

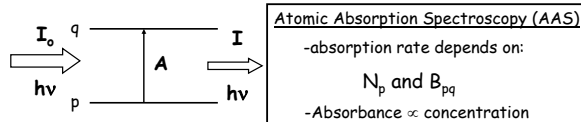
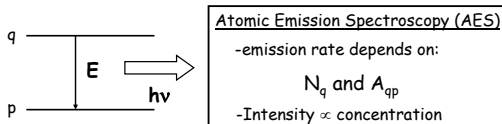
Spectroscopy:

Atomic Absorption and Emission Spectrometry

Chem 221
Instrumental Analysis
Spring 2005

Fundamentals

- **Atoms** can also absorb and emit EMR:



AAS versus AES?

- **AAS:** Absorbance $\propto N_p$
- **AES:** Emission Int. $\propto N_q$

But: concentration $\propto N_T$

For a *thermal* population distribution, we use the Boltzmann Equation to relate N_p and N_q to N_T :

$$\frac{N_q}{N_T} = \frac{g_q e^{-(E_q/kT)}}{\sum(g_i e^{-(E_i/kT)})}$$

Where: T = absolute temp., k = Boltzmann's constant, and g_i = statistical weight of state i

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Impact of Boltzmann

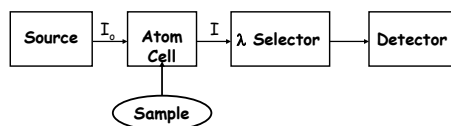
- Population of *any state* is **temperature dependent**
- **BUT:** even at high temperatures, N_q/N_T is usually very small ($\sim 10^{-3}$ - 10^{-7} @ 3000 K)
- **So:** N_p (ground state population) $\approx N_T$ (99+% of atoms are in the ground state)
 - So: absorbance $\propto N_T$
 - And: absorbance is relatively temp indep
- **Also:** N_q/N_T is very temperature sensitive, but at **constant temperature:**

$$N_q = N_T K \propto \text{conc} (\propto I)$$

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Instrumentation

- Let's start with AAS:

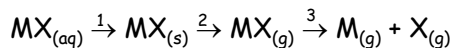


-lets first look at Atom Cells and how a sample is converted to gas phase atoms

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Obtaining Gas Phase Atoms

- From an *aqueous solution*:



1. **Desolvation**
-conversion of analyte to solid crystals
2. **Vaporization**
-conversion of solid to molecular vapor
3. **Atomization**
-dissociation of molecular vapor into atomic vapor

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Flame Atom Cells:

Laminar Flow Pre-mix Spray Chamber Burner

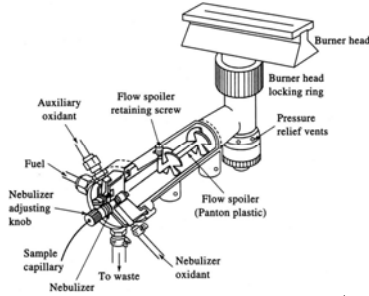
■ Requirements:

stable, quiet, long path-length, "cool"

(H₂/air: 2000°C,
C₂H₂/air - 2300 °C)

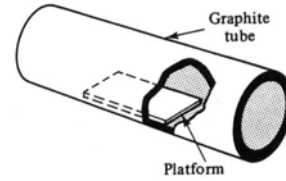
■ Limitations:

- flashback!
- inefficient



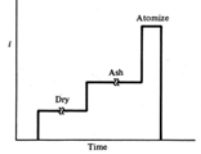
Electrothermal Atomizers: The Graphite Furnace

■ Resistively heated carbon tube:



• Sample micropipetted (5-50 μL)
onto platform in tube

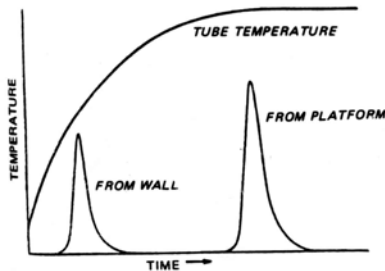
3-stage heating cycle:



- Dry (~120°C) - desolvation
- Ash (~500 - 1000°C)
- atomize matrix
- Atomize (~1000 - 3000°C)
- atomize analyte

Graphite Furnace Atomization: Why Use a Platform?

■ Ideally, atomize into an isothermal environment:



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Flame-AAS versus GFAAS

Flame-AAS

- Continuous
- 1-5% sample consumption
- mL samples
- short residence time (ms)
- high sample throughput
- ppm - ppb det. limits

GFAAS

- Pulsed/Transient
- 100% sample consