



REVIEW ON ATOMIC EMISSION SPECTROSCOPY

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ABSTRACT

Atomic Emission Spectroscopy (AES) is a chemical analysis method that employs the intensity of light produced at a certain wavelength from a flame, plasma, arc, or spark to quantify the quantity of an element in a sample. The identification of the element is determined by the wavelength of the atomic spectral line in the emission spectrum, while the intensity of the emitted light is related to the number of atoms in the element. Various methods can be used to excite the sample. By examining the radiation released by atoms, atomic emission spectroscopy can be used to establish their identification, structure, and surroundings. We may determine the energy levels (or stationary states) of the atom from wavelength measurements, and this offers an experimental basis for atomic structure theories in this review its consists of history, principle, instrumentation and detectors.

1. INTRODUCTION

Atomic emission spectroscopy (AES or OES) uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration. Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized, and atomized by a flame, discharge, or plasma. These high-sufficient energy to promote the atoms into high energy levels. The atoms decay back to lower levels by emitting light. Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow. The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer. Since all atoms in a sample are excited simultaneously, they can be detected simultaneously, and is the major advantage of AES compared to atomic-absorption (AA) spectroscopy.

2. HISTORY

Atomic Emission Spectroscopy (AES) has a long history; as far back as the 1550s, where qualitative applications based on the color of flames were used in the smelting of ores. It is based on the physical and

chemical principle of atoms that, after being heated by a flame, return to a normal energy state and give off excess energy in the form of light.

2.1 The 17th Century

In 1666, Sir Isaac Newton showed that white light from the sun could be separated into different colors of light; he also introduced the word 'spectrum'.

The idea was developed over time, with work from William Herschel, JW Ritter, Joseph Fraunhofer, and William Bunsen, all of whom studied spectra from sparks, arcs, and flames.

2.2 The 19th Century

In 1859, Gustav Kirchhoff recognized that each element and compound had its own unique spectrum and by studying the spectrum of an unknown source, you can determine its chemical composition. Kirchhoff's laws also state that emitted power and absorbed the power of light at a given wavelength is the same for all bodies at the same temperature.

Although the quantitative application based on atomic emission from electric sparks was developed by Sir Norman Lockyer, a British scientist and astronomer credited with discovering helium in the

1870s, it was Henrik Lundegårdn who pioneered the technique. Very early in its history, AES was understood to be a very powerful tool, but it was not utilized extensively until the 1930s

3. PRINCIPLE

AES is based on the principle that when energy is applied to a molecule in the form of light or heat, molecules are excited and move from a lower energy level state to a higher energy level state. At the higher energy level state, the molecules are unstable and jump back to the lower energy level state on emitting radiations in the form of photons. The wavelengths of emitted photons are recorded in the emission spectrometer. The level of emissions for a molecule is the energy differential between the excited energy and lower stable energy. Each element has its own level of emission frequencies, which helps to detect the elements. The frequencies of the emissions are recorded in the emission spectrometer. According to Bohr, this frequency (ν) occurs when the excited element undergoes a transition between two discrete states with energies E_1 and E_2 . Energy conservation leads to the well-known relationship between the energy of the photon and the energy difference between these states:

$$\Delta E = E_2 - E_1 = h\nu = h\frac{c}{\lambda}$$

where h is Planck's constant.

4. INSTRUMENTATION

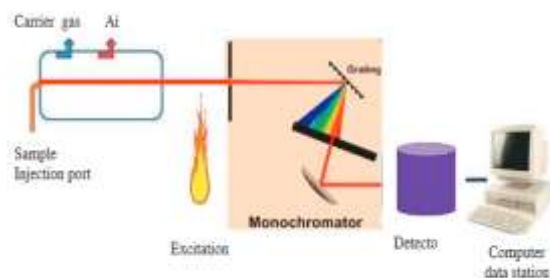


Fig.1 Instrumentation of atomic emission spectroscopy.

4.1 Sample Introduction

Sample preparation and introduction of the sample into the plasma is the critical part of the analytical process of AES. A process flow diagram for sample preparation is given in Fig.2. The sample that needs to be analyzed should be first converted into highly excited free atoms. To transport the liquid samples to the source of excitation an inert gas is introduced, typically argon flowing at 0.3–1.5L/min. The most convenient method for the introduction of liquids into the gas stream is as an aerosol from a nebulizer. The aerosol could be formed from the action of a high-speed jet across the tip of the small orifice or by other means, e.g., by using an ultrasonic transducer. Stability of the spectral emission is highly dependent on these droplet sizes. Hence it is critical to select the appropriate nebulizer type for the production of uniform droplet sizes. Appropriate nebulizer selection depends on the characteristics of the sample such as density, viscosity, organic content, total dissolved solids, and total sample volume.

