Chapter

Atomic Spectroscopy

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Abstract

Atomic spectroscopy includes a number of analytical techniques used to determine the elemental composition of a sample (it can be gas, liquid, or solid) by observing its electromagnetic spectrum or its mass spectrum. Element concentrations of a millionth (ppm) or one billionth part (ppb) of the sample can be detected. There are different variations of atomic spectroscopy, emission, absorption, fluorescence, and mass spectroscopy. Determination of an appropriate technique requires a basic understanding of each technique since each has its individual strengths and limitations. This chapter is designed to provide a basic overview to the atomic spectroscopy techniques and how can you select the one that best suits our analytical problems.

Keywords: atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), atomic fluorescence spectroscopy (AFS), X-ray fluorescence (XRF), mass spectroscopy (MS)

1. Introduction

Spectroscopy is the study of interactions between matter and different forms of electromagnetic radiation; when practiced to quantitative analysis, the term spectrometry is used.

Atomic spectroscopy includes the techniques of atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), atomic fluorescence spectroscopy (AFS), X-ray fluorescence (XRF), and inorganic mass spectroscopy (MS). AAS, AES, and AFS exploit interactions between UV-visible light and the valence electrons of free gaseous atoms. In XRF, high-energy charged particles collide with inner-shell electrons of atom, initiating transitions with eventual emission of X-ray photons. For inorganic MS, ionized analyte atoms are separated in a magnetic field according to their mass to charge (m/z) ratio [1].

2. Atomic spectroscopy: general principles

Every element has a characteristic atomic structure, with a small, positively charged nucleus surrounded by a sufficient number of electrons necessary to maintain neutrality. Electrons settle into orbitals within an atom and one of the electrons can also jump from one energy level to the higher level by acquiring the necessitated energy (**Figure 1**). This energy is provided by colliding with other atoms, such as heating-AES, photons derived from light-AAS and AFS, or high-energy electrons-XRF. Possible transitions happen, when the required energy reaches to the difference between two energy states (ΔE). A neutral atom may exist at a low energy shell

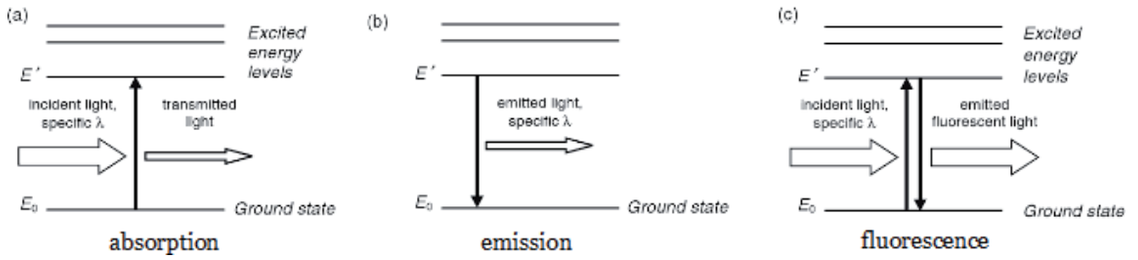

Figure 1.
Energy level diagrams to show transitions associated with (a) AAS, (b) AES, and (c) AFS. The vertical arrows indicate absorption or emission of light.

or ground state (E_0), or at any of a group of excited states depending on how many electrons have been jumped to higher energy levels (E′,) although it is normal to think for the first transition. Each element has a unique energy level and the ΔEs associated with transitions between those levels.

The ΔE for movements of *valence* electrons in most elements meets the energy equal to UV/visible radiation. The energy of a photon (E) is computed with the following equation:

$$E = h\upsilon \tag{1}$$

where h is Planck's constant (6.63×10^{-34} Js) and υ the frequency of the wave-form corresponding to that photon. The relationship between wavelength and frequency is showed by the equation below:

$$\upsilon = \frac{c}{\lambda} \tag{2}$$

where c is the speed of light and λ the wavelength. Thus,

$$E = \frac{hc}{\lambda} \tag{3}$$

and a specific transition, ΔE, is associated with a unique wavelength.

