**Atomic absorption spectroscopy (AAS)**

Dear students welcome for the lecture series on food technolog , in today's session we are concentrating on the topic Atomic absorption spectroscopy.

The topic can be studied under the five modules, they are

- Introduction
- Historical background
- Types of atomic absorption spectroscopy
- Inductively Coupled Plasma Optical Emission Spectroscopy
- Applications of atomic spectroscopy in various fields

## I. Introduction

- Atomic Absorption Spectrometry (AAS) is a technique for measuring quantities of chemical elements present in environmental samples by measuring the absorbed radiation by the chemical element of interest.
- This is done by reading the spectra produced when the sample is excited by radiation.
- The atoms absorb ultraviolet or visible light and make transitions to higher energy levels.
- Atomic absorption methods measure the amount of energy in the form of photons of light that are absorbed by the sample.

- A detector measures the wavelengths of light transmitted by the sample, and compares them to the wavelengths which originally passed through the sample.
- A signal processor then integrates the changes in wavelength absorbed, which appear in the readout as peaks of energy absorption at discrete wavelengths.
- The energy required for an electron to leave an atom is known as ionization energy and is specific to each chemical element.
- When an electron moves from one energy level to another within the atom, a photon is emitted with energy E.
- Atoms of an element emit a characteristic spectral line.
- Every atom has its own distinct pattern of wavelengths at which it will absorb energy, due to the unique configuration of electrons in its outer shell.
- This enables the qualitative analysis of a sample.
- The chemical methods used are based on matter interactions, i.e. chemical reactions.
- For a long period of time these methods were essentially empirical, involving, in most cases, great experimental skills.
- In analytical chemistry, Atomic Absorption Spectrometry is a technique used mostly for determining the concentration of a particular metal element within a sample.

- Atomic Absorption Spectrometry can be used to analyze the concentration of over 62 different metals in a solution.

## II. Historical background:

- The technique of Atomic Absorption Spectrometry can be thought of as having its origin in 1666 with Isaac Newton who used a prism to separate the colours of the solar spectrum.
- Wollaston in 1802 recorded his observation that the spectrum of sunlight which was at the time thought to be continuous was in fact interrupted by dark lines.
- Later in 1814 Fraunhofer found a series of lines in the visible region of the solar spectrum and labeled the principal lines alphabetically without identifying their chemical origin.
- In 1832, Brewster, who is associated with the invention of the kaleidoscope investigated the absorption of light by various vapours and suggested that Fraunhofer lines were due to certain vapours in the sun's atmosphere.
- Kirchhoff in 1860 deduced from Fraunhofer's results the presence of certain elements in the solar atmosphere and with Bunsen in 1861 laid the foundations of a new method of chemical analysis using flames.
- Fraunhofer and Kirchhoff had been observing atomic absorption and atomic emission respectively.
- Foucault demonstrated the reversal of spectral lines, for example when the spectral source is surrounded by atomic vapours from the substance emitting

the spectrum and the atomic vapours absorb the radiation that they themselves are emitting.

- In 1902 Wood illustrated the emission-absorption relationship by heating sodium in a partially evacuated glass bulb and irradiated the bulb with light from a sodium flame.
- He demonstrated an increase in absorption effect by heating the bulb more strongly.
- Wood named the lines emitted and absorbed by sodium atoms as resonance lines and carried out experiments to show the possibility of using the resonance effect to detect traces of mercury.
- This may have been the first analysis carried out by atomic absorption spectrometry.
- Wood does not seem to have been able to impress either chemists or spectroscopists who were more interested in emission spectroscopy and few followed in the field of atomic absorption and its applications.
- The advances made by Kirchhoff, Bunsen, Foucault and Wood did interest astronomers who used atomic absorption to study the composition of the solar and stellar atmospheres.
- In 1924 Angerer and Joos studied the atomic absorption spectra of metals in the iron group and Frayne and Smith in 1926 of indium, gallium, aluminium and thallium.
- Hughes and Thomas in 1927 studied the absorption and resonance effects of mercury.

- Lunegardh in 1928 demonstrated atomic emission spectroscopy (AES) in an air-acetylene flame using a pneumatic nebulizer.
- In 1930 Mueller and Pringsheim published an atomic absorption method of measuring mercury content of air thereby carrying on Woods original project of 1913 and 1919.

