratory.

At the beginning of the 20th century, the development of quantum mechanics theory provided mathematical patterns explaining the phenomena, which is the interaction of radiation with the matter. Considering this point, the necessary theoretical basis to develop a new technique of elementary analysis using the phenomenon of atomic absorption was established, but only in 1955, the first proposal of a practical instrument was introduced. At the beginning of the 60s, the first commercial equipment appeared and so far, equipments have been using the same basic components, although with more technologically involved. Understanding this technique requires understanding the phenomenon of emission and absorption of radiant-energy through the matter or, more specifically, through atoms.

3. Basic principles

3.1 Wave-particle duality: Light

Electromagnetic radiation is a form of energy described by classical physics as a wave made up of mutually perpendicular, fluctuating electric and magnetic field that propagates at a constant speed. It is characterized by wavelength (λ), (distance between two adjacent waves) and by frequency ν (number of waves per unit of time). The speed of light propagated in a vacuum is $C=299.792.458 \text{ m s}^{-1}$.

This model explains the energy propagation, but cannot explain its interaction with the matter. That interaction can be explained if we treat energy as a particle, called photon. A photon is characterized by frequency and wavelength and can transfer energy amount $E = h\nu / \lambda$, where h is Planck constant ($4.135667516 \times 10^{-15} \text{ eV s}$).

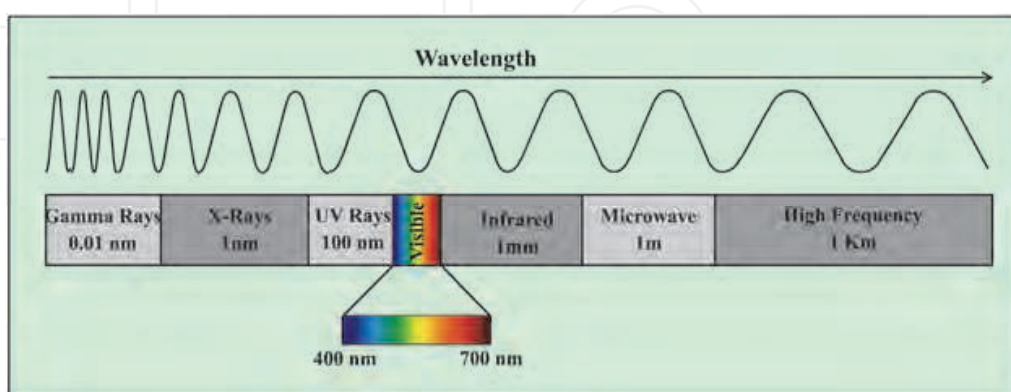


Fig. 1. Regions of the electromagnetic spectrum.

Electromagnetic spectrum is conveniently divided in wavelength rates with specific names (from gamma rays to radio waves) as shown in figure 1. That wavelength division does not

have a physical meaning itself, being only a practical classification in accordance with the available technological equipment for its generation and detection. For example, the visible region of light between 400 and 700 nanometers (nm) is directly detected by the human eye and perceived as visible light ($1 \text{ nm} = 10^{-9} \text{ m}$).

3.2 The atom, energy of a quantum state and electronic transitions

Bohr model has an atom consisting of a nucleus containing protons and neutrons surrounded by a cloud of electrons in fact inhabit specific regions in space. This is known as an orbital. The further an orbital gets from the nucleus, the more they gain potential energy associated to a determined orbital.

Quantum Mechanics explains that orbitals have quantized energy levels and for moving an electron to another level, it has to receive or emit the exact amount of energy corresponding to the difference between the two electronic levels ($\Delta E = E_1 - E_0$).

The amount of energy required to move an electron from energy level E_0 to energy level E_1 can be provided by heat due to a collision with other particles or absorb the energy of a photon. In this case, the energy of a Photon ($E = h\nu = hc/\lambda$) should be equal to the difference between the orbitals (ΔE), this is, only a Photon of a particular wavelength is absorbed and can promote that transition. This phenomenon is known as atomic absorption.

A more stable electron configuration of an atom is the one with less energy, also known as ground state configuration. The difference of energy between the last full orbital and the next empty orbital of the atom in a ground state is of the same order of magnitude of photons with wavelengths between 200 and 800 nm, this means, photons in ultraviolet regions and visible light of electromagnetic spectrum.

Sodium atom in ground state, e.g., has an electronic configuration of $1s^2 2s^2 2p^6 3s^1$. The 3s electron can receive a photon with energy of 589.0 nm ($E=2.2 \text{ eV}$) and passes to 3p orbital, which is an unstable state known as excited state. Being unstable, the excited atom loses its energy quickly (approximately in 10^{-8} s) and returns to ground state.

One way to lose excitation energy is by emitting a photon of 589.0 nm, a phenomenon known as atomic emission. A photon of 330.3 nm can also be absorbed by sodium. This is the difference of energy between 3s and a 4p orbital (3.6eV), but one photon of 400 nm cannot be absorbed because there are not two orbitals in a sodium atom with the same difference of energy. The return of electron from 4p orbital to ground state can also occur in two steps: first to 4s and then to 3s by emitting two photons with energies correspondent to the two transitions in a phenomenon known as atomic fluorescence.

The sodium atom can also receive enough energy to remove an electron, turning into sodium ion (Na^+), known as ionization. In this case, a change occurs in orbitals of different energy levels, so that the ion has a new set of transition being able to absorb or emit photons of wavelengths differently from metallic sodium.

Each chemical element has a unique electronic structure that differentiates from others. This implies in a possible and unique set of transitions, a set of characteristic absorption/emission lines that can be used for identification. Although the set of transitions is unique for each element, there may be a coincidence of spectrum in some lines of two or more elements, which means that different atoms can absorb or emit photons of same wavelength.

Even though the theoretical basis was established in the beginning of the twentieth century, only in the early 1950s an Australian physicist, Sir Alan Walsh, proposed the phenomenon

of atomic absorption as an elementary analysis technique. However, the first scientific equipment was made in the early of 1960s. Despite unavailable technology by that time, two main problems of the technique were solved: to obtain a source that would emit radiant energy of specific wavelength for each element and to generate and to put atoms into a ground state from a sample so they can absorb energy from the source.

3.3 Basic instrumentation

Every atomic absorption spectrometer presents the same basic components, however, each manufacturer differentiates the configuration due to the analytical demand and according to technological advance. Figure 2 shows the main components of an atomic absorption spectrometer.

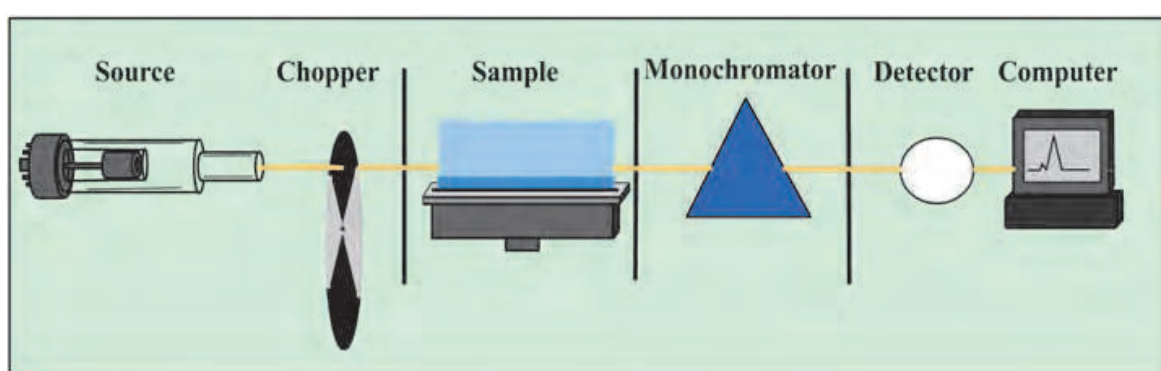


Fig. 2. Main components of an atomic absorption spectrometer.

The radiation source may be continuous, emitting from visible to infrared wavelengths or from lines that emit discrete lines, specifically from each chemical element. The modulator helps to differentiate radiation emitted by radiation lamp coming from the environment and, mainly, from the atomization system. The atomization system removes analyte atoms in solution and generates atomic vapor composed of atoms in ground state, putting them between the source and the detector to absorb the radiation emitted. The monochromator is responsible for the selection of photons due to the wavelength that will reach the detector. The detector transforms the energy of photons into a proportional electronic signal and amplifies it. The signal intensity obtained is treated by systems for data acquisition and processing.