When light of a specific wavelength enters an analytical system, outer shell electrons of the corresponding atoms will be excited as energy is absorbed. As a result, the amount of light transmitted from the system to detector will be reduced, this is understood as AAS (**Figure 1a**).

Under appropriate circumstances, outer shell electrons of vaporized atoms may be excited by heating. As these electrons return to the more stable ground state, energy is lost. As **Figure 1b** shows, some of this energy is emitted as light, which can be measured with a detector, this is AES.

Some of the radiant energy absorbed by ground state atoms can be emitted as light as the atom returns to the ground state i.e. AFS (**Figure 1c**).

When high-energy photons strike to a massive particle, it can excite an inner shell electron of the atom. The forming inner orbital vacancy can be filled with an outer shell electron. The transition is created by an emission of an X-Ray photon. This process is *called* X-ray fluorescence (XRF) [2–6].

The energy of the emission i.e. the wavelength is characteristic of the atom (element) from which it originated while the intensity of the emission is related to concentration of the atoms in the sample [7].

The high temperature inductively coupled plasma has been successfully used as an effective ion source for a mass spectroscopy, the type of method of inductively coupled plasma-mass spectroscopy (ICP-MS) is routinely used for measurements of trace elements in clinical and biological samples [8, 9].

It follows from Eqs. 1–3 that the wavelengths of the absorbed or emitted light are unique to a given element.

3. Atomic spectroscopy: instrumentation

Formation of the atomic vapor i.e. atomization is the major principle of emission, absorption, and fluorescence techniques. The most critical component of instruments used in atomic spectroscopy is the atomization sources and sample introduction devices with an associated spectrometer for wavelength selection and detection of light. Atomization involves the several key (the basic) steps: solvent removal, separation from anion and other elements of the matrix, and reduction of ions to the ground state atom. The design of an AFS instrument is similar to those for AAS and AES except that the light source and the detector are located at a right angle (**Figure 2**).

A light source which emits the sharp atomic lines of the element to be determined is selected. There are two types of light sources used in these instruments: continuous sources and line sources. A continuous source, also called to as a broad-band source, emits radiation over a broad range of wavelengths. A line source, on the other hand, emits radiation at specific wavelengths, but this source of radiation is not as pure as radiation from a laser. **Table 1** provides a list of most common kinds of lamps considered to be light sources.

The atomizer is any device which will produce ground state atoms as a vapor into the light path. Many atomizers utilized for AFS are similar to those used for AAS and AES. The atomizers most commonly used in these techniques are flames and electrothermal atomizers [10]. The flame provides for easy and fast measurements with few interferences and is preferred at any *appropriate concentration* for the analyte. Flame atomizers contain a pneumatic nebulizer, an expansion chamber, and an air-acetylene laminar flame with a 10 cm path length. The typical pneumatic nebulizer for sample introduction is insufficient, and although elements such as Na and K can be determined in biological samples by flame AES, flame atomization is more suitable for AAS and AFS. AAS measurements can detect concentrations at approximately 1 μg/ml (ppm) or more. Devices are being developed to overcome these limitations of the typical nebulizer. Atomization can be reached to 100% and the devices can also generate the sample as a pulse flow rather than the continuous flow. Most systems use a graphite tube which is heated electrical energy, a technique called graphite furnace atomization, although other materials are sometimes employed. A programmed sequence of the furnace temperature is used in electrically heated graphite tube. With this atomizer, 10–50 μl of test solution is dried, organic material is destroyed, and the analyte ions dissociated from anions for reduction to ground state atoms. This atomizer also produces *temperatures* up to 3000 K which allows to form an atomic vapor of refractory elements such as aluminum and chromium. Since the analyte is atomized and retained within a small volume furnace, this procures a dense atom population. The technique is extremely sensitive as it allows one to detect a few μg/ml concentrations of the analyte. Although the technique is widely used for AAS, electrothermal atomization will

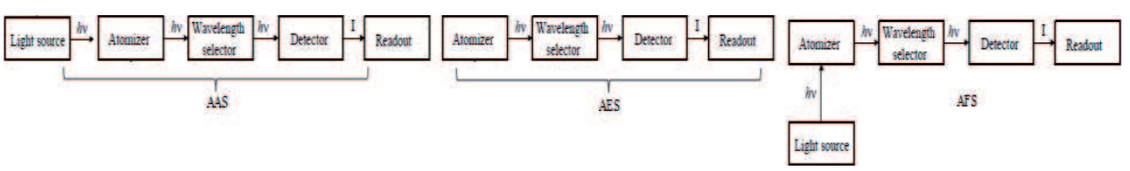

Figure 2.
Schematic diagram of an AAS, AES, and AFS instrument.