**What Is Atomic Absorption Spectrometry (AAS)?**

- Atomic absorption is a process involving the absorption by free atoms of an element of light at a wavelength specific to that element, or put more simply, it is a means by which the concentration of metals can be measured.
- In Atomic Spectrometry, emission, absorption and fluorescence, energy is put into the atom population by thermal, electromagnetic, chemical and electrical forms of energy and are converted to light energy by various atomic and electronic processes before measurement.
- Atomic Absorption Spectrometry is useful not only for the identification but also the quantitative determination of many elements present in samples.
- The technique is specific, in that individual elements in each sample can be reliably identified and it is sensitive, enabling small amounts of an element to be detected down to around 1µg g-1 (1ppm) i.e. one part in one million using straightforward flame procedures.

## III. Types of atomic absorption spectroscopy

**Flame Atomic Absorption Spectroscopy**

- Atomic Absorption (AA) occurs when a ground state atom absorbs energy in the form of light of a specific wavelength and is elevated to an excited state.

- The amount of light energy absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases.
- The relationship between the amount of light absorbed and the concentration of analytes present in known standards can be used to determine unknown sample concentrations by measuring the amount of light they absorb.
- Performing atomic absorption spectroscopy requires a primary light source, an atom source, a monochromator to isolate the specific wavelength of light to be measured, a detector to measure the light accurately, electronics to process the data signal and a data display or reporting system to show the results.
- The light source normally used is a hollow cathode lamp (HCL) or an electrodeless discharge lamp (EDL).
- In general, a different lamp is used for each element to be determined, although in some cases, a few elements may be combined in a multi-element lamp.
- In the past, photomultiplier tubes have been used as the detector. However, in most modern instruments, solid-state detectors are now used.
- Flow Injection Mercury Systems (FIMS) are specialized, easy-to-operate atomic absorption spectrometers for the determination of mercury.
- These instruments use a high-performance single-beam optical system with a low-pressure mercury lamp and solar-blind detector for maximum performance.

- Whatever the system, the atom source used must produce free analyte atoms from the sample.
- The source of energy for free-atom production is heat, most commonly in the form of an air/acetylene or nitrous-oxide/acetylene flame.
- The sample is introduced as an aerosol into the flame by the sample introduction system consisting of a nebulizer and spray chamber.
- The burner head is aligned so that the light beam passes through the flame, where the light is absorbed.

**Limitations of atomic absorption spectroscopy**

- The major limitation of Flame AA is that the burner-nebulizer system is a relatively inefficient sampling device.
- Only a small fraction of the sample reaches the flame, and the atomized sample passes quickly through the light path.
- An improved sampling device would atomize the entire sample and retain the atomized sample in the light path for an extended period of time, enhancing the sensitivity of the technique.

**Graphite Furnace Atomic Absorption Spectroscopy**

- With Graphite Furnace Atomic Absorption (GFAA), the sample is introduced directly into a graphite tube, which is then heated in a programmed series of steps to remove the solvent and major matrix components and to atomize the remaining sample.

- All of the analyte is atomized, and the atoms are retained within the tube (and the light path, which passes through the tube) for an extended period of time.
- As a result, sensitivity and detection limits are significantly improved over Flame AA.
- Graphite Furnace analysis times are longer than those for Flame sampling, and fewer elements can be determined using GFAA.
- However, the enhanced sensitivity of Graphite Furnace Atomic Absorption, and its ability to analyze very small samples, significantly expands the capabilities of atomic absorption.
- Graphite Furnace Atomic Absorption allows the determination of over 40 elements in microliter sample volumes with detection limits typically 100 to 1000 times better than those of Flame AA systems.

## IV. Inductively Coupled Plasma Optical Emission Spectroscopy

- ICP is an argon plasma maintained by the interaction of an RF field and ionized argon gas.
- The plasma can reach temperatures as high as 10,000 ˚K, allowing the complete atomization of the elements in a sample and minimizing potential chemical interferences.

- Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is the measurement of the light emitted by the elements in a sample introduced into an ICP source.
- The measured emission intensities are then compared to the intensities of standards of known concentration to obtain the elemental concentrations in the unknown sample.
- There are two ways of viewing the light emitted from an ICP. In the classical Inductively Coupled Plasma Optical Emission Spectroscopy configuration, the light across the plasma is viewed radially (Figure 3a), resulting in the highest upper linear ranges.
- By viewing the light emitted by the sample looking down the center of the torch or axially, the continuum background from the ICP itself is reduced and the sample path is maximized.
- Axial viewing provides better detection limits than those obtained via radial viewing by as much as a factor of 10.
- The most effective systems allow the plasma to be viewed in either orientation in a single analysis, providing the best detection capabilities and widest working ranges.
- The optical system used for Inductively Coupled Plasma Optical Emission Spectroscopy consists of a spectrometer that is used to separate the individual wavelengths of light and focus the desired wavelengths onto the detector.

- Older, “direct reader” types of Inductively Coupled Plasma Optical Emission Spectroscopy systems used a series of photomultiplier tubes to determine pre-selected wavelengths.
- This limited the number of elements that could be determined as the wavelengths were generally fixed once the instrument was manufactured.
- Sequential-type systems can select any wavelength and focus it on a single detector.
- However, this is done one element at a time, which can lead to longer analysis times. In today’s modern Inductively Coupled Plasma Optical Emission Spectroscopy systems, solid-state detectors based on charge-coupled devices (CCD) are used, providing very flexible systems and eliminating the need for large numbers of single photomultiplier detectors.

**Inductively Coupled Plasma Mass Spectrometry**

- With Inductively Coupled Plasma Mass Spectrometry (ICP-MS), the argon ICP generates singly charged ions from the elemental species within a sample that are directed into a mass spectrometer and separated according to their mass-to-charge ratio.
- Ions of the selected mass-to-charge ratio are then directed to a detector that determines the number of ions present .
- Typically, a quadrupole mass spectrometer is used for its ease-of-use, robustness and speed.
- Due to the similarity of the sample-introduction and data-handling techniques, using an Inductively Coupled Plasma Mass Spectrometry is very

much like using an ICP-OES system. Inductively Coupled Plasma Mass Spectrometry combines the multi-element capabilities of ICP techniques with exceptional detection limits equivalent to or below those of Graphite Furnace Atomic Absorption.

- It is also one of the few analytical techniques that allows the quantification of elemental isotopic concentrations and ratios, as well as precise speciation capabilities when used in conjunction with HPLC or GC interfaces. This feature enables the analytical chemist to determine the exact form of a species present – not just the total concentration.
- However, due to the fact that the sample components are actually introduced into the instrument, there are some limitations as to how much sample matrix can be introduced into the Inductively Coupled Plasma Mass Spectrometry.
- In addition, there are also increased maintenance requirements as compared to Inductively Coupled Plasma Optical Emission Spectroscopy systems.
- Generally, Inductively Coupled Plasma Mass Spectrometry systems require that the total dissolved solids content of a sample be below 0.2% for routine operation and maximum stability.
- There are several items, such as the interface cones and ion lens, located between the ICP torch and the mass spectrometer, that need to be cleaned on a periodic basis to maintain acceptable instrument performance.
- Recent developments have led to new technologies to increase the robustness and stability of Inductively Coupled Plasma Mass Spectrometry.

- Orthogonal ion lens systems increase the ability of the Inductively Coupled Plasma Mass Spectrometry to handle higher total dissolved solids content and dramatically improve longterm stability for high matrix solutions.
- Interference control has been made even easier by using universal cell technologies that include both collision (using Kinetic Energy Discrimination KED) and Dynamic Reaction Cell (DRC) in a single instrument allowing the analyst to choose the best technique for their samples.

| Technique | Strengths | Limitations | Applications |
|---|---|---|---|
| Flame AA – Flame Atomic Absorption Spectroscopy | • Very easy-to-use<br>• Widely accepted<br>• Extensive application information available<br>• Relatively inexpensive | • Low sensitivity<br>• Single-element analytical capability<br>• Cannot be left unattended (flammable gas) | Ideal for laboratories analyzing large numbers of samples for a limited number of elements and for the determination of major constituents and higher concentration analytes. |
| GFAA – Graphite Furnace Atomic Absorption Spectroscopy | • Exceptional detection limits<br>• Well-documented applications<br>• May be left unatteneded | • Limited analytical working range<br>• Sample throughput somewhat less than other techniques | Ideal for laboratories analyzing a limited number of elements and requiring excellent detection limits. |
| ICP-OES – Inductively Coupled Plasma Optical Emission Spectroscopy | • Best overall multi-element atomic spectroscopy technique<br>• Excellent sample throughput<br>• Very wide analytical range<br>• Good documentation available for | • Higher initial investment | Ideal for laboratories analyzing multiple elements in a moderate or large number of samples. |

