Fundamentals of Atomic Spectroscopy: **Hardware**

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Introduction Classification

Spectroscopy is a broad field with many subdisciplines, which can be classified by the type of material being analyzed. This presentation will focus on the first category, **atomic spectroscopy**.

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Introduction General

Atomic spectroscopy includes a number of analytical techniques used to determine the **elemental composition** of a sample by examining its electromagnetic spectrum or its mass spectrum.

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Introduction Timeline of Early Developments

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Introduction What's Measured?

- 1. Absorption of energy causes an electron to move to a higher energy level (E2) **AA**
- 2. The excited electron will eventually drop back to the ground state and emit light at a particular wavelength (emission) **MP-AES, ICP-OES**
- 3. If there is enough energy, the electron will leave the atom completely and leave behind a positively charged ion Electron (ionization) > ICP-MS

See notes for details

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Atomic Absorption Spectroscopy Principles of Operation

Atomic absorption spectroscopy (AAS) techniques rely on the fact that an atomized element will absorb light of a characteristic wavelength, elevating it from the ground state to an excited

The amount of light energy absorbed is proportional to the number of analyte atoms in the light path.

The technique is calibrated by introducing known concentrations of analyte atoms into the light path and plotting the absorption versus concentration curve.

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state.

Atomic Absorption Spectroscopy General Set Up

- Lamp emits light for element of interest
- Atomizer converts liquid sample into free atoms which absorb energy from the lamp
- Monochromator selects wavelength used for measurement
- Detector measures light absorbed by free atoms

Atomic Absorption Spectroscopy Lamp

The source of light primarily used with the atomic absorption technique is the hollow cathode lamp (HCL).

Typically each lamp is dedicated to the analysis of a single element, though in some cases a few elements can be combined into a single lamp.

Because of this limitation, atomic absorption is typically used for analysis of either a single element or a small number of elements.

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Typical hollow cathode lamp construction

See notes for details

Atomic Absorption Spectroscopy Atomizer

Atomization is the process that converts a liquid sample into free atoms.

The diagram shows the different steps that occur during atomization, starting with the element being prepared as a solution.

Element M undergoes different stages:

- Solution: MA_{liquid} (compound)
- Nebulization: MA*liquid* (compound)
- Desolvation: MA*solid* (A = solution anion)
- Vaporization: MA*gas*
- Atomization: M⁰
- Excitation: M*
- Ionization: M+

Atomic Absorption Spectroscopy Atomizer

Atoms can absorb discrete amounts of energy:

- Heat
- Light at discrete wavelengths

An electron may change energy levels

- An atom can pick up (absorption) or release (emission) energy.
- Atom becomes "excited"
- Excitation is explained by the transition of an electron from an inner orbit (higher energy) to an outer orbit.

Atomic Absorption Spectroscopy Flame AAS Atomizer

In **flame AAS (FAAS)** the sample is prepared as a liquid and nebulized into the flame.

The fundamental characteristic of this technique is the atomization that happens in the flame.

Schematic diagram of flame or graphite furnace atomic absorption spectrometer system

Flame AAS Advantages • Short analysis time possible • Good precision • Easy to use • Cheap **Limitations** • Sensitivity • Dynamic range • Requires flammable gases • Unattended operation is not possible because of flammable gases • Must not contain excessive amounts of dissolved solids

[Source: Atomic spectroscopy applications in the contract](http://www.chem.agilent.com/Library/primers/Public/Primer_Environmental_elemental_analysis.pdf) environmental laboratory

Atomic Absorption Spectroscopy Graphite Furnace AAS Atomizer

Dissolution of sample into a liquid form is required in most cases.

Sample is injected into a graphite tube and electrothermally heated in different stages to atomize the analyte.

In graphite furnace atomic absorption (GFAAS) the atomization happens in three stages:

- Drying
- Ashing
- Atomization

Graphite furnace operation is a complementary technique to conventional flame AA and adds some advantages to the analysis.

Graphite furnace

Advantages

- High sensitivity due to
	- − entire sample is atomized at one time
	- − free atoms remain in the optical path longer
- Reduced sample volume
- Ultra trace analysis possible
- Can run unattended, even overnight

Limitations

- Very slow
- Fewer elements can be analyzed
- Poorer precision
- More chemical interferences (compared to flame AA)
- Method development requires skill
- Standard additions calibration required more frequently (compared to flame AA)
- Expensive consumables (graphite tubes)

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Atomic Absorption Spectroscopy Graphite Furnace AAS Atomizer

The graphite tube sits in this apparatus which supplies an inert gas and a powerful to heat the tube, which then desolvates and atomizes the sample.

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Atomic Absorption Spectroscopy Elemental Coverage in AAS

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Atomic Absorption Spectroscopy Other Atomizers

Hydride generation technique

Suitable for elements forming volatile hydrides (As, Sn, Bi, Sb, Te, Ge and Se) when reacted with a reducing agent, such as sodium borohydride.

Advantages

- Separation of specific elements as hydrides which can eliminate matrix interference
- Good sensitivity due to 100% sampling efficiency
- Good precision
- Faster than graphite furnace AA

Limitations

- Limited to specific elements
- Some chemical interferences
- Requires specific sample preparation (analyte must be converted to a specific oxidation state)

Cold vapor technique

Used specifically for mercury (has a large enough vapor pressure at ambient temperature) which can be reduced to atomic state by a strong reducing agent, such as sodium borohydride, tin (II) chloride).

Advantages

- Eliminates many matrix interferences
- Good sensitivity due to 100% sampling efficiency
- Good precision
- Faster than graphite furnace AA

Limitations

- Limited to mercury only
- Mercury must be stabilized in solution

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Atomic Absorption Spectroscopy System

Key Applications

- Determination of trace metals/ impurities in oil, plants, water
- Analysis of elements in fluids, water, soil, food, serum, semiconductor material
- And many more

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Example Flame AAS: Determination of Low Levels of Gold in Mineral Ore

[Source: Extending the Analytical Range for Gold Using](http://www.agilent.com/cs/library/applications/a-aa10.pdf) Agilent UltrAA Lamps

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Example GF AAS: Measuring Cd, Cu, Pb, Co, Ni in Marine Invertebrates

Signal graphics for Ni in CRM 786 R Mussel Tissue

[Source: Sequential Determination of Cd, Cu, Pb, Co and Ni](http://www.chem.agilent.com/Library/applications/aa129.pdf) in Marine Invertebrates by Zeeman GFAAS

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Example Hydride Generation AAS: Determination of As, Sb and Se

Sample preparation and typical calibration data for As using hydride generation

[Source: Determination of As, Sb and Se in Difficult](http://www.chem.agilent.com/Library/applications/aa105.pdf) **[ToC](#page-2-0) Environmental Samples by Hydride Generation**

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One sample preparation

25 mL HCl added.

Atomic Emission Spectroscopy General

Due to the limitations in AAS, techniques that don't require dedicated lamps for each element have come into use. These techniques, called **atomic emission spectroscopy (AES)**, rely on the fact that once an atom of a specific element is excited (as in atomic absorption), it emits light in a characteristic pattern of wavelengths (an emission spectrum) as it returns to the ground state.

The flame is not an ideal excitation source for atomic emission. Therefore hotter sources are used.

We will discuss the following techniques:

- Microwave plasma atomic emission spectroscopy (MP-AES)
- Inductively coupled plasma optical emission spectroscopy (ICP-OES)

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Atomic Emission Spectroscopy Microwave Plasma Atomic Emission Spectroscopy

Nitrogen plasma is used to desolvate, atomize, and excite the atoms in the liquid sample that has been nebulized into it. The nitrogen plasma is considerably hotter (up to $5,000^\circ$ K) than the air-acetylene flame used in AA.

The atomic emission is quite strong for most elements, leading to improved detection capability and linear dynamic range over flame AA for most elements.

The intensity of the light emitted is measured using optical detection at the wavelengths characteristic of the elements of interest.

MP-AES

Advantages

- Safe (no flammable gas)
- Low operating costs as nitrogen can be extracted from compressed air using a nitrogen generator
- No lamps required for analysis
- Identification and quantitation of virtually all metals and many metalloids.
- Better performance than flame AAS

Limitations

- Higher initial cost than AAS
- More interferences compared with flame AA (including spectral interferences)
- Not as sensitive as graphite furnace AAS or ICP-MS

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- Not as productive as ICP-OES
- No isotope determination

Microwave Plasma Atomic Emission Spectroscopy System

Key Applications

- Trace elements in geological samples
- Metals in soil extracts
- Major elements in food and beverages
- Analysis of petroleum
- Analysis of waste water

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Microwave Plasma Atomic Emission Spectroscopy How Does It Work?

Agilent MP-AES runs from nitrogen extracted from air using a nitrogen generator.

- Axial magnetic and radial electrical fields sustain the nitrogen plasma
- Sample aerosol is introduced into nitrogen plasma

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Microwave Plasma Atomic Emission Spectroscopy How Does It Work?

- Axial emission from the nitrogen plasma is directed into the fast-scanning monochromator optics
- Wavelength-specific emissions are detected using a high-efficiency CCD

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Microwave Plasma Atomic Emission Spectroscopy Determination of Nutrients in Soil (Multielement Testing)

MP-AES results for Cu, Fe, Mn, and Zn in DTPA extraction of soil, compared to FAAS

[Source: Determination of available nutrients in soil](http://www.chem.agilent.com/Library/applications/5991-5675EN_app_note_4200_mp-aes-nutrients_soils.pdf) using the Agilent 4200 MP-AES

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Microwave Plasma Atomic Emission Spectroscopy Measuring Major and Minor Elements in Milk

Determination of Ca, K, Mg, Na, P, Fe, Zn and Cu in TMAH, Triton X-100, EDTA and ionization buffer by MP-AES 4200

[Source: Measuring major and minor elements in milk using](http://www.chem.agilent.com/Library/applications/Elements_Milk_MPAES_v2.pdf) the Agilent MP-AES 4200

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Inductively Coupled Plasma Optical Emission Spectroscopy Principles of Operation

An argon inductively coupled plasma (hotter than MP, up to $10,000^{\circ}$ K) is used to desolvate, atomize, and excite the atoms in the liquid sample that has been nebulized into it.

The intensity of the light emitted is measured using optical detection at the wavelengths characteristic of the elements of interest.

ICP-OES is capable of measuring both atomic and ionic emission so more wavelengths can be monitored

These measurements can be compared to a standard to quantify the concentration of the elements in the sample.

ICP- OES

Advantages

- Fastest sample throughput
- Simultaneous multi-element analysis (up to 73 elements)
- Wide dynamic range (from sub-ppb to % level)
- Tolerates complex matrices
- Low argon gas consumption
- Safe (no flammable gas)

Limitations

- Higher initial costs than AAS or MP-AES
- More spectral interferences compared with MP-AES
- Not as sensitive as graphite furnace AAS or ICP-MS
- No isotope determination

Inductively Coupled Plasma Optical Emission Spectroscopy General Set Up

Plasma torch can be viewed axially or radially. Some "dual view" instruments allow viewing of both orientations, depending on the analysis being performed. (Axial view gives longer path length and thus greater sensitivity.)

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Simplified schematic diagram of ICP-OES spectrometer system

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Inductively Coupled Plasma Optical Emission Spectroscopy System

Key Applications

- Monitoring of water/wastewater/solid wastes
- Determination of trace elements in water
- Mercury monitoring in environmental samples
- Quantitative analysis of multiple elements in water/soil/sediment environment samples
- Analysis of soil analysis of micronutrient content (Agriculture)
- Determination of precious metals and gold

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Inductively Coupled Plasma Optical Emission Spectroscopy Analysis of Milk Powder

Analysis of NIST milk powder 8435 SRM using the 5100 SVDV ICP-OES

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Source: Analysis of milk powders based on Chinese **[ToC](#page-2-0)** [standard method using the Agilent 5100 SVDV ICP-OES](http://www.chem.agilent.com/Library/applications/5991-4900EN.pdf)

Inductively Coupled Plasma Optical Emission Spectroscopy Analysis of Biodiesel Oil

P (213.618 nm) Calibration 6,500 6,000 5,500 5,000 4,500 4,000 ity $3,500$ $E = 3,000$ 2,500 **Standards Concentration (ppm)** % Error 2,000 Blank Ω N/A 1,500 Standard 1 0.51 5.47 $1,000$ Standard 2 1.03 0.19 0.26 Standard 3 2.14 500 1.00 2.00 0.00 Concentration (ppm)

Calibration curve for P 213.618 nm line, using FBC background correction, shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99986.

Agilent 5100 ICP-OES wavelengths and calibration parameters. All results are shown in solutions.

> [Source: Analysis of biodiesel oil \(as per ASTM D6751 &](http://www.chem.agilent.com/Library/applications/5991-5333EN_AppNote5100_ICP-OES-biodiesel.pdf) EN 14214) using the Agilent 5100 SVDV ICP-OES

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Inductively Coupled Plasma Mass Spectrometry General

- **ICP-MS** combines two advantages:
- 1. Argon ICP as a highly efficient ion source
- 2. A mass spectrometer for fast scanning, high ion transmission and unit mass resolution

The main difference to ICP-OES is to analyze atomic ions. Most elements have the first ionization potential of 4 to10 eV, which are efficiently ionized in argon ICP.

Ions are passed into the high vacuum region for separation and detection. Photons and neutral species are rejected.

The mass spectrometer separates ions based on their mass-to-charge ratio (*m/z*).

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Inductively Coupled Plasma Mass Spectrometry General

An electron multiplier detector generates a pulse for each ion reaching it.

Since the charge on a singly ionized element is 1, the *m/z* is equal to the mass, so ICP-MS measures the elements as a simple spectrum of characteristic atomic (isotopic) mass from 6Li to 238 U.

ICP-MS

Advantages

- Most sensitive technique
- Multi-element analysis
- Isotopic information (IR, ID analysis)
- Wide dynamic range
- Tolerates complex matrices

Limitations

- Less matrix tolerance than ICP-OES
- Most expensive technique (purchase and running costs)
- Subject to isobaric interferences

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Inductively Coupled Plasma Mass Spectrometry General Set Up

Simplified schematic diagram of the major components of a quadrupole ICP-MS system.

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Inductively Coupled Plasma Mass Spectrometry System

Inductively Coupled Plasma Mass Spectrometry How Helium Collision Cell Mode Removes Spectra Interference

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Inductively Coupled Plasma Mass Spectrometry ICP-MS as a Chromatography Detector

In addition to its common use as a standalone metals analyser, ICP-MS is increasingly applied as a detector for a range of chromatographic separation methods

- Capillary electrophoresis (CE)
- Field-flow fractionation (FFF)
- Ion chromatography (IC)
- Liquid chromatography (HPLC)
- Gas chromatography (GC)

In this configuration, the front-end technique separates the different species (with time), and the ICP-MS operates as a mass selective detector to measure the element(s) associated with the compound(s) of interest as they elute from the chromatograph.

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Inductively Coupled Plasma Mass Spectrometry Speciation with LC-ICP-MS and GC-ICP-MS

HPLC-ICP-MS application examples:

- Inorganic vs. organic arsenic
- Organo-tin
- Methyl-mercury

GC-ICP-MS examples:

- **Pesticides**
- OP nerve agent residues
- PBDEs
- **Nanoparticles**

Seven overlaid chromatograms of apple juice spiked with 500 ng/L As standard.

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Inductively Coupled Plasma Mass Spectrometry Drinking Water Analysis

Most developed countries have enacted regulations and monitoring programs to ensure that the supply of drinking water is free from potentially harmful chemicals. The fast, multi-element technique of ICP-MS is widely used for this.

Inductively Coupled Plasma Mass Spectrometry Trace Metallic Impurity Analysis in High Purity HCl

HCl is frequently used to remove metallic impurities on the surface of silicon wafers. The manufacturing process of semiconductor devices requires routine monitoring of ultra-trace contaminants in HCl.

As, which suffers ArCl+ interference, can be measured at trace levels.

[Source: Direct analysis of trace metallic impurities in high](http://www.chem.agilent.com/Library/applications/5990-7354EN_AppNote_7700s_HCL.pdf) purity hydrochloric acid by Agilent 7700s ICP-MS

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Summary Atomic Spectroscopy Techniques

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Abbreviations

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