Source	Wavelength Region	Useful for...
H_2 and D_2 lamp	continuum source from 160–380 nm	molecular absorption
tungsten lamp	continuum source from 320–2400 nm	molecular absorption
Xe arc lamp	continuum source from 200–1000 nm	molecular fluorescence
nernst glower	continuum source from 0.4–20 μm	molecular absorption
globar	continuum source from 1–40 μm	molecular absorption
nichrome wire	continuum source from 0.75–20 μm	molecular absorption
hollow cathode lamp	line source in UV/Visible	atomic absorption
Hg vapor lamp	line source in UV/Visible	molecular fluorescence
laser	line source in UV/Visible/IR	atomic and molecular absorption, fluorescence, and scattering

Table 1.
The most common kinds of light sources.

provide a better performance for both AES and sample introduction into an inductively coupled plasma. Traditional sources usually include arcs and sparks but modern instruments use argon or some other inert gas to create plasma. The plasma may be produced when gas atoms are ionized, $Ar + e^- \rightarrow Ar^1 + 2e^-$—a process generated by seeding ions from a high-voltage spark—and is sustained from a radio frequency generator in the area of the induction coil. This is known as *inductively coupled plasma* (ICP). Plasma exists at temperatures of up to 10,000 K and the instrument prevents the torch from melting. XRF requires that sample should be irradiated by high energy photons. In most instruments, the source is the polychromatic primary beam from *X-Ray tubes*. Of interest to biological applications, however, it is the use of radioactive isotopes such as ^{244}Cm, ^{241} Am, ^{55}Fe, and ^{109}Cd [11, 12].

An ideal *wavelength selector* has a high throughput of radiation and a narrow effective bandwidth. There are two major types of wavelength selectors —**filters and monochromators**. A simple example of an absorption filter is a piece of colored glass. Absorption filters provide effective bandwidths of 30–250 nm, although the throughput can be only 10% of the source's emission intensity at the low end of this range. Interference filters constructed of a several optical layers deposited on a glass or transparent material. Typically, effective bandwidth is 10–20 nm, with maximum throughputs of at least 40% [11]. *A monochromator* is used to convert a polychromatic source of radiation at the entrance slit to a monochromatic source of restricted effective bandwidth at the exit slit. These devices are classified as either fixed-wavelength or scanning. The wavelength selects by manually rotating the grating in a fixed-wavelength monochromator. A scanning monochromator includes a drive mechanism that continuously rotates the grating, allowing sequential wavelengths to exit from the monochromator (**Figure 3**) [11].

Detectors use a sensitive **transducer** that converts a signal comes from light energy into electrons An ideal detector produces signal, *S*, is a linear function of the electromagnetic radiation's power, *P*,

$$S = kP + D$$

where *k* is the detector's sensitivity and *D* is the detector's **dark current**, or the background current when no radiation of source reached to the detector.

Phototubes and photomultipliers include a photosensitive surface that absorbs radiation in the ***UV-visible***, or near-IR, generating an electrical current proportional to the number of photons reaching the transducer (**Figure 4**). Other *photon*