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| | applications<br>• May be left unatteneded<br>• Easy-to-use | | |
| ICP-MS – Inductively Coupled Plasma Mass Spectrometry | • Exceptional multi-element capabilities<br>• Ability to perform isotopic analyses<br>• Well-documented interferences and compensation methods<br>• Rapidly growing application information<br>• Detection limits equal to or better than GFAA with much higher productivity<br>May be left unattended | • Highest initial investment<br>• Method development more difficult than other techniques<br>• Limited solids in sample | Ideal for laboratories analyzing multiple elements in a large number of samples and requiring a system capable of determining trace and ultratrace analyte concentrations. |

## V. Applications of atomic spectroscopy in various fields

### Environmental

- In the environment we live in, understanding heavy-metal contamination is critical. The accurate measurement of concentrations of these metals is imperative to maintain clean air, water and soil for a safer world.

### Food

- Accurate analysis of food for nutritional content, contamination or authenticity – the exact geographic source of the product – is critical for regulatory and quality assurance.

**Pharmaceutical**

- Drug research, development and production is dependent on elemental analysis, starting with the testing of individual ingredients and continuing through production to final quality control, as impurities can affect drug efficacy and metabolism.

**Petrochemical**

- From petroleum refining to a broad spectrum of applications using lubricants and oils, many industries require the determination of metals – particularly analytes that can lead to degradation and contamination – to ensure conformity as well as monitor and control processes.

**Chemical/Industrial**

- From the analysis of raw materials and components to finished product testing and quality control, industrial and chemical manufacturers require accurate analytical techniques to ensure the safety and performance of their products.

**Geochemical/Mining**

- With myriad applications from date stamping to precious metals testing, atomic spectroscopy offers a fast, accurate solution for broad geological surveys as well as an invaluable means of testing potential mining areas before incurring the high costs associated with digging.

**Biomonitoring**

- Instrumentation for accurate measurements of metals in biological matrices is vital when assessing human exposures to natural and synthetic chemicals.
- Speciation is also becoming increasingly important due to its ability to provide additional information on element valence state or molecular form.

**Agriculture**

- Trace metals are essential for plant growth. Atomic spectroscopy also facilitates precise soil analysis to ensure that metals are not at levels that could unduly affect the food source (livestock and/or crops).

**Semiconductor**

- Determining lower and lower values in a variety of materials – rapidly and affordably – has become necessary in the increasingly competitive semiconductor industry.

**Nuclear Energy**

- Operating under constant scrutiny, the nuclear field is required to monitor and measure the levels of a variety of elements to an exacting degree.
- Atomic spectroscopy is commonly used to determine trace elements in everything from process water to low-level waste.

**Renewable Energy**

- As the world continues to move toward eco-friendly technologies and energy sources, there’s an ever-increasing need for accurate elemental analysis.
- Applications include testing biofuels for batch consistency and quality control, as well as trace elemental analysis on solar panels to ensure optimum performance.

**Nanomaterials**

- As research science defines more novel applications for nanomaterials, the need to eliminate material uncertainty on a particleby-particle basis continues to grow.
- Whether there is a need to solve an environmental issue or apply a manufacturing QA/QC solution to a synthesis or formulation process, there is a growing requirement for sensitivity to conduct accurate, precise work.

## Conclusion

**Today we studies about AAS, Historical background, What Is Atomic Absorption Spectrometry (AAS)? Types of atomic absorption spectroscopy, Flame Atomic Absorption Spectroscopy, Limitations of atomic absorption spectroscopy, Graphite Furnace Atomic Absorption Spectroscopy, Inductively Coupled Plasma Optical Emission Spectroscopy**

**Inductively Coupled Plasma Mass Spectrometry, Applications of atomic spectroscopy in various fields, in Food we sdudied the Pharmaceutical area, Petrochemical, Chemical/Industrial, Geochemical/Mining, Biomonitoring, Agriculture, Semiconductor,**

**Nuclear Energy and Nanomaterials.**