Atomic spectroscopy methods

- Atomic spectroscopy methods are based on light absorption and emission of atoms in the gas phase. The goal is elemental analysis - identity and concentration
- of a specific element in the sample; chemical and structural information are lost. The sample is destroyed.

Design of instrumentation to probe a material

- Signal Generation-sample excitation
- Input transducer-detection of analytical signal
- Signal modifier-separation of signals or amplification
- Output transducer-translation & interpretation

Characterization of Properties

- chemical state
- structure
- orientation
- interactions
- general properties

Molecular Methods

- macro Vs micro
- pure samples Vs mixtures
- qualitative Vs quantitative
- surface Vs bulk
- large molecules (polymers, biomolecules)

Elemental Analysis

- bulk, micro, contamination (matrix)
- matrix effects
- qualitative Vs quantitative
- complete or specific element
- chemical state

Techniques for reducing matrix effects include:

1. Matrix substitution - dissolving sample into liquid or gas solution, grinding sample with KBr powder.
2. Separation - using chromatography, solvent extraction, etc. to isolate analyte from complex matrix.
3. Preconcentration - collecting the analyte from sample into a much smaller volume to raise its concentration.
4. Derivatization - chemically modifying the analyte to improve volatility, light absorption, complex formation, etc., so that the instrument can more easily measure concentration.
5. Masking - modifying interferences so that they are no longer detected by the instrument.

Extreme trace elemental analysis

- Direct instrumental determination - multi-element - direct excitation---should be least expensive
- These are relative physical methods requiring appropriate standards & systematic errors like spectral interferences occur
- NAA, XRF, sputtered neutral MS

Extreme trace elemental analysis

- Multi-stage procedures --- sample separation and preparation before quantitation
- Standards are less of a problem
- Time consuming & subject to losses or contamination
- Chromatography coupled with analysis

Molecular Spectroscopy IR, UV-Vis, MS, NMR

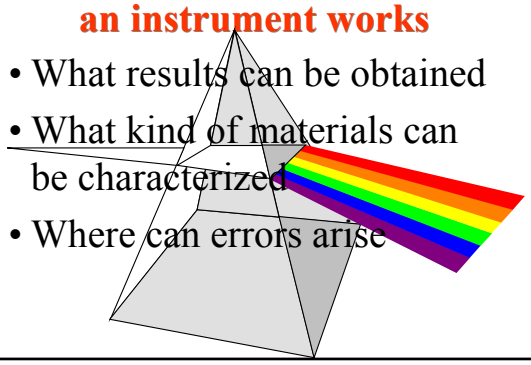
- What are interactions with radiation
- Means of excitation (light sources)
- Separation of signals (dispersion)
- Detection (heat, excitation, ionization)
- Interpretation (qualitative easier than quantitative)

Techniques

- spectroscopy (UV, IR, AA)
- NMR
- mass spectrometry
- chromatography (GC, HPLC)
- measure radioactivity, crystallography, PCR, gas phase analysis

Reason to understand how an instrument works

- What results can be obtained
- What kind of materials can be characterized
- Where can errors arise

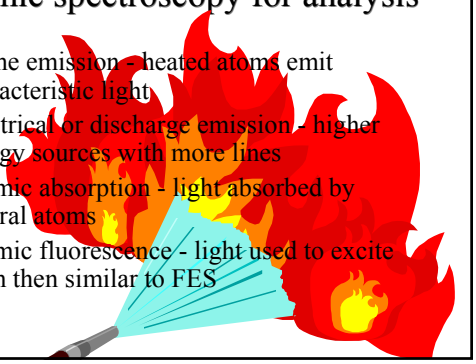


Atomic spectroscopy

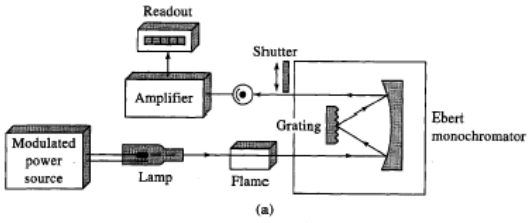
- **Outer shell electrons excited to** higher energy levels
- Many lines per atom (50 for small metals over 5000 for larger metals)
- Lines very sharp (inherent linewidth of 0.00001 nm)
- Collisional and Doppler broadening (0.003 nm)
- Strong characteristic transitions

Atomic spectroscopy for analysis

- Flame emission - heated atoms emit characteristic light
- Electrical or discharge emission - higher energy sources with more lines
- Atomic absorption - light absorbed by neutral atoms
- Atomic fluorescence - light used to excite atom then similar to FES



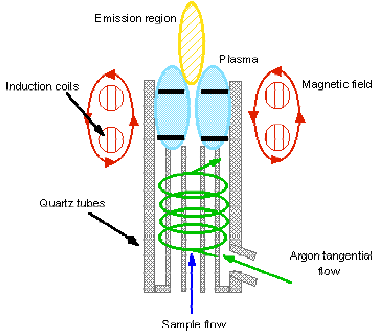
AAS Spectrophotometers:



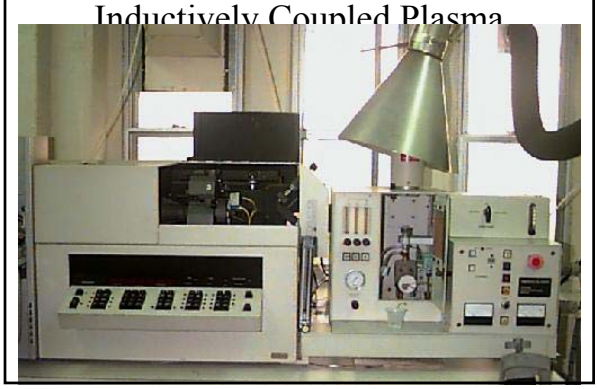
General issues with flames

- Turbulence / stability / reproducibility
- Fuel rich mixtures more reducing to prevent refractory formation
- High temperature reduces oxide interferences but decreases ground state population of neutrals (fluctuations are critical)

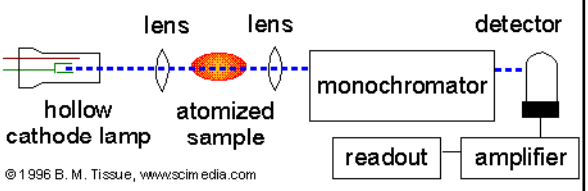
Inductively Coupled Plasma



Inductively Coupled Plasma



AA Instrument Schematic



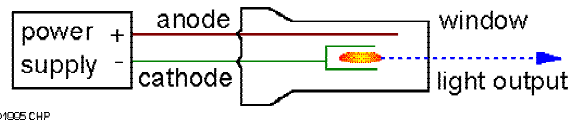
Atomic Absorption

AA instrumentation

- Radiation source (hollow cathode lamps)
- Optics (get light through ground state atoms and into monochromator)
- Ground state reservoir (flame or electrothermal)
- Monochromator
- Detector , signal manipulation and readout device

Hollow Cathode Lamp

Emission is from elements in cathode that have been sputtered off into gas phase



Light Source

- **Hollow Cathode Lamp** - seldom used, expensive, low intensity
- **Electrodeless Discharge Lamp** - most used source, but hard to produce, so its use has declined
- **Xenon Arc Lamp** - used in multielement analysis
- **Lasers** - high intensity, narrow spectral bandwidth, less scatter, can excite down to 220 nm wavelengths, but expensive

Atomizers

- Flame Atomizers - rate at which sample is introduced into flame and where the sample is introduced are important

AA - Flame atomization

- Use liquids and nebulizer
- Slot burners to get large optical path
- Flame temperatures varied by gas composition
- Molecular emission background (correction devices)

Sources of error

- solvent viscosity
- temperature and solvent evaporation
- formation of refractory compounds
- chemical (ionization, vaporization)
- salts scatter light
- molecular absorption
- spectral lines overlap
- background emission

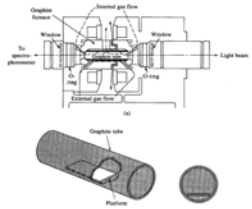
Atomizers

- Flame Atomizers - rate at which sample is introduced into flame and where the sample is introduced is important
- Graphite Furnace Atomizers - used if sample is too small for atomization, provides reducing environment for oxidizing agents - small volume of sample is evaporated at low temperature and then ashed at higher temperature in an electrically heated graphite cup. After ashing, the current is increased and the sample is atomized

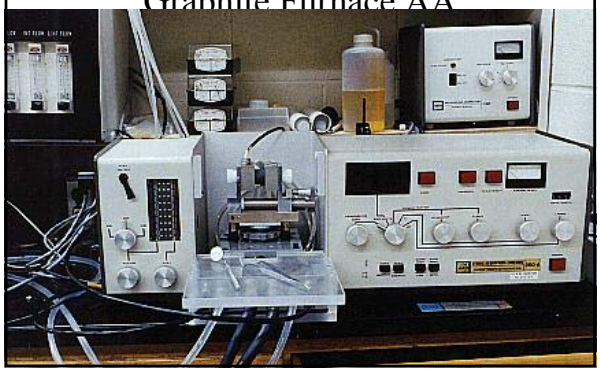
Electrothermal atomization

- Graphite furnace (rod or tube)
- Small volumes measured, solvent evaporated, ash, sample flash volatilized into flowing gas
- Pyrolitic graphite to reduce memory effect
- Hydride generator

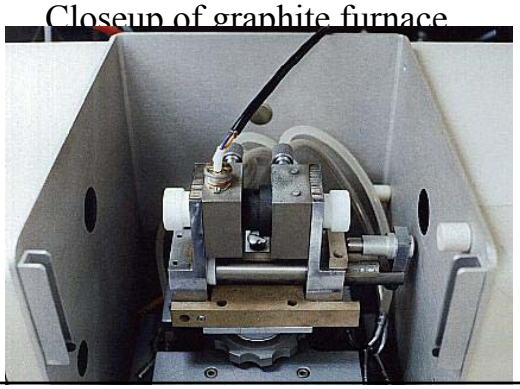
Graphite Furnace



Graphite Furnace AA



Closeup of graphite furnace



Controls for graphite furnace

Detector

- Photomultiplier Tube
  - has an active surface which is capable of absorbing radiation
  - absorbed energy causes emission of electrons and development of a photocurrent
  - encased in glass which absorbs light
- Charge Coupled Device
  - made up of semiconductor capacitors on a silicon chip, expensive

Background corrections

- Two lines (for flame)
- Deuterium lamp
- Smith-Hieftje (increase current to broaden line)
- Zeeman effect (splitting of lines in a strong magnetic field)

Atomic Absorption

- Assumptions: (i) Beer's law holds for the atoms in the flame or graphite furnace, and (ii) the concentration
- of atoms in the flame or furnace is proportional to the concentration of analyte in the sample.
- **Calculations:** The usual calibration curves or standard addition problems.

Beer's Law

$A = \varepsilon bC$ (Beer's Law)

where ε = molar absorptivity (units $M^{-1}cm^{-1}$); b = sample thickness (cell pathlength) in cm; and C = conc. in M (mol/L). , is a property of the analyte and of wavelength; identification of the analyte (qualitative analysis) is possible from the spectrum (ε vs 8). Note that the sensitivity m is equal to ε b.

Problems with Technique

- Precision and accuracy are highly dependent on the atomization step
- Light source
- molecules, atoms, and ions are all in heated medium thus producing three different atomic emission spectra

Problems continued

- Line broadening occurs due to the uncertainty principle
  - limit to measurement of exact lifetime and frequency, or exact position and momentum
- Temperature
  - increases the efficiency and the total number of atoms in the vapor
  - but also increases line broadening since the atomic particles move faster.
  - increases the total amount of ions in the gas and thus changes the concentration of the unionized atom

Interferences

- If the matrix emission overlaps or lies too close to the emission of the sample, problems occur (decrease in resolution)
- This type of matrix effect is rare in hollow cathode sources since the intensity is so low
- Oxides exhibit broad band absorptions and can scatter radiation thus interfering with signal detection
- If the sample contains organic solvents, scattering occurs due to the carbonaceous particles left from the organic matrix