At this point, it is important to stand out that the element cannot be directly determined by the atomic absorption spectrometer; even though the system provides that response. A spectrometer measures the amount of electromagnetic energy coming from the source before and after passing through a sample; this is, an indirect measurement of the absorption of energy by atoms present in the sample. To obtain a final result, a series of physical and chemical phenomenon should occur under controlled conditions and the measurement performed should be treated by an appropriate mathematical model. As each component of the equipment plays a part on this work, a more detailed study is essential to understand the performance of this analytical technique as well as its power and limitations.

3.3.1 Radiation source

Around 1952, when the development of the technique was starting, sources of continuous emissions were used. This means that it was used light in the visible and adjacent

ultraviolet ranges. First experiments showed the necessity of a spectrometer with 0.002 nm resolution for using this source, which was impossible with the equipment available by that time. A solution was found changing the emission sources of discrete lines. Then, the first sealed hollow cathode lamp (HCL) was manufactured (Welz et al., 2010), a high intensity atomic emission light source essential for developing the technique and widely used today.

3.3.2 Hollow cathode lamp (HCL)

HCL as shown in figure 3 consists of a sealed glass tube filled with inert gas, argon or neon, where an anode (positive pole) and a cathode (negative pole) are placed. The cathode contains an element whose spectrum is required basically in a pure source or an appropriate alloy. For elements that emit radiation in the ultraviolet region, the front window of emission is made of quartz because the glass of the tube absorbs UV radiation.

When an appropriate difference of power is applied, some atoms of Argon (filling gas) are ionized (Ar^+) and accelerated in the cathode direction where they are struck enough with force to eject atoms of the element of interest (M^0). These atoms are struck by other filling gas ions and pass from the ground state into the excited state (M^*), which will return rapidly to the ground state by emitting photon with a characteristic wavelength.

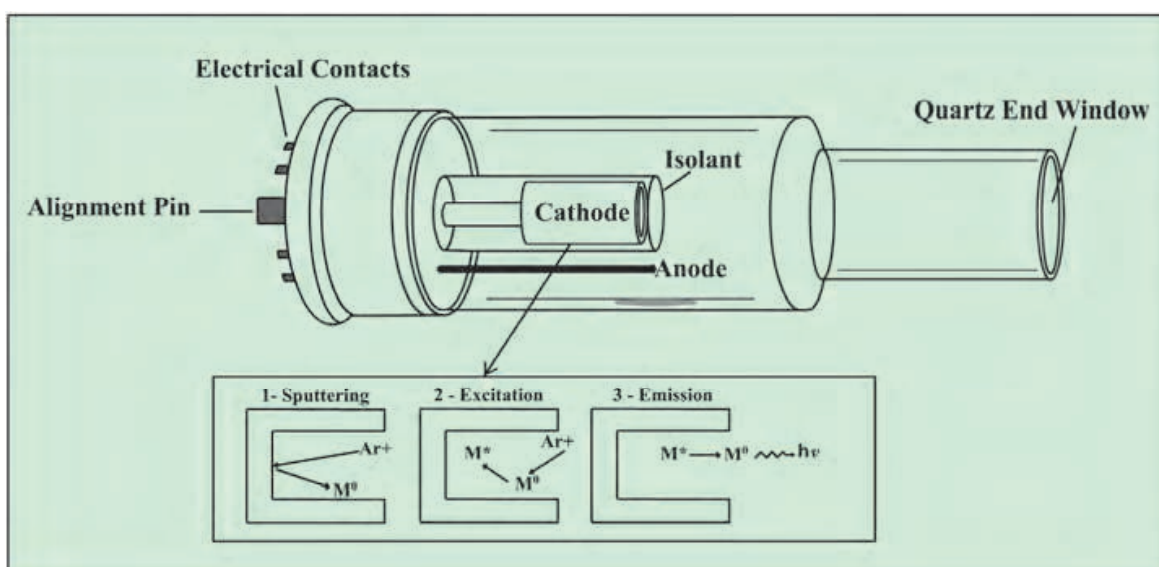


Fig. 3. Scheme of the hollow cathode lamp (HCL).

The HCL is a source of high intensity that emits simple spectra lines permitting the use of a low resolution monochromator. The disadvantage is the need of a different lamp for each element. The analysis turns slow and become expensive for multi-element analysis (determination of more than one element in the same sample).

To reduce these problems, there are multi-elemental lamps, whose cathodes are manufactured with a mixture of elements so they emit a characteristic spectrum for each one. The elements that form the cathode should be compatible. It is possible to form an alloy with them and the main lines of spectrum cannot overlap. The disadvantage is that the intensity of emission for each element is lower than a monoelemental lamp, which increases the signal-to-noise ratio and decreases the sensitivity of the analyses.

3.3.3 Electrodeless Discharge Lamp (EDL)

An electrodeless discharge lamp (EDL) is a discrete light source and was presented as an alternative to HCLs (hollow cathode lamps), but with high intensity emissions. They are very useful for more volatile elements with emission lines in UV region, where HCL has a lower performance.

EDLs consist of the element or a salt of the element sealed in a quartz bulb containing an inert gas. The capsule is placed inside a ceramic cylinder involved with a metallic wire coil. A radio-frequency power source distributes energy that passes through a conducting coil creating an oscillating electric field that ionizes gas inside the bulb. As the electric field is oscillating, the ions are accelerated so that they all have enough kinetic energy to excite the metal atoms inside the bulb when colliding with them. When they return to the ground state, the excited atoms release absorbed energy by emitting light with characteristic element spectrum.

Despite of HCLs efficiency, the cost-effective asset acquisition of EDLs is higher over its lifetime so it is normally used when HCLs are not enough to solve a specific analytical problem. Thus, it is more common to find a big quantity of HCLs in laboratories and none or only few units of EDLs.

3.3.4 Modulators

The atomic absorption spectrometric method is based on measuring the amount of radiation coming from the lamp before and after passing through the sample. However, there are other light sources as the environment and, mainly, atomization system captured in the monochromator. The other light sources interfere in the measurement by reducing signal-to-noise ratio, sensitivity and accuracy of analysis. The solution to this problem is the modulated drive signal of the lamp and combined with the synchronization of the detector to amplify selectively the signal of the lamp. The modulation can be mechanical or electrical and, practically, both of them have similar results.

With old equipments, mechanical modulation is normally performed by a rotating shield located between the lamp and the atomization system, so that the light of the lamp alternately passes through the atomizer or is blocked, at a general frequency of 50 to 60 Hz. Electronic modulation is the most common among new equipments, where the current of the lamp is on and off rapidly. The equipment electronic circuits compensate variations of the lamp's current, filtrate interfering sources and measure analytical signals.

3.3.5 Atomization system

Although there are some different techniques used to work with solid and gaseous samples in most of the atomic absorption equipments, these samples are introduced in solution.

To determine the contamination level and amount of lead in fish, e.g., a representative sample of fish is collected, treated, and dissolved in acid or in an appropriate acid mixture. The resulting solution has its volume adjusted and finally taken to the equipment for respective analysis. The lead in the solution is used as an ionic form (Pb^{2+}) but the radiation emitted by the lamp is specific to metallic lead (Pb^0), and is not absorbed by the ion lead.

To make a determination, the lead ion has to be separated by a solution, reduced to metallic lead (gaseous form) and placed in the optical path between the lamp and the monochromator. This all is done by the atomization system and mostly common by using a flame to provide necessary energy so that the atomization process occurs. When this kind of

atomizer is used, the technique is known as Flame Atomic Absorption Spectrometry (FAAS).

Figure 4 shows an atomizer with a pre-mixture chamber, actually, most commonly used in FAAS. The solution containing the analyte is aspirated by a nebulizer, mixed in a nebulization chamber with the gases. The obtained mixture is directed to the burner, where they are burned, occurring sample atomization and absorption.