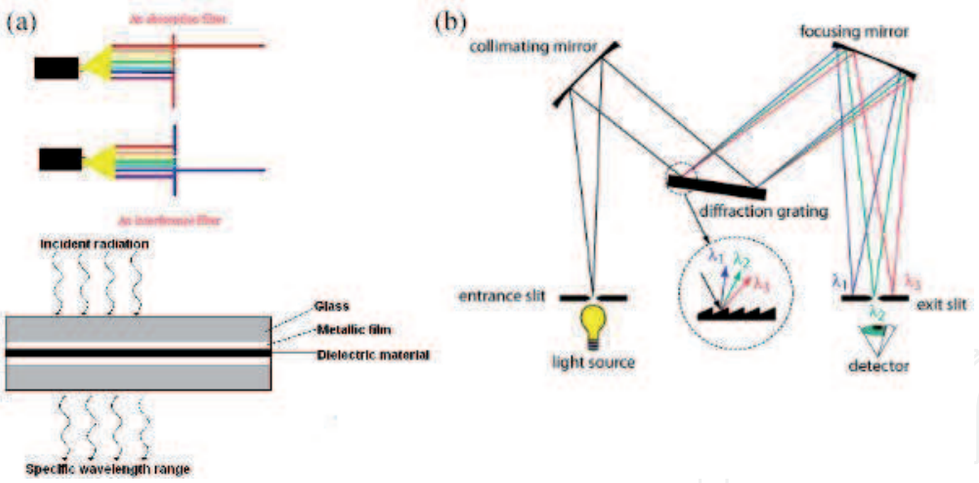

Figure 3.
Schematic diagram of wavelength selectors: (a) filters and (b) a diffraction grating monochromator.

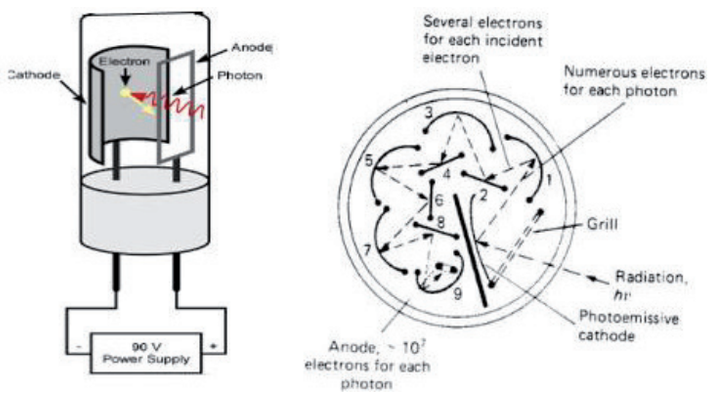

Figure 4.
Diagram of a phototube and a photomultiplier tube.

detectors use a semiconductor compound as the photosensitive surface. One advantage of the Si photodiode manufactured utilizing semiconductor process is that it is easy to miniaturize. Infrared photons do not have enough heat to generate a measurable current with a photon transducer [11].

A transducer's electrical signal is sent to a **signal processor** where it is displayed in a form that is more convenient *to* explain. The analog meters, digital meters, recorders, and computers equipped with data acquisition boards are good examples of signal processors. A signal processor is used in calibrating the detector's

Detector	Class	Wavelength Range	Output Signal
phototube	photon	200–1000 nm	current
photomultiplier	photon	110–1000 nm	current
Si photodiode	photon	250–1100 nm	current
photoconductor	photon	750–6000 nm	change in resistance
photovoltaic cell	photon	400–5000 nm	current or voltage
thermocouple	thermal	0.8–40 μm	voltage
thermistor	thermal	0.8–40 μm	change in resistance
pneumatic	thermal	0.8–1000 μm	membrane displacement
pyroelectric	thermal	0.3–1000 μm	current

Table 2.
Examples of detectors for spectroscopy.

response, amplificating the transducer's signal, removing noise by filtering, or mathematically transforming the signal [11] (**Table 2**).

4. Atomic spectroscopy: sample preparation

An ideal sample preparation should remove interfering components from the matrix and to adjust of analyte to facilitate the actual measurement. Methods for destruction of the organic matrix by simple heating or by acid digestion have been developed and are thoroughly approved. Microwave heating is used for this purpose, with the specifically designed a compatible *equipment* to avoid dangerous of excessive pressure within reaction flask. Although the number of samples that can be processed is not large, microwave heating affords rapid digestion and low reagent blanks. More recent developments include continuous flow systems for automated digestion which has a direct link with the instrument [12].