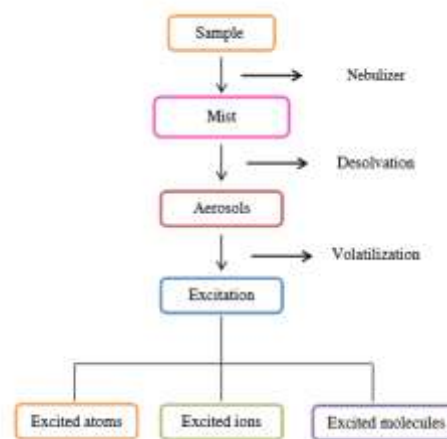


Fig.2 Process diagram for sample preparation

4.2 Excitation Sources

An excitation source is used to dissolve, atomize, and excite the atoms of the sample. The ideal excitation source will allow the excitation of all the elements in the sample and does it repeatedly until it encompasses the entire elemental excitation in the sample. A number of excitation sources can be used for these purposes, which include but are not limited to the following.

4.2.1 Direct-Current Plasma

This excitation process involves using two electrodes to produce an electrical discharge to heat the plasma gas, typically argon. This method of excitation is more suitable for samples that contain a high portion of solids.

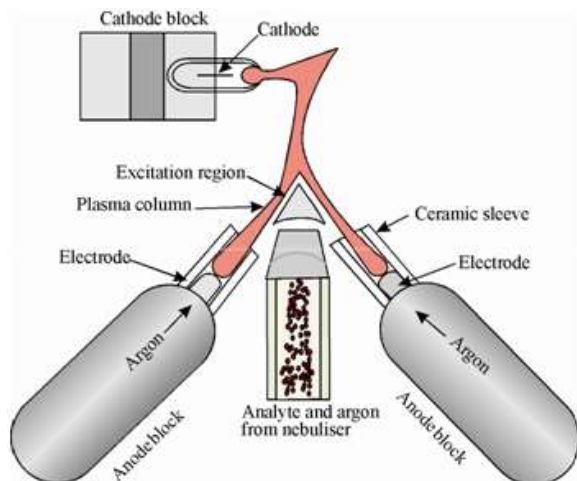


Fig.3 Schematic of a three electrode, Note the inverted-"Y" Shape of the plasma

4.2.2 Inductively coupled plasma

This is the most commonly used excitation process and it requires a plasma torch made up of concentric quartz tubes to induce excitation in the sample. The inner tube contains argon and the sample, and argon gas flows through the outer tube and acts as a cooling agent. A radiofrequency generator having a range of 1–5kW at 27 or 41MHz creates an oscillating current within an induction coil that surrounds the tubes. An oscillating magnetic field is produced by this induction coil and this induces a change in the electric field. The flowing gas seeded with electrons undergoes acceleration and gains energy that is required to excite and ionize the gaseous atoms by collision. This produces the plasma and the sample particles entering the plasma then undergo desolvation, dissociation, atomization, and excitation

4.2.3 Flame

The flame is a high-temperature source that is used to desolvate and vaporize the sample to generate free atoms for spectroscopic study.

4.2.4 Laser-Induced Breakdown

A high-energy laser pulse is utilized in this method to provoke the elemental excitation in the sample.

4.2.5 Microwave-Induced Plasma

In this method, typically a 2.45GHz microwave generator (a magnetron) is required to produce a microwave that travels through a cable and is focused via a tuning system where a torch sits in the center of the cavity. The torch has a carrier gas that flows in the outer portion of the torch, and plasma is ignited by a spark. Ozbek and Akman [3] reported that MP-AES is the most versatile new generation analytical method, which operates at a 2.45GHz magnetic field with nitrogen as the carrier gas.

4.2.6 Laser-Induced Plasma

In this method, heated plasma is maintained by a support gas, typically argon, which is focused by a high-energy CO₂ laser source.

4.2.7 Spark or Arc

Spark and arc excitation sources employ a spark or an electric pulse or an arc of continuous electrical discharge between two electrodes for vaporizing and exciting the atoms of the sample.