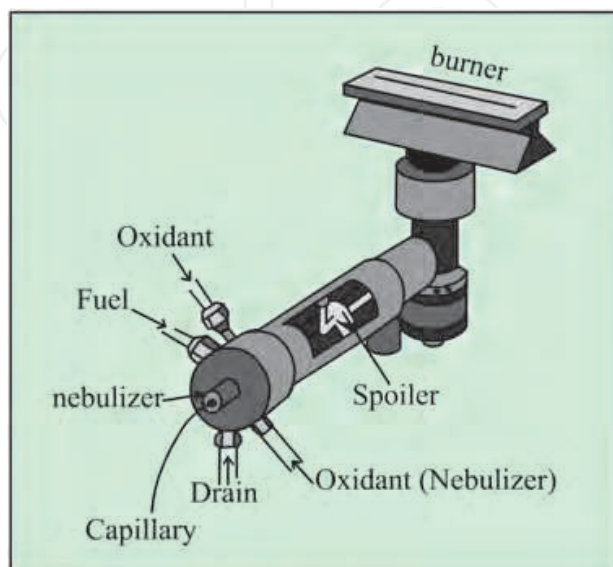


Fig. 4. Scheme of the pre-mixture atomizing.

The nebulizer has an orifice for gases and a central capillary tube where the solution to be analyzed is introduced. The gas, generally the oxidant, goes at a high speed and causes a pressure decrease in the capillary that pulls the solution (venture effect) and injects it in the nebulizer chamber as a thin aerosol. This kind of nebulizer typically has a flow rate measurement of 3 to 5 ml per minute and a constant and stable flow is obtained in less than 30 s after starting the aspiration.

The mixture, oxidant and fuel gas are homogenized in the nebulizer chamber with the aerosol coming from the nebulizer. It is coated with a resistant material to acid, alkali and various kinds of organic solvent. At the entrance to the chamber, in front of the nebulizer, there is a flow spoiler used to select aerosol droplets: the smaller ones are pulled by gas flow that passes around the spoiler and goes into the burner. This is necessary because small droplets improve the atomization and its homogenized size helps to produce a stable signal. The bigger ones, as they have more mass, are not deviated by the flow of gases, colliding with the spoiler, falling into the back of the chamber and are released by a drain. Approximately 95% of solution is discarded, being one the main restrictions to increase the technique sensitivity.

After passing through the chamber, solution and gases get to the burner. A burner is a metallic piece, generally a titanium based-alloy or another with high chemical and thermal resistance with a slit of 5 to 10 cm length and 1 to 2 mm width. Gases escape through that slit and are incinerated by forming an aligned thin layer of fire with optic axis of the equipment where the analyte atomization and selective radiation absorption emitted by the lamp occurs. The length of the slit defines the optical path, term used in spectrometry to describe the size of the sample cell, this is, the distance covered by radiation at the same

means of the absorbent species. In this case, the flame is the sample cell with 5 or 10 cm of optical path, depending on the burner used. The amount of radiation absorbed is proportionally directed to the optical path, thus, the size of the burner influences the sensitivity and the detection limit that can be obtained with this technique.

Figure 5 shows several steps that occur during the atomization process of any element M, initially in solution of ionic M^+ . The nebulizer and the chamber of nebulizer are responsible for transferring part of a flask solution to the burner, in continuous flow of very small droplets.

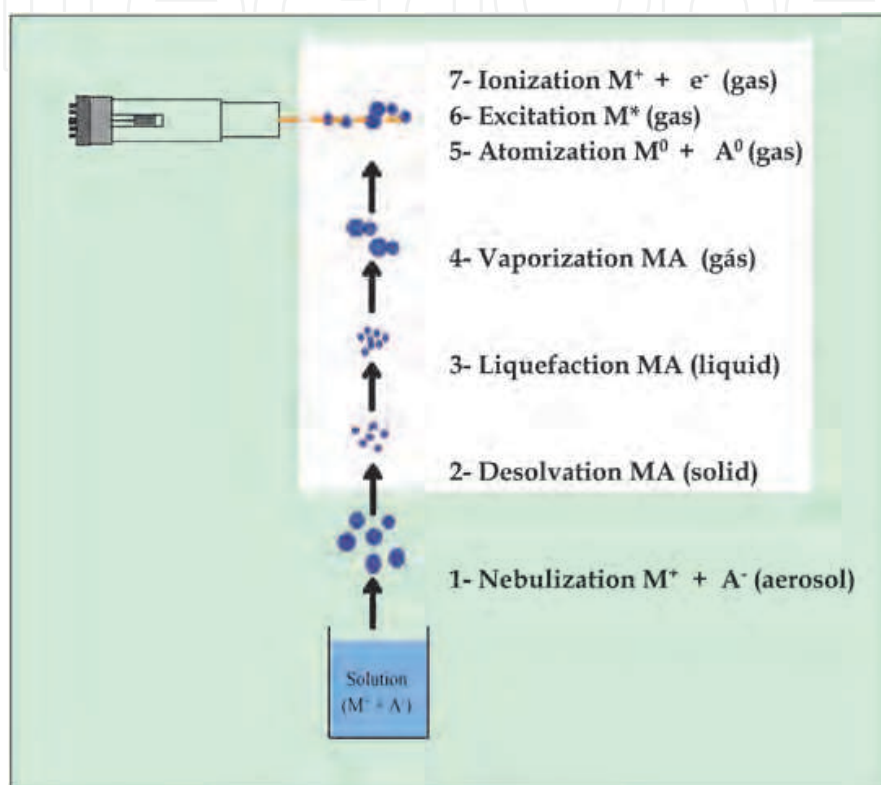


Fig. 5. Scheme of atomization mechanism.

When getting to the flame, the solvent dries fast and a solid MA compound is formed where A is an anion present in the solution. The heat is enough to liquefy, vaporize and break the bond of compound MA, releasing gaseous atomic specie M^0 in the ground state. This species absorbs a specific wavelength radiation emitted by the lamp. If the temperature were high enough, M^0 could be excited to M^* or lose an electron and passed to M^+ , but these two species do not absorb the wavelength that is measured by decreasing the analytical signal.

The temperature is the variable that most influences the atomization process. The best way to control this variable is through a critical choice of fuel and oxidants gases, and varying the percentage to a fine adjustment among them. As examples of fuel gases, we can cite propane, hydrogen and acetylene. As examples of oxidant gases, we can cite air, oxygen and nitrous oxide (Skoog et al., 2006).

Although this is a dynamic process, the solution is pulled with constant speed and, therefore, the population of M^0 species at the light path is also fairly constant over the time, producing a well stable absorption signal. The number of readings and its respective time

can be freely adjusted by the operator (generally between 0.5 and 2s), however, it can be obtained quickly a very reliable and reproducible average.

A relative concentration on each species of elements M (M^+ , MA, M^0 , M^* , etc.) varies according to different factors, as the temperature and nature of the flame (oxidation or reduction), composition and speed of the solution aspiration, M ionizing power, stability of MA species and flame region observed. As only gaseous species M^0 produces the desired analytical signal, all variables are optimized and their concentration can reach a maximum value exactly in the flame region aligned of the optical path.

Air-acetylene is one of the most used flames for elements that show fewer tendencies to form thermally stable compounds. Nitrous oxide-acetylene is used because of its high temperature and low and safe speed burn. For safety measures, the burner with a slit of 5 cm is used for nitrous oxide-acetylene. When air-acetylene mix is used, the preference is about 10 cm. Other compositions are rarely used and only for very specific analyses.

Pneumatic atomizing systems for FAAS are simple, robust and reliable demanding little maintenance, however their technique sensitivity is limited because they discard most of the solution away and also for the little time of residence of the absorption species in the optical path. This was noticeable since the first beginning of its development and, along the last five decades, several authors proposed alternative ways of atomization. Some of them were developed until the commercialization phase, initially, as basic equipment accessories, achieving then, the status of alternative analyses techniques.

3.3.6 Other kinds of atomizers

Using a same spectrometer, three more basic atomizers can be used to produce ground state atoms, which are used for specific techniques. These atomizers were adapted because of its limitation to flame AA sensitivity. Despite FAAS is a rapid and precise method of analysis, the need for trace metal analyses at $\mu\text{g L}^{-1}$ level calls for a more sensitive technique. By examining the flame AA process, a number of areas limit the sensitivity of the technique: the concentration of analyte, nebulizer for flow-low rate liquid sample, and the major sample loss during the nebulizer process until reaching a burner, little time of the sample in the flame and, finally, chemical interferences occurred during the atomization process.

With exception of analyte concentration, these limitations occur practically with a large amount of atoms in an optical one-way for a longer period of time. This is the basic principle of three different atomization processes that, noticeably, receive the following analytical techniques denomination: Hydride Generation, Cold Vapor Mercury and Graphite Furnace Atomic Absorption.

Hydride Generation Technique – First, elements forming volatile hydrides (As, Pb, Sn, Bi, Sb, Te, Ge and Se) can react with reducing agents in mid-acid, generally with sodium borohydride. The gaseous hydrides are transported by the stripping argon flow directly to a cell on the central burner head (air/acetylene) and perfectly adjusted in the optical path of the atomic absorption spectrometer. In either case, they hydride gas is dissociated in the heated cell into free atoms, occurring the absorption process. The maximum absorption reading, or peak height, or the integrated peak area is taken as the analytical signal. For these elements, detection limits below $\mu\text{g L}^{-1}$ range are achievable. The great advantage of this technique is the separation of specific elements as hydrides (pre-concentration stage), eliminating the interference from the matrix. Figure 6 shows a schematic hydride generator being atomized into the cell by the flame.

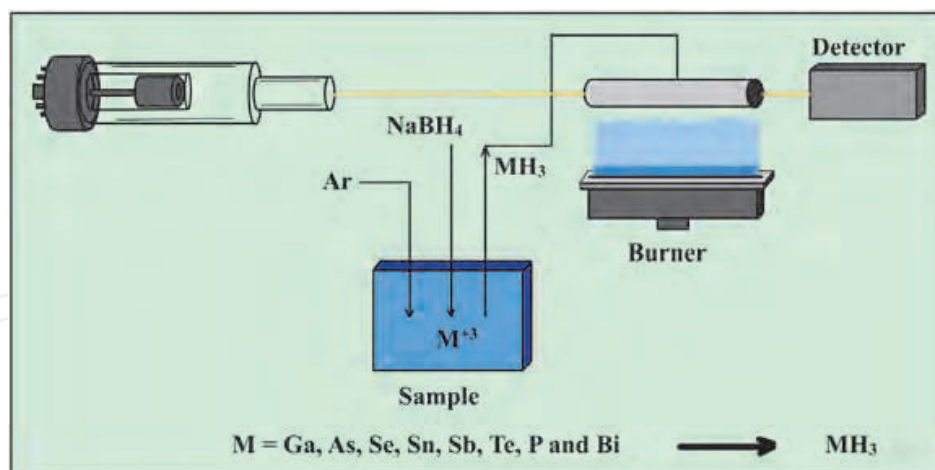


Fig. 6. Scheme of the hydride generation technique.

The major limitation to the hydride generation technique is that it is restricted primarily to the elements listed above, and results depend heavily on the valence state of the analyte, reaction time, gas pressures, acid concentration, and cell temperature. The formation of the analyze hydrides is also suppressed by a number of common matrix components, leaving the technique subject to chemical interference.

Cold Vapor Mercury Technique - This technique is only used to determine mercury due to its chemical characteristic reduced to atomic state by a sample reaction with a strong reducing agent as tin chloride or sodium borohydride in a closed reaction system. Similar to the previous system, the volatile free mercury is then driven from the reaction flask by air or argon bubbling through the solution, being carried in the light path of the AA spectrometer. Also, all of the mercury in the sample solution placed in the reaction flask is chemically atomized and transported to the sample cell for measuring the absorbance. The advantage of this technique is that sensibility can be increased by simply addition of the amount of the sample. The detection limit for mercury by this technique is approximately $0.02 \mu\text{g L}^{-1}$.

Graphite Furnace Technique - So far the most advanced and widely used high sensitivity sampling technique for atomic absorption is the graphite furnace. In this technique, a tube of graphite is placed inside a furnace with rigorous control of temperature, where it can be cooled by current inert gas. The furnace is aligned to permit the passage of the lamp light beam. The importance of this technique requires a more detailed discussion in the following items.

3.3.7 Monochromator

Lamps used in atomic absorption, as previously mentioned, emit discrete spectral lines. The number of lines depends on different factors as the number of possible electronic transitions from the emitter element, applied current, presence of other emitter elements, and others. Besides that, the atomizing system is a powerful radiation emitter.

The mathematical description to relate radiation absorption with the concentration of analyte in the solution (Beer-Lambert's Law) is based on the measurements with monochromatic radiation, this means, a unique wavelength. On the other hand, the detectors are sensitive to photons and all the range of ultraviolet and visible radiation. Though, it is necessary to have a device between the source and the detector to select and isolate the appropriate wavelength.

The chosen wavelength is emitted and absorbed with greater intensity by the element and is related to the most probable electronic transition for the atom in ground state. The more transition probability, more frequently it will occur, so, more photons from the wavelength will be emitted. That wavelength or spectral line is known as resonance line. Due to its intensity, it provides a better signal-to-noise relation and the best sensitivity for the analysis. The monochromator is responsible for selecting the appropriate wavelength for analysis. It is a hermetical closed box with entrance and exit slits of 0.2 to 2nm, lenses and mirrors to focus the radiation and a dispersed element that can be a prism or a diffraction grating or a combination of them. It is filled up with inert gas to avoid ultraviolet radiation absorption by the air and normally has the walls painted in matte black to avoid reflection and scattered radiation. The polychromatic radiation enters through the entrance slit, it is separated and only the chosen wavelength of radiation reaches the exit slit and goes on to the detector.

In practice, the monochromators are not able to isolate a unique wavelength. So, a wavelengths range goes to the detector. The bandwidth depends on the resolution, which is the ability to distinguish between two near wavelengths. The more sophisticated an expensive the monochromator is, the better its resolution is. Most of the lamps used emit simple spectra and the monochromator can have a low resolution, around 0.1nm.

Figure 7 shows a design of a Czerny-Turner monochromator used in atomic absorption. In this project, the radiation enters through the entrance slit and is focused in the diffraction grating (dispersant element) by a spherical mirror. The grating is set up in a gyratory support that allows determining the angles of incidence and reflection and, after separated, the chosen wavelength is focused in the exit slit by another spherical mirror until reaching the detector. This is known as sequential monochromator, because it is possible to determine the selection of any wavelength by only revolving the diffraction grating.

In this case, the dispersed element is a diffraction grating. The grating is made on a substratum glass or quartz struck with grooves, cut with very precise angles and covered with a reflexive surface. When reaching this surface, the radiation is reflected at an angle that depends upon the wavelength of the incident ray. Different wavelengths are reflected at different angles, occurring dispersion of radiation. The more the number of grooves, the bigger the resolution of grating and separation are. Although this is not unique, the grating resolution is one of the main factors affecting the monochromators' performance. Monochromators used in atomic absorption equipments generally have grating up to 1000 slots per millimeter.

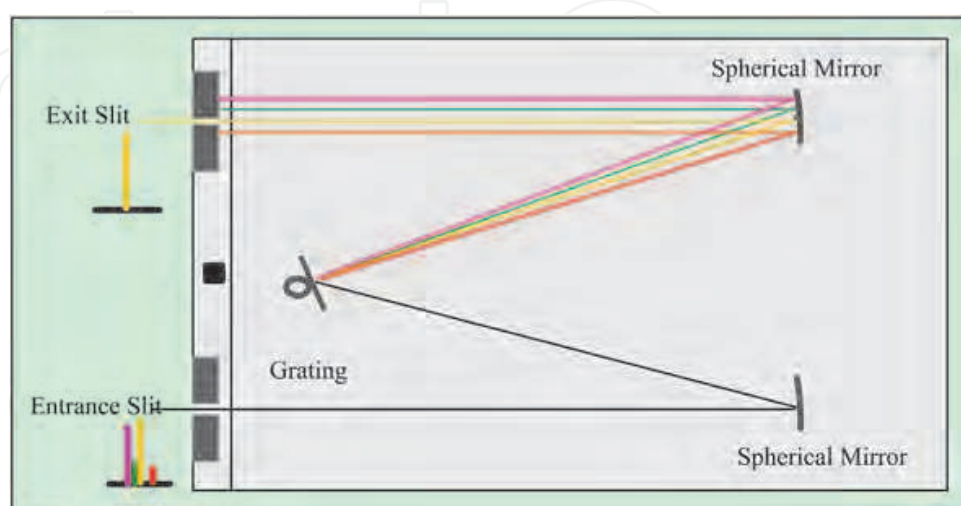


Fig. 7. Diagram of a discrete light diffraction in a Czerny-Turner monochromator.

