

Atomic Spectroscopy

- Atomic Energy Diagrams Revisited
- Information Provided:
 - Energies of atomic orbitals, degeneracy
 - “allowed” transitions
 - Resonance vs. nonresonance lines
- Atomic Processes:
 - Emission
 - Absorption
 - Fluorescence

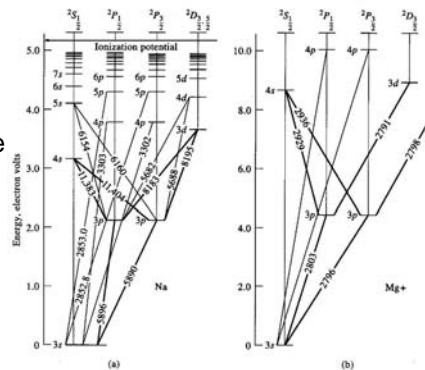


Figure 8-1 Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

Factors that Influence Atomic Spectra: Line Widths

- Ideally should observe a transition occurring at a single wavelength (λ_0)
 - In practice, lines have finite width ($\Delta\lambda_{1/2}$)
 - Effective line width, $\Delta\lambda_{1/2}$: width of line at half of maximum intensity
 - Several factors contribute
1. Uncertainty Broadening
 - Because excited state lifetimes are finite (and small), the uncertainty principle leads to an uncertainty in the measured energy of the transition
 - Remember $\Delta t \Delta E > h$?
 - Relatively small contribution

Factors that Influence Atomic Spectra: Line Widths

2. Doppler Broadening

- Doppler Effect: Apparent frequency of wave depends on the relative motion of the source and the observer
 - source moving toward observer =
 - source moving away from observer =
- In an atomic spectroscopy experiment, the atom is the source and the detector is the observer
- Since the motion of atoms is typically random, the result is symmetrical broadening of the atomic line.
- Major source of broadening in atomic spectroscopy

3. Collision (Pressure) Broadening

- Collisions cause changes in ground state energy levels
- Collisions can be with atoms of same kind or different species
- Also major source of broadening

Factors that Influence Atomic Spectra

• Temperature Effects:

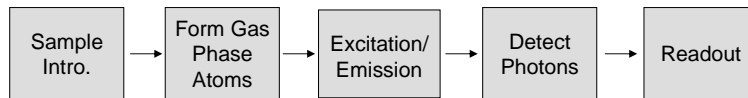
- Temperature influences the ratio of ground state to thermally excite atoms (ions...)
 - Boltzmann Relationship

$$\frac{N}{N_0} \propto e^{-E/kT}$$

- So, small change in T results in large change in population
- Most important in?

Atomic Spectroscopy Experiments

- **Steps in Atomic Spectroscopy Experiments**



- Each step influences accuracy and precision of results

Sample Introduction for Atomic Spec.

- Need reproducible means for transferring sample to atomizer
 - Different requirements for solids and liquids
- **Solution Methods:**
 - Nebulization:
 - Electrothermal Vaporization:
 - Hydride Generation:
- **Methods for Solids**
 - Much more challenging
 - Can result in ejection of small particles or atoms
 - May also induce excitation: ETV, Arc and Spark, Glow Discharge

Atomization Methods for Atomic Spectroscopy

- Techniques for AS require the production of **gas-phase atoms**
 - Multi-step process
 - Elevated temperature
- Three common methods (plus many others)
 - Flames
 - Furnace (electrothermal)
 - Plasma: *ionized Gas*: Gaseous mixture containing atoms, cations and electrons

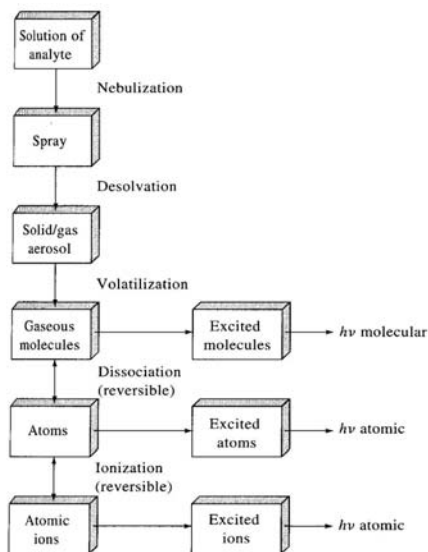


Figure 9-1 Processes occurring during atomization.

Flame Atomization Sources

- Nebulized sample (solution) is mixed with fuel and oxidant and ignited
 - Identity and ratio of fuel and oxidizer determine temperature of flame
 - also influence efficiency of atomization
 - Continuous signal → helps precision (1%)
 - Much of the sample gets thrown away

TABLE 9-1 Properties of Flames

Fuel	Oxidant	Temperatures, °C	Maximum Burning Velocity (cm s ⁻¹)
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	285

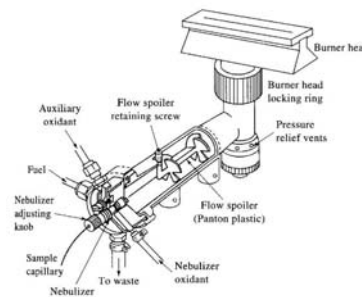


Figure 9-5 A laminar flow burner. (Courtesy of Perkin-Elmer Corporation, Norwalk, CT.)

Flame Atomization Sources

- Composition of the flame is non-uniform - Three "Zones"

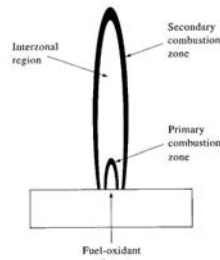


Figure 9-2 Regions in a flame.

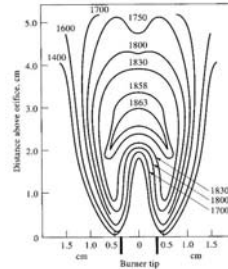
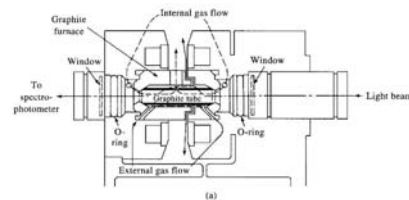


Figure 9-3 Temperature profiles in °C for a natural gas/air flame. (From B. Lewis and G. vonElbe, J. Chem. Phys., 1943, 11, 24. With permission.)

- Primary combustion zone: Relatively cool, products of incomplete combustion
 - Secondary combustion zone: outermost region, also fairly cool, oxide formation
 - Interzonal region: Where the action is. Hottest part of the flame → lots of atoms
- Position in flame for maximum efficiency of atomization varies from element to element.
 - Depends on relative ease of atomization and oxidation
 - General guidelines exist

Electrothermal Atomization Sources

- Graphite furnace is most common
 - Graphite tube with horizontal platform for sample (L'vov platform)



- Inert gas streams serve two purposes:

- Sample must be mechanically inserted into tube
 - affects precision (5-10 % typical)
- BUT all of the sample is used
 - affects accuracy and LOD (0.1 ng to 0.1 pg possible)
- Multi-step heating: Drying, Ashing, Atomization...
- Discontinuous signal

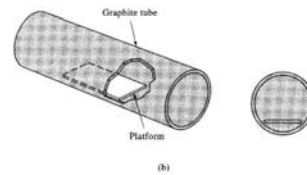


Figure 9-6 (a) Cross-sectional view of a graphite furnace. (Courtesy of the Perkin-Elmer Corporation, Norwalk, CT.) (b) The L'vov platform and its position in the graphite furnace. (Reprinted with permission from W. Slavin, Anal. Chem., 1982, 54, 689A. Copyright 1982 American Chemical Society.)