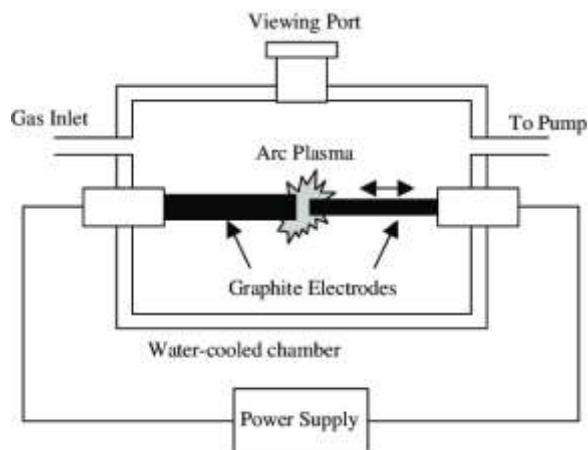


Fig.4 Schematic representation of an arc-discharge apparatus

4.3 Spectrometer

The spectrometer is used to view and analyze a range of given characteristics for a sample. The atomic emission source will excite the atoms or ions from its lower energy stable state to a higher energy state. These excited atoms or ions will then spontaneously return to their stable or lower energy state. During this transition an emission spectrum is produced

when a photon of energy is generated. This emitted energy is directly proportional to the concentration of atoms or ions in the sample. The spectrometer is used to measure this energy by using optics to separate the characteristic elemental wavelengths from the plasma background. The spectra of samples containing many elements can be very congested, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer. The spectrometer consists of a dispersive element and image transfer assembly.

In the AES spectrometer, the gratings are used as a dispersive element to disperse the incident light into component wavelengths. This grating works by reflecting the light off the angled grating surface, causing the wavelengths to be dispersed through constructive interference at wavelength-dependent diffraction angles. Since all atoms from multiple elements in a sample are excited simultaneously, they can be detected sequentially by using a monochromator or simultaneously by using a polychromator with multiple detectors. The image transfer assembly of the spectrometer consists of entrance and exit slits through which light enters and exits, producing a line separated from the rest of the spectrum, and concave mirrors or lenses.

4.4 Detector

Detectors are transducers that transform the analog output of the spectrometer into an electric signal that is viewed and analyzed using a computer. Photon detectors work generally by either causing electrons to be emitted or developing a current when photons strike the detector surface and measuring the intensity of the emission line. Examples include a photomultiplier tube (PMT), charge-coupled device (CCD), and charge-injection device (CID). PMTs are the most widely used detector in inductively coupled plasma atomic emission spectroscopy (ICP-AES). The PMT detector consists of a photocathode in a vacuum tube and ejects electrons when struck by light. These electrons travel to a dynode that produces secondary electrons that strike another diode and produce new secondary electrons, and so on. The anode is situated in the last end of the last dynode that collects the electrons. One photon produces about a million secondary electrons on striking the photocathode in the tube. At the phototube the electrical current at the anode is measured as elemental line intensity per unit time. The advent of multichannel solid-state detectors provides more flexibility to carry out multiple elemental analyses. PMT detectors are durable and extremely reliable

when carrying out elemental analyses. However, they limit the number of elements that can be determined simultaneously, because a separate detector is required for each wavelength

To overcome this challenge, modern AES instruments are equipped with solid state detectors. These solid-state detectors can measure the continuous emitting spectra. There are two types of solid-state detectors: CID and CCD. These detectors have multiple pixels rows, which are sensitive to light. When struck by radiation, both these detectors generate and store the charge. The magnitude of the charge generated in the detectors is directly proportional to the intensity of the incident radiation. The major difference between these two detectors is how the signal is read from the chip. In CCD detectors, the charge is measured by moving the charge from the detector element, where it is collected by a charge-sending amplifier. However, in CID detectors the charge is measured in terms of voltage change induced by the movement of the charge within the detector element. CID detectors have the advantage of collecting signals at their optimal signal-to-noise ratio. CCDs are used to measure very sensitive and low-level light applications and have the capacity to monitor any wavelength between 170 and 780nm. CIDs can monitor any wave-length between 165 and 800nm.

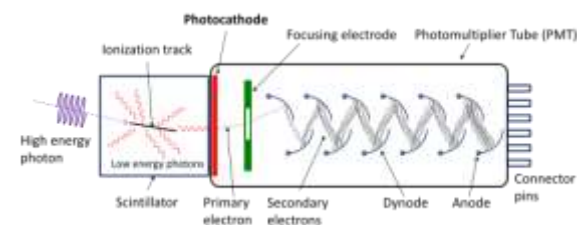


Fig.5 Schematic diagram of photo multipliertube

4.5 Data processing and instrumentation control:

The electrical current measured at the anode of the photomultiplier tube is converted into some form of signal that can be passed onto a computer and accessed immediately for analysis. The current generation of AES instruments use a computer to control the spectrometer and to collect, manipulate, and report the analytical data. The amount of computer control over all these functions varies from model to model

5. CONCLUSION

AES is a qualitative technique, it allows scientists to figure out what metal they are looking at, and it



only concerns visible light. It is an incredibly powerful means of determining the elemental composition of samples based on the emission of light.

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