Echelle monochromators, use a diffraction grating and a prism as dispersing elements that spread the spectrum in two dimensions. In the last decade, this kind of monochromator has been mainly chosen because they are well adapted to solid-state detectors are available today. These monochromators are called simultaneous or multi-channels and the measured wavelengths depend on the relative positions of dispersing elements and detector. In this case, it is not possible to determine any wavelengths for the determination, but only the ones that are pre-determined when the equipment is built. In the practice, this is not a very serious limitation, because the solid-state detectors are formed by millions of pixels and each one of them can work as an individual detector. This way, there are hundreds of available lines to be determined.

One of the advantages of these monochromators is that they do not have mobile parts that avoid mechanical defects such as misalignments and looseness occurring with sequential types. Besides that, they permit to determine several elements simultaneously. It does not have much utility when used with lines emission lamps, but there are equipments using continuous sources associated to monochromators of high resolution, which permit a simultaneous determination of over 60 elements in few seconds. These equipments can solve one of the main limitations of the technique with enough time to determine several elements in one same sample.

3.3.8 Detector

The detector is placed in front of the exit slit and receives the determined photons by the monochromator. It transforms lightning energy in an electrical signal, that is amplified and measured. Detectors mostly used in old equipments are photo-multiplier valves. With modern equipments, they are being substituted by a system based on solid-state detectors type CCD (charge coupled device). They are similar to digital cameras sensors with a set of sensitive pixels to electromagnetic radiation in the UV regions and visible that transforms the energy of photons coming from the monochromator into a digital signal.

Modern CCDs have from 1 to 50 millions of pixels (megapixels) working each one of them as individual detectors. When coupled to an Echelle monochromator of high resolution and to a continuous radiation source, they can transform the atomic absorption spectrometry in a simultaneous technique of analysis. This is a technological advance of great importance and, in practice, this means to pass the determination of one to tens elements every five minutes. Equipments with that configuration are still unusual and much research is being performed about this matter, however, many researchers believe than in a close future this will turn into a standard configuration.

3.3.9 Acquisition of data processing

In the beginning, the signal obtained in the detector was read in an analogical amperemeter. The value was written down and then, all the calculation was done manually. Nowadays, everything is made by a microcomputer equipped with a specific program for operational control and data processing.

Each manufacturer develops a program according to the characteristics and implemented accessories in the spectrometry, so that everything can be done by software, e.g., how to turn on, how to pre-heat and align the lamps, how to control the gases flow, how to change and align the atomization system, how to program and control automatic samplers and graphite furnace, among others.

In the acquisition and data processing part, the number of repetitions and the time of reading integration, number of samples and number and concentration of the analytical curve solutions, etc. can be programmed. Once the readings are obtained, the program draws the analytical curve, performs interpolation values of absorption and calculates the concentration of the sample solutions. If the mass of a solid sample and the dilutions done after solubilization are provided, the program will directly calculate the concentration of the analyte in the solid sample.

4. Sample preparation

Atomic absorption analyses are most commonly performed with standards and samples in solutions. Before introduction into the equipment, the solid samples need to be solubilized in a process generically known as sample preparation. This is a very slow process in the development of an analytical methodology. Considering all analytical operations, this is the most critical and most time-consuming. This analysis might present a large possibility of errors, which may result in a more expensive cost (Kingston & Jassie, 1988).

There are two large categories of analytical matrices: organic and inorganic samples. The inorganic samples incorporate soil, inorganic substance, sediment, clay and metal. The organic samples or carbon-based includes biological, polymeric, petrochemical and pharmaceutical samples. Organic samples can be solubilized in a dry or wet basis, and in a open or closed systems. These methods guarantee the elimination of organic material and the quantitative recovery of analyte in solution (Kingston & Jassie, 1988; Oliveira, 2003).

Decomposition methods via dry ashing consist of burning the sample at elevated temperatures (450-550°C), O₂ atmosphere to atmosphere pressure. This method allows to calcinate big amounts of samples and to dissolve the ash in a small volume of acid facilitating the sample analysis in case the element of interest comes in small quantity. Some problems may result in the loss of volatile elements due to high temperatures, reaction of the analyte with the crucible material or difficulty with the dissolution of the residue (Hoenig & Kersabiec, 1996; Watson, 1994).

Wet digestion in open systems consists of the oxidation by an acid or by a mixture of acids aided by heating. This is a technique that requires hard work and can evolve a great amount of toxic products (nitrogen oxides) (Hoenig & Kersabiec, 1996), it also increases the risk of constituent loss and contamination. These problems could be minimized if they were performed in closed places, digestion pumps of PTFE (Teflon), and heated by conduction or convection. In this case, the increase of temperature and pressure increases the speed of the reaction; however, it would take time-consuming or long hours for the digestion/cooling (Figueiredo et al., 1985). The use of digestion procedure in microwave systems is an alternative. Besides reducing the time of decomposition, it avoids contaminating the sample with maximal efficiency of solubilization (Kingston & Jassie, 1988). The microwave has been widely used in the solubilization of samples with high organic content (Binstock, 2000; Costa et al., 2001; Pouzar et al., 2001; Wasilewsk et al., 2002).

Some kinds of inorganic samples take much time to be solubilized via wet digestion methods, even using closed systems in microwaves-assisted. As for example, samples of silicate cement, refractory oxides, minerals and others. Here, a fusion method can be used. It consists of a fusion and reaction of the sample with high-temperature fluxes (300 to 1000°C), followed by the solubility product formed by an acid or a mixture of acids (Oliveira, 2003). Some common fondants used are lithium metaborate, sodium carbonate and potassium

nitrate, among others. Additional quantity of fondants varies between 5 to 50 times of the sample mass and the high-temperature reaction transforms insoluble compounds in products that can be easily solubilized. As a reference example it can be mentioned silica (SiO_2 , insoluble in acids except for HF) with sodium carbonate, forming soluble sodium silicate (Na_2SiO_3). The disadvantage of this method is the time and sample manipulation for its performance and the possible contamination of the samples by impurity fondants. This factor is critical for trace and ultra trace analyses.

After solubilization, other procedures are required for adequate samples and conditions of analysis as the separation of interferences or pre-concentration of elements of interest. The ideal solubilization method should be the simplest to get to dissolve the sample completely and, the most important, the final solution should contain all analytes of interest.

5. Interferences

Atomic absorption is a very specific technique with a few interferences. Such interferences can be classified into six categories: chemical interference, ionization interference, matrix interference, emission interference, spectral interference, background interference. Since they are very precise, there are available methods that can overcome most of the problems.

5.1 Chemical interference

If the sample in the flame can produce a thermal stable component of the analyte to be analyzed and if it does not dissociate completely in the flame, the population of analyte atoms that can absorb will be reduced. This will decrease the sensitivity analysis. This problem is normally solved in two ways: with temperature higher than the flame (where the compound is unstable and can be broken down), or adding a sequestering agent. This sequestering agent is a cation that competes with analyte of interest by formation of the stable compound. If the sequestering agent has a higher concentration, the analyte of interest is released to form the atom. A good example of a sequestering agent is the addition of lanthanum to determine Ca in samples that contain phosphate. A high concentration of lanthanum, which also forms a thermally stable compound with phosphate, releases calcium to the atomic state and allows it to be detected with good sensitivity, even when air-acetylene is used as a mix to produce flame. In case of using nitrous oxide-acetylene, this technique is not necessary since the flame is hotter and can break down the calcium phosphate.

5.2 Ionization interference

Ionization interference occurs when the flame temperature is too high for the analyte and, therefore, has enough energy to take it beyond the neutral atomic state and to produce ions. This also decreases the population of atoms that can absorb. A strategy to solve this problem is by adding ionization suppression to the sample, standards and white. The most common ones are K, Na, Rb and Cs, alkali metals that are easily ionizable and increase the electrons population in the flame, minimizing the formation of other cations. The analyte in the sample will not be ionized so easily. Another strategic is by working with cooler flames, which reduce ionization effects.

5.3 Matrix interference

Matrix interferences may increase or decrease the signal. They occur because the physicochemical characteristics of the sample matrix (viscosity, burn speed, surface tension)

may differ substantially from the calibration curve standards. This may occur because of the difference on concentration of dissolved salts, acids and bases, because of the use of different solvents, or when the patterns and sample temperatures are very different. When it is not possible to reproduce the matrix or there are no standardized samples, it is recommended to use the matrix spike test.

5.4 Emission interference

If the emission intensity of the interest analyte is high, the analyte absorption may decrease due to its reduction of the ground state atoms population. The modulation of the lamp signal eliminates the problem of the detector to measure the emission signal mixed with signal coming from the lamp. The use of cooler flames may reduce the absorption.

5.5 Spectral interference

There are rare cases in which two elements present in the sample absorb the same spectral line. If the problem is detected, the simplest solution is to change the spectral line. It is very important to obtain previous information about the elements that may interfere in the line used and whether they are likely to be in the sample so that it can be confirmed and solved.

5.6 Background interference

This problem cannot be corrected by the matrix spike test and it occurs due to the light distribution caused by particles present in the flame, or for the light absorption caused by molecular fragments of materials coming from the sample matrix. To solve this problem, the background absorption must be determined and subtracted from the total. This determination is obtained since the analyte absorbs in a straight line and the background forms a wide absorption band. Therefore, an accessory lamp, as a deuterium lamp, that emits a continuous spectrum can be used, either the sample gets the light from the hollow cathode lamp or from the deuterium lamp. As the analyte absorbs very little from the continuous spectrum, the continuous absorption is all from the interference and can be subtracted from the total absorption measured by the hollow cathode lamp.

6. Quantitative analysis in absorption (flame atomization)

Quantitative analysis, as mentioned before, is possible due to the relation of the absorbance signal by the concentration of the analyte (Lambert-Beer Law). Basically, the atomic absorption spectrometry analysis consists of comparing absorbance signals of a group from patterns and samples.

In order to have a good instrumental performance, that is, to work with maximum analytical sensitivity, it is imperative the evaluation of some of the instrumental parameters. Every part of an atomic absorption equipment needs to be adjusted in order to have an optimization. Basically, these parameters according to figures of merit in AAS are: selection of the wavelength in relation to the concentration of analyte, adjustment of the lamp current, adjustment of oxidant and reducing gases flow, adjustment of the height of the burner and nebulizer pressure, due to the distance of the needle to the nebulizer chamber, selection of the monochromator exit slit and adjustment of the background effect, if necessary. In modern equipments, most of the adjustments are automatic.

Once adjusted all parameters, the determination starts reading the absorbance of the analytical blank, followed by the standards with increasing concentrations. Considering the

obtained values, an analytical curve is constructed. If the correlation for this curve is significant, it is possible to start the aspiration of the sample solutions and to read the respective absorbance values. By interpolation in the analytical curve, it is obtained the sample solution analyte concentration value. The concentration value of the original sample is calculated considering the amounts of the samples (mass or aliquot) and respective dilutions.

7. Introduction to graphite furnace atomic absorption

Differently from other spectrometric techniques, electrothermal atomization can get a total atomization of the sample inside the graphite tube, the signal observed depends on analyze mass rather than concentration, the term "characteristic mass (m_0)" is used as a measure of the sensitivity of the furnace. Characteristic mass is analogous to characteristic concentration for flame AA except that mass, rather than concentration, is related to absorbance. The characteristic mass of an analyte is defined as the mass of analyte in picograms required to produce a peak height signal of 0.0044 absorbance or an integrated peak area signal of 0.0044 absorbance-seconds (A.s), which corresponds to only 1% of the total light absorbed ($\log 100/99$). This way, the detection limits in graphite furnace are usually defined in mass units (pg) instead of concentration units.

A basic graphite furnace atomizer is comprised of the following components: graphite tube, electrical contacts, enclosed water cooled housing and inert purge gas controls. Figure 8 shows the basic constituents of graphite furnace atomizer.

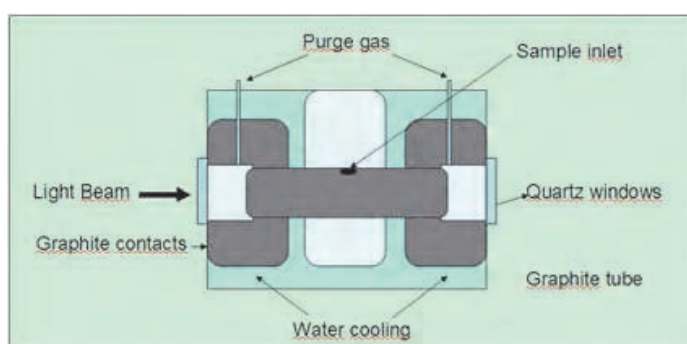


Fig. 8. Scheme of the longitudinally-heated graphite furnace atomizer.

The tube is held in place between two graphite contact cylinders, which provide electrical connection. An electrical potential applied to the contacts causes current to flow through the tube, leading to the heating of the tube and the sample. All this system is placed and aligned with the light beam.

Basically, GFAAS methodology consists of 5 steps that, evidently, can be in greater number according to the complexity of the sample. First, the sample (5 to 50 μL) is introduced by an automatic injector, and the analytical programming begins. The temperature of the furnace is slowly increased up to the temperature in which the solvent vaporizes, remaining at this temperature for a certain time. The elapsed time on each analytical phase is crucial, since loss of the analyte by evaporation may occur, or the physicochemical process of the sample may be incomplete, especially in this drying phase, in which the amount of volatile constituents present in the samples is bigger. After the drying phase, the temperature is gradually increased until it reaches the pyrolysis value (Ash), when fusion and evaporation

of the more volatile constituents in relation to the volatilization temperature of the analyte of interest will occur, remaining for a while to be effective. Immediately and quickly, the temperature of the furnace reaches the temperature of the analyte atomization, differently from others in this phase, the inert gas, usually argon, is interrupted so that the maximum interaction of the atomic cloud with the electromagnetic lamp may occur. This also helps to maximize sample residence time in the tube and increase the measurement absorbance signal. Finally, the cleaning phase (Clean Out) occurs, by using higher temperatures in order to assure there is no remaining residual causing memory effect, which interferes with future atomizations. After all these steps, the system cooling takes place (Cool Down). Besides helping cooling the system and not interfering with the chemical properties of the sample inside the tube during the analysis phase, the inert gas is used to minimize graphite oxidation of the tube and furnace.

The figure 9 shows a typical programming in graphite furnace atomization, the characteristic effect inside the tube (lateral side) and the absorption measurement profile.

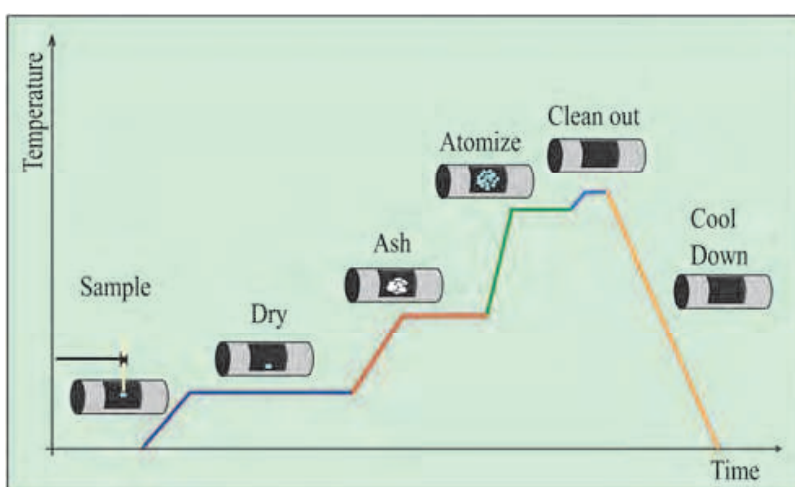


Fig. 9. Furnace thermal stages.

A significant characteristic of the graphite furnace is its high sensitivity. This technique has been implemented as an analytical routine in several kinds of samples, especially the ones related to environmental. Also, with the possibility of controlling the atmosphere and temperature inside the graphite tube, complex samples can be modified physically and chemically (the later with the addition of the so called chemical modifiers) during the analysis phases, enabling, therefore, a “cleaner” sample during the atomization phase and minimizing matrix interference. Due to advancements in technology and scientific researches, new materials and new modifiers have enabled better sensitivity and the increase of chemical elements can be quantified by this technique. They have made it possible to analyze very complex sample matrices, such as those frequently found in biological and geological samples. The microliter sample sizes used, offer additional benefits in which the amount of sample available for analysis is limited, as in many clinical analysis. Opposite to the significant sensitivity, the signal handling requirements for graphite furnace atomic absorption are much more demanding than those for flame atomic absorption. Graphite furnace signals change rapidly, background levels are higher, and signal interpretation needs are more extensive. Only with the development of an analysis protocol known as the Stabilized Temperature Platform Furnace (STPF), the GFAAS implementation

has been intensified due to the analytical efficiency acquired. This way, combining the stability in the analyte atomization provided by background correction (Zeeman) and the experimental conditions that minimize graphite furnace interferences, this development is mainly financed by the manufacturers of AA equipment and a large number of scientific work have been published.

These factors (STPF) contribute significantly to precision and detection limit performance: the L'vov platform (pyrolytic coating), whose function is to delay atomization and longitudinal heating until the furnace tube has reached steady state conditions; fast electronics to accurately follow the changing signal absorbance with symmetrical profiles; use of integrated peak absorbance signals to accurately quantitative the analyte regardless of changes in peak shape caused by the matrix; matrix modifiers to convert the analyte to less volatile compounds in the step atomization and which are atomized only after the furnace tube has reached a steady state temperature or to make the matrix components more volatile that are eliminated in the ash step, and maximum power heating to bring the furnace to a steady state temperature before the analyte is atomized.

The Zeeman Effect with the magnet on the analyte is an ideal performance to perform background correction for graphite furnace analyses. Correction occurs at precisely the same wavelength used for analysis, thus correcting properly even when the background is structured. The Zeeman Effect uses the identical light source with the same electrical source conditions to produce both the analytical and background signals. This corrects at the same time for source or detector drift and for non-atomic absorption.

In fact, with the condition of STPF applications, the diverse kinds and powerful background corrections and high sensitivity make electrothermal atomization be one of the most used among the atomic absorption techniques. Allied to other separation techniques (chromatography), continuous measurement systems (CMS) and solid sample, this latter in a vertiginous application in diverse matrices, GFAAS stands out not only in the use of analytical routine for diverse industrial segments, but also in scientific aspects and they will be referred in the application item of atomic absorption spectrometry.

7.1 Background correction

Radiation from lamp is attenuated by non-atomic source: molecular species, solid particles, absorption and scatter. The signal is added to atomic signal results in falsely high signal. This problem is more severe in graphite furnace than in FAAS.

Small analyte signals should not be measured in the presence of high background since it reduces energy at detector according to the high absorbance, reduces signal-to-noise-ratio and degraded precision and accuracy. Several techniques allow subtraction of background from total absorbance measurement.

The measurement of signal absorption in a determination by AAS is given according to the following sequence: first, the detector receives the signal: atomic + non-specific after the atomization; then, the same detector receives the signal only from the background correction: non-specific only; finally, measurements are timely separated in a few milliseconds, atomic absorption calculated: total absorbance - background absorbance = atomic absorbance.

Common background correction techniques are Deuterium for the atomization flame, Zeeman for the atomization graphite furnace and the least common Smith-Hieftje setup.

8. Technological innovations

8.1 Tungsten filament

Studies about the use of tungsten filament, tantalus and other metals date back from 1960. However, Berndt & Schaldach (1988) presented and developed an open system to work with tungsten filaments. Results obtained as reference solutions demonstrated the power of the tungsten filament as an atomizer for Ba, Cd, Co, Cr, Eu, Mn, Pb, Sn and V determination.

The scientific community, therefore, got more interested in this kind of study where tungsten filaments were used as atomizers with different spectrometry techniques. Nowadays, mechanisms to introduce samples in ICP OES and ICP-MS based on electrothermal heat used in graphite and filaments furnace are commercialized. These mechanisms have permitted, besides the liquid sample, solid sampling and slurries samples. However, the literature shows little work related to the use of tapes, tubes or tungsten filaments that can also help the vaporization for sample introduction in different spectrometric techniques.

8.2 Flame tubular furnace and thermal aerosol

The use of thermal aerosol in the sample introduction of the tube atomizer (TS-FFAAS, or thermo spray flame furnace atomic absorption spectrometry) in flame (air-acetylene) was initially proposed by Gaspar & Berndt (2000). The system consists of an auto sampler, a peristaltic pump, a ceramic capilar where the sample is introduced into a flame-heated nickel tube (Figure 10).

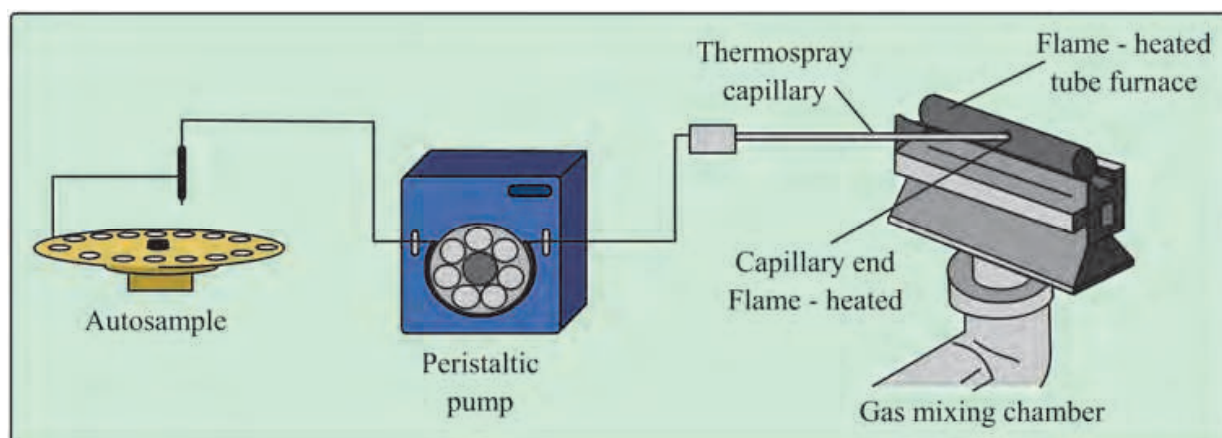


Fig. 10. Representation of a sample introduction system (From: Gáspar & Berndt, 2000).

The complete introduction of the sample in the atomizer tube as well as the increase of the residence time of the atomic cloud in the optical path (137ms) promote the improvement of the analytical signal to various volatile metals as: Ag, As, Au, Bi, Cd, Cu, Hg, In, K, Pb, Pd, Rb, Sb, Se, Te, Tl and Zn. Consequently, a considerable gain-sensitivity is obtained when compared to FAAS. The detection gain varies according to the element, being able to oscillate by a factor of three (Cu, of $14 \mu\text{g L}^{-1}$ in FAAS for $4.2 \mu\text{g L}^{-1}$ in TS-FF-FAAS) or, as observed for Cd, in a factor of 110 (Cd, of $34 \mu\text{g L}^{-1}$ in FAAS for $0.31 \mu\text{g L}^{-1}$ in TS-FF-FAAS). The aerosol formation is based on Leidenfrost effect, in which the heated surface of the capillary generates an increasing temperature and a steam layer in the capillary wall that helps with the drop and pulverization. This makes that the steam phase of the sample be

superior to the liquid phase present in the tube. Pereira-Filho et al., (2002) published the first work involving analytical application of TS-FF-AAS for the determination of Cd, Cu and Pb in biological samples suspensions. Perspective techniques have found direct injection of slurries as a good alternative to contour problems with the sample preparation, being chemical analysis the most difficult ones. Another possibility aims for synergistic effects with multi-elementary measurements, high sensitivity and selectivity of a high resolution continuum source atomic absorption, because there are no reports applying metallic atomizers with this technique.

8.3 High resolution continuous source atomic

Although the first atomic absorption spectrometry developed in the 19th century used a continuous source. Only at the end of the 20th century, it was possible to use atomic absorption spectrometry with continuum source. Improving the background corrections and diffraction patterns allied to studies and development proposed by the group of Harnly and Becker-Ross, the necessary technological maturity resulted in the atomic absorption spectrometry of high resolution and continuum source (HR-CS-AAS). This equipment is composed by Xenon arc lamp, ellipsoidal mirror, atomizer (flame or graphite furnace); entrance slit, paraboloid mirrors, prism, adjusted intermediate slit, echelle and CCD detector. This equipment contains a small Xenon arc lamp operating at 15 bar high pressure in a hot spot mode with a continuous emission monitoring system between 190 to 850 nm allowing a multi-elementary analytical determination.

Relating to measurements and background correction, the high resolution of the monochromator and CCD detector permit to identify the origin of atoms or molecular and eliminate them with an adequate procedure. Besides that, the atomic absorption measurement and the background are strictly simultaneous, permitting to visualize background signals. Some advantages of HR-CS-AAS and the use on a unique radiation source for all elements can be mentioned, multi-elementary determination, improvement of signal-noise-ratio due to the high emission intensity of Xenon lamp and, consequently, increase of the calibration range with variation until 5 orders of magnitude, simultaneous background correction in the proximity of the analytical line and better analytical performance of trace elements in complex samples.

9. New tendencies

In atomic absorption spectrometry or AAS, both with the classical flame AAS and with furnace AAS innovation took place. Remarkable efforts, however, were made to use all types of methods allowing volatile species generation with metals. Flame atomic absorption spectrometry (FAAS) is a mature analytical method, which is present in almost any analytical laboratory as a working horse for elemental determinations of metals. Innovation, however, is still going on with respect to the introduction of the sample into the atomizer and the increase of the analyte sampling efficiencies and residence times in the atomizer. By the so-called furnace in flame approach for volatile elements or volatile species forming elements especially, the sampling efficiency can be considerably increased as compared to conventional pneumatic nebulization with the improvement of limit of detection for lots of elements. A further technique for sample introduction which remains to attract the interest is thermospray. The use of cloud point extraction for isolating and pre-enriching heavy

metals from complex samples is another strategy for sample preparation and interesting for environmental sample application (Bings et al., 2010).

Addition to the elements that form volatile hydrides, also, a number of metals could be employed for analytical purpose. During the last years much research was done to widen the circle of metals which could be determined in this way and to know more about the volatile species generation mechanisms. Room temperature ionic liquids further were found to enhance the chemical vapor generation of transition elements following reduction in acidified aqueous solution with KBH_4 .

In relation to sample introduction by electrothermal systems the background correction further remains a topic of methodological development in GFAAS and SIMAAS (simultaneous atomic absorption spectrometry with electrothermal atomization). In the case of diode laser electrothermal atomization, both Zeeman and wavelength modulated atomic absorption could be shown to be valuable, and the detection limits obtained were shown to be at the same level as in coherent forward scattering in the case of crossed polarizers. With diode lasers in GFAAS, also, isotopic dilution could be applied for calibration, as Doppler-free measurements are possible. Apart from graphite furnace, also, tungsten furnaces remain a topic of investigation. Though they do not have the advantages of graphite furnaces in the sense of a reduction of the analytes from the oxides to the elemental form nor do they have the precision as a result of a good sample uptake, they have the advantage of being cheaper and without risks for stable carbide formation.

Furnace atomic absorption spectrometry retained its original form stemming from L'vov and Massmann's work, however, in every part of the system, considerable innovation occurred. In graphite furnace atomic absorption spectrometry (GFAAS), special attention has been paid to the thermochemical processes responsible for the atom cloud formation, as they are of crucial importance for the signal magnitude and form and, accordingly, for the accuracy and precision achievable. The stabilized temperature platform principle by a number of groups has been shown to be very powerful to eliminate a number of volatilization interferences in GFAAS. Similarly, lots of work have been published with the surface of graphite tube modified, mainly covered with refractory carbides that, besides improving atomization conditions, increases considerably the life cycle of the tube. Works have been published for the formation of refractory carbides and tubes and graphite platforms by using different methodologies and proving the efficiency through physical analyses (Izário Filho et al., 2001a, 2001b, 2001c). Direct solids sampling can be realized in flame AAS but innovation especially occurs in the case of electrothermal atomization. The less manipulation of sample is the great advantage of solid sampling when compared with sample preparation with dry or wet digestion. The use of the solid sample is associated to determinations of semi-metallic and non-metallic elements into the atomic absorption system, the HR-CS AAS, mainly for determination of phosphorous and sulphur in samples of petroleum, fuel and other derivatives. Welz and Curtius are exponents who developed applications of HR-CS AAS for elementary analysis and molecular analysis.

On the other hand, special problem in direct solids analysis is the calibration. In direct solids GFAAS, it has been proposed to use spiked filter papers for the determination of transition elements in vegetable samples. For a sampling of powders, the use of slurries is very convenient, e.g., in the direct determination of elements in gel forming konjac samples by enzymatic hydrolysis assisted slurry sampling GFAAS. The direct sampling of powder

samples and the injection of slurries under the use of a modifier mixture of Pd and Mg salts, where the solid sampling technique was found to be the most sensitive and easy technique.

10. Technical applications and research

As discussed in this text, Atomic Absorption Spectrometry have been used for the quantitative and qualitative determination of chemical elements on samples such as aqueous solutions, waters, sea-waters, metals and alloys, glass, drugs, food, environmental samples, industrial wastes, biological samples among others. Studies have been conducted using variations of the AAS, as flame (FAAS), hydride generation (HG-AAS) and graphite-furnace or electro-thermal (GFAAS or ETAAS) (Vogel et al., 2002). Quite whole work proposed some differential aspects related to the methodology or to the equipment. In some cases, association with other procedures or techniques, results in a hybrid technique, as occurs when AAS is used together with continuous flow-injection (FIA) or high-performance liquid chromatography (HPLC). Other technical advances are proposed too, as the use of integrated contact furnace (ICF), tungsten coil, or the association of TS-FF-AAS, acronym of thermal spray flame furnace AAS.

To estimate the importance of a subject to the scientific world is a very complex matter. Many criteria may be used, each one with vantages and disadvantages. In order to only illustrate the importance and the evolution of the atomic absorption spectrometry, we did a rapid search in the Science Direct <<http://www.sciencedirect.com>>, considering "atomic absorption spectrometry" as key-word in TITLE-ABSTR-KEY. Two periods were considered: the whole period (about half-century, since the first article was published) and the most recent one (from 2010 until present data, july 2011). Our rapid search returned 5,637 scientific papers, considering the whole period. A significant fraction of the works (463 articles, or 8.2%) concentrates in the most recent period. Considering graphite furnace atomic absorption 1,953 articles (34,6%) were found for the whole period, and 95 articles (4,9%) was found from 2010 until the present data.

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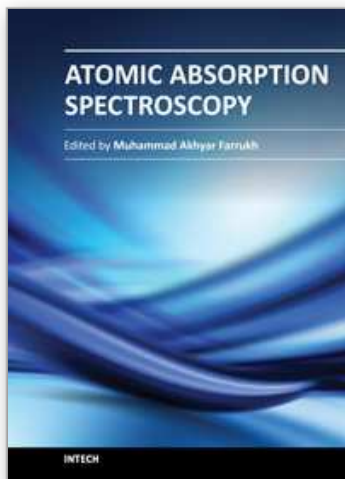
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Atomic Absorption Spectroscopy

Edited by Dr. Muhammad Akhyar Farrukh

ISBN 978-953-307-817-5

Hard cover, 258 pages

Publisher InTech

Published online 20, January, 2012

Published in print edition January, 2012

Atomic Absorption Spectroscopy is an analytical technique used for the qualitative and quantitative determination of the elements present in different samples like food, nanomaterials, biomaterials, forensics, and industrial wastes. The main aim of this book is to cover all major topics which are required to equip scholars with the recent advancement in this field. The book is divided into 12 chapters with an emphasis on specific topics. The first two chapters introduce the reader to the subject, its history, basic principles, instrumentation and sample preparation. Chapter 3 deals with the elemental profiling, functions, biochemistry and potential toxicity of metals, along with comparative techniques. Chapter 4 discusses the importance of sample preparation techniques with the focus on microextraction techniques. Keeping in view the importance of nanomaterials and refractory materials, chapters 5 and 6 highlight the ways to characterize these materials by using AAS. The interference effects between elements are explained in chapter 7. The characterizations of metals in food and biological samples have been given in chapters 8-11. Chapter 12 examines carbon capture and mineral storage with the analysis of metal contents.

How to reference

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Hélcio José Izário Filho, Rodrigo Fernando dos Santos Salazar, Maria da Rosa Capri, Ângelo Capri Neto, Marco Aurélio Kondracki de Alcântara and André Luís de Castro Peixoto (2012). State-of-the-Art and Trends in Atomic Absorption Spectrometry, Atomic Absorption Spectroscopy, Dr. Muhammad Akhyar Farrukh (Ed.), ISBN: 978-953-307-817-5, InTech, Available from: <http://www.intechopen.com/books/atomic-absorption-spectroscopy/state-of-the-art-and-trends-in-atomic-absorption-spectrometry>

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