Plasma Atomization Sources

- Combination of atoms, ions, and electrons results in higher temperatures
 - Results in lower interference
 - Better efficiency
- Two main types
 - ICP:
 - DCP:
- **Inductively Coupled Plasma**
- Relatively high argon flow rate (Liters per minute)
- After ignition, coupling of ionic charge with RF magnetic field “forces” ions to move
 - Heating results, plasma is sustained

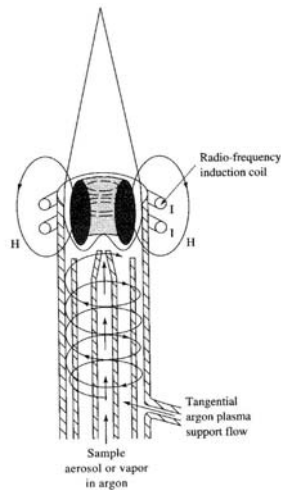


Figure 10-1 A typical inductively coupled plasma. (From V. A. Fassel, Science, 1978, 202, 185. With permission. Copyright 1978 by the American Association for the Advancement of Science.)

Plasma Atomization Sources

- Sample can be introduced via nebulization, electrothermal methods, or ablation
 - transported into plasma with argon
- Continuum background is produced in the core
 - also contains argon spectrum
- Background fades above the core
 - allows improvement in sensitivity
- High temperature allows efficient atomization, but electron concentrations result in minimal ionization

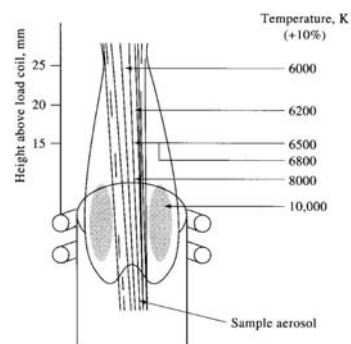


Figure 10-4 Temperatures in a typical inductively coupled plasma source. (From V. A. Fassel, Science, 1978, 202, 186. With permission. Copyright 1978 by the American Association for the Advancement of Science.)

Plasma Atomization Sources

- **Direct Current Plasma**
- DC Power supply
 - (high voltage)
- Plasma becomes self-sustaining
- ~5000K in Excitation Region
- Similar sensitivity as ICP, higher maintenance

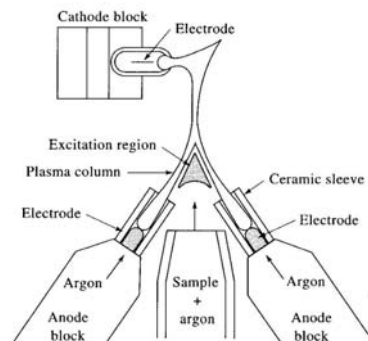


Figure 10-5 A three-electrode dc plasma jet. (Courtesy of Spectra Metrics, Inc. Haverhill, MA.)

Excitation Sources for AA

- Monitoring narrow lines, need narrow source
- Hollow Cathode Lamp

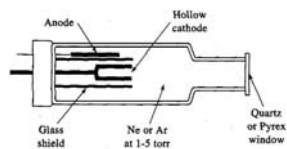


Figure 9-11 Schematic cross section of a hollow cathode lamp.

- Cathode is coated with atom of interest
- Tube is filled with Ar or Ne
- High voltage ionizes gas, charged ions are accelerated toward electrodes
 - Produces sputtering of atoms (ground and excited)
 - Excited atoms emit light at atomic lines
- Design of HCL results in redeposition of metal atoms onto electrodes - recycling
- Need to avoid excessively high potentials
 - Line broadening (Doppler)
 - Self-absorption
- Need separate lamp for each element

Excitation Sources for AA

- Absorption in atomic spectroscopy
- Several lines produced by source
 - filter or monochromator selects (nothing fancy)
- Because bandwidth of absorption peak is large compared to excitation line, Beer's Law applies
 - Why is $\Delta\lambda$ for absorption greater than $\Delta\lambda$ for excitation?

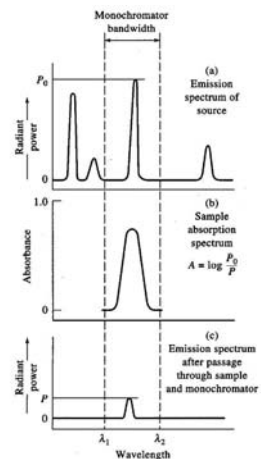


Figure 9-10 Absorption of a resonance line by atoms.

Interferences in Atomic Spectroscopy

- Processes that affect the efficiency of producing gas-phase atom or the interaction of these atoms with light
- Two main classes:
 - Spectral Interferences:
 - Chemical Interferences

Spectral Interference:

- Several sources
 - Overlapping lines due to contaminants
 - Correct by:
 - Broadband processes due to combustion products
 - Correct by:
 - Scattering by particulates formed in the flame
 - Correct by:
 - Matrix effects
 - Correct by:

Interferences in Atomic Spectroscopy

- Background correction methods can (to an extent) compensate for interference in electrothermal methods
- Two-Line Method
 - compare response of a line that is absorbed by the analyte to a line that isn't absorbed
- Continuum-Source Method (our instrument)
 - compare response to narrow band excitation to a broadband (wide slitwidth = large bandwidth)
- Zeeman Effect
 - Introduction of a magnetic field causes splitting of absorption lines
 - Result is polarization-dependent absorption
 - analyte absorption only occurs in one polarization
- Source Reversal
 - at high source current, self absorption takes place
 - decreases intensity of source at the peak
 - Alternating current results in background correction (like continuum source method)

Interferences in Atomic Spectroscopy

- **Chemical Interferences:**
 - Think of atomization process as an equilibrium
Gas-Phase Atoms = Interfering Species
- **In an optimized method, the equilibrium is shifted as far to the left as possible**
 - Goal is to choose conditions to ensure this
 - Take advantage of existing knowledge!
- **Volatility:**
 - some salts have inherently low volatility
 - Slow atomization rate = fewer atoms in the GP
 - Correct by:
 - Increasing temperature
 - Adding *Release Agents*
 - Adding *Protective Agents:*

Interferences in Atomic Spectroscopy

- **Formation of gas-phase compounds:**
 - Many materials form fairly stable gas-phase oxides or halides...

$$M + O_x = MO_x$$
 - Correct by:
- **Ionization Interference:**

$$M = M^+ + e^-$$
 - Strongly dependent on Temperature and Ionization Potential
 - As temperature increases, the probability of ionization also increases
 - more ions = fewer atoms = decreased absorption (or emission)
 - Correct by:
 - Adding an *ionization suppressor*.
- **Advantages of Plasmas:**
 - High Temperature leads to:
 - more efficient volatilization
 - fewer chemical interferences
 - Few ionization interferences
 - Why?

Atomic Spectroscopy Instruments

- Requirements (ideal):
 - Relatively narrow bandwidth → good wavelength discrimination
 - Ability to cover wide wavelength range → flexibility
 - Background correction capability
 - Good sensitivity
 - Good stability
- General Instrument Design
 - In most cases, plasma (ICP, DCP) can be substituted for HCL and Flame

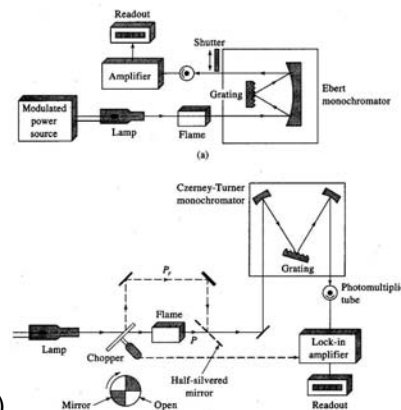


Figure 9-13 Typical flame spectrophotometers: (a) single-beam design and (b) double-beam design.

Atomic Spectroscopy Instruments

- Since we are typically only interested in a small number of regions of the spectrum, scanning across all λ regions is a waste of time
 - Slew-Scan
 - Multichannel instruments
- Echelle optics
 - Two dispersing elements
 - Coarsely ruled grating
 - Prism
 - Forms two-dimensional array of lines
- Echelle Polychromator
 - fix exit “slits” in strategic places on focal plane
 - Scan single PMT across slits
 - Fix several PMTs, one per slit
 - Use multichannel detector (CCD, CID)

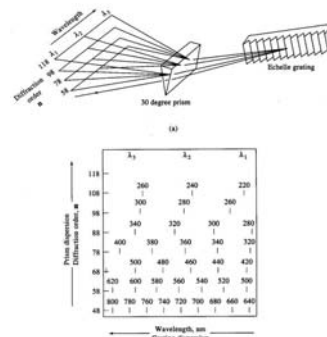


Figure 21 An echelle monochromator: (a) arrangement of dispersing elements, and (b) schematic end-on view of the dispersed radiation from the point of view of the transducer.

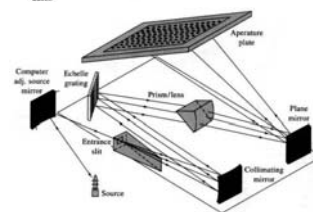


Figure 10.7 Schematic of an echelle polychromator system.

Detection Limits in Atomic Spectroscopy

- Combination of contributions: volatility, susceptibility to interference, etc.

TABLE 9-3 Detection Limits (ng/mL)* for Selected Elements†

Element	AAS‡ Flame	AAS‡ Electrothermal	AES‡ Flame	AES‡ ICP	AFS‡ Flame
Al	30	0.005	5	2	5
As	100	0.02	0.0005	40	100
Cs	1	0.02	0.1	0.02	0.001
Cd	1	0.0001	800	2	0.01
Cr	3	0.01	4	0.3	4
Cu	2	0.002	10	0.1	1
Fe	5	0.005	30	0.3	8
Hg	500	0.1	0.0004	1	20
Mg	0.1	0.00002	5	0.05	1
Mn	2	0.0002	5	0.06	2
Mo	30	0.005	100	0.2	60
Na	2	0.0002	0.1	0.2	—
Ni	5	0.02	20	0.4	3
Pb	10	0.002	100	2	10
Sn	20	0.1	300	30	50
V	20	0.1	10	0.2	70
Zn	2	0.00005	0.0005	2	0.02

*Nanogram/milliliter = 10^{-3} $\mu\text{g/mL}$ = 10^{-3} ppm.

†AAS = atomic absorption spectroscopy; AES = atomic emission spectroscopy; AFS = atomic fluorescence spectroscopy; ICP = inductively coupled plasma.

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§From C. W. Fuller, *Electrothermal Atomization for Atomic Absorption Spectroscopy*, pp. 65-83. London: The Chemical Society, 1977. With permission, The Royal Society of Chemistry, Burlington House, London.

Utility of Atomic Spectroscopy

- THE tool of choice for metals analysis
- Depends on:
 - required sensitivity
 - optical characteristics
 - sample composition (matrix effects)
- Sample Prep. also plays a major role (as usual!)

TABLE 10-3 Comparison of Detection Limits for Several Atomic Spectral Methods*

Method	Number of Elements Detected at Concentrations of				
	<1 ppb	1–10 ppb	11–100 ppb	101–500 ppb	>500 ppb
Inductively coupled plasma emission	9	32	14	6	0
Flame atomic emission	4	12	19	6	19
Flame atomic fluorescence	4	14	16	4	6
Flame atomic absorption	1	14	25	3	14

*Detection limits correspond to a signal that is twice as great as the standard deviation for the background noise. Data abstracted with permission from V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, 1974, 46(13), 1111A. Copyright 1974 American Chemical Society.