Liquid-liquid portioning has been widely applied for preconcentration procedure. Analyte atoms in a large volume of aqueous solution are complexed with a suitable agent and collected into a small volume of solvent. Vapor generation procedures permit the rapid introduction of 100% of the sample into the atomizer and are used for AAS, AES, AFS, and ICP-MS. Certain elements such as arsenic, selenium, and bismuth readily evolve gaseous hydrides and transferred by a flow of inert gas to an AES, and ICP-MS or to a heated silica tube positioned in the light path for AAS, AFS. The tube can be heated using the air-acetylene flame or an electric current. The obtained heat is enough to cause decomposition of the hydride and atomization of the analyte. Thus, there is no loss off analyte, which in all the atoms flow the light path with in few seconds and they are trapped within the silica tube that was retarded their dispersion. Any sample volume added to the reaction container, hydride generation AAS has detection limits a few nanograms of analyte. Mercury can quickly form a vapor in the ambient temperature, and this property is the basis for cold vapor generation. When a reducing agent is added to sample solution, Hg^{2+} converts to the elemental mercury. Agitation or bubbling of gas through the solution is used to enhance rapid vaporization of the atomic mercury and to improve the transfer of mercury to a flow through cell located in the light path. As with hydride generation, the detection limit is a few nanogram and some manufacturers have been developed common instrumentation to accomplish both procedures. Chromatographic or electrophoretic techniques have been also developed that are coupled directly to the atomic spectroscopic instrument to develop integrated analytical arrangements [13].

5. Atomic spectroscopy: detection limits

The detection limits are important parameters of analytical techniques. Typical detection limit ranges for the major atomic spectroscopy techniques are shown in **Figure 5**. AAS detection limits are generally better in all cases where the element can be atomized. Detection limits for refractory elements such as bor, titanium, and vanadium are better by ICP than by AAS. Nonmetals and the halogens can only be determined by ICP. Optimum detection of nonmetals such as sulfur, nitrogen, and halogens by ICP-ES can only be achieved when a vacuum monochromator is used. For mercury and those elements that form hydrides, the cold vapor mercury or hydride generation techniques offer exceptional detection limits [14].

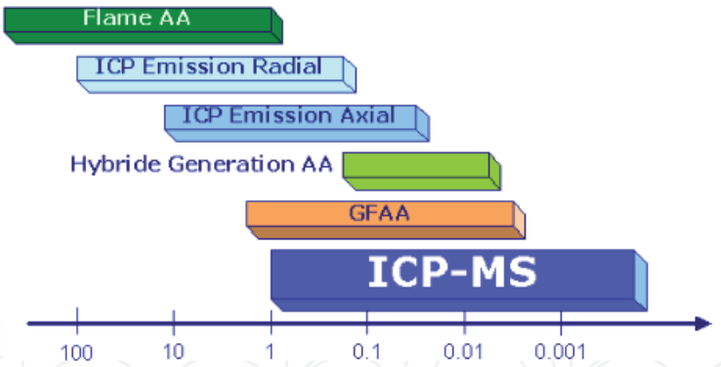

Figure 5.
Typical detection limit ranges for the major atomic spectroscopy techniques.

6. Atomic spectroscopy: analytical working range

The analytical working range can be considered as the concentration range over which quantitative results can be obtained without recalibration for system. Selecting a technique with an analytical working range based on the expected analyte concentrations, minimizes the analysis times by allowing the samples with different analyte concentrations to be analyzed together. For example; ICP-MS, once considered only an ultratrace element technique, can now run concentration ranges from low parts-per-trillion (ppt) level up to high parts per million (ppm). A wide analytical working range also can reduce, for example handling requirements, minimizing potential errors. **Figure 6** shows typical analytical working ranges with a single set of instrumental conditions [15].

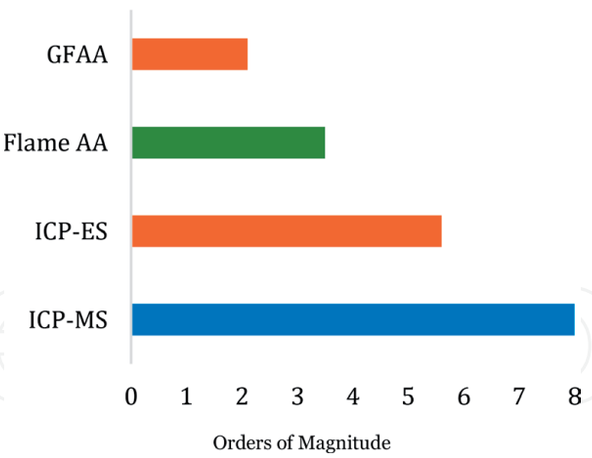

Figure 6.
Analytical working ranges for the major atomic spectroscopy techniques.

7. Atomic spectroscopy: interferences

Spectroscopic interferences have been determined and documented, and methods have been used to correct or compensate for those interferences which may occur. For example; ICP-AES provides a wide dynamic range and minimal chemical interferences [15]. A summary of the types of interferences seen with atomic spectroscopy techniques, and the corresponding methods of compensation are shown in **Table 3**.

Technique	Type of interference	Method of compensation
Flame AA	lonization Chemical Physical	lonization buffer Releasing agent or nitrous oxide-acetylene flame Dilution, matrix matching, or method of additions
GFAA	Physical and chemical Molecular absorption Spectral	STPF conditions Zeeman or continuum source background correction Zeeman background correction
ICP emission	Spectral Matrix	Background correction or the use of alternate analytical lines Internal standardization
ICP-MS	Mass overlap Matrix	Inter element correction, use of alternate mass values, or higher mass resolution Internal standardization

Table 3.
Atomic spectroscopy interferences.

8. Atomic spectroscopy: other performance criteria

Performance criteria for analytical techniques include the ease of use, required operator skills, and availability of documented methodology. **Table 4** summarizes comparative advantages and limitations of the most common atomic spectroscopy techniques.

Criteria	Flame AA	Flame AE	AFS	ICP	X-RF
Costs	Low (~$10–15 K)	Moderate	Moderate	Highest (~$200 K)	Highest
Instrumental ion	Low	Low	High	High	High
Maintenance	Low	Low	Low	High	High
Sample preparation	Moderate	Low		Moderate	High
Speed	Slow	Medium		Fast	Fast
Operator skill	Lower	Moderate	Higher	Higher	Higher

Table 4.
Comparison of spectroscopic techniques performance.

9. Atomic spectroscopy: recent developments and applications

Analytical methods of atomic spectroscopy have been used for elemental analysis identification, and quantitation in varieties of samples. Recently, most all of the spectroscopic techniques available are used in the analysis of metals and trace elements in samples of industrial and environmental origin.

Progress continues to develop in analytical spectroscopy as improvements are made to sensitivity, limits of detection, and availability. Recent development depends on instrumental adjustments and slight modifications to allow new types of measurements. Advancements in materials science have revealed demand for new methods of measurement using instruments already accessible, pushing the boundaries of what was previously available. For example, some new and interesting miniaturized plasma sources and a new distance of flight (DOF) mass spectrometer have been to the fore in developments. In addition, several novel methods have been developed, such as laser ablation molecular isotopic

spectrometry (LAMIS) for isotope ratio analysis, and stand-off LIBS techniques such as "underwater LIBS" [16].

10. Conclusion

This chapter summarizes the key principles and application areas of atomic spectroscopy techniques. For example, a medical laboratory could determine the type and amount of heavy metals that could be present in patient's serum or urine. Environmental scientists could monitor heavy metal contamination of water and soil. The pharmaceutical industry uses these techniques to determine metals and metalloids in drug products [17, 18].

Important criteria for selecting an analytical technique include detection limits, analytical working range, sample preparation, cost, ease of use, and the availability of proven methodology. Atomic spectroscopy techniques have provided a rapid, simple, accurate, and highly sensitive means of determining the concentrations of the elements.

In the future, it seems more likely that *maximum permissible* limits for elements in drinking water, the drug product etc. will be reduced, rather than increased, therefore more sensitive techniques, such as ICP-MS, will begin to play a greater role in the analysis of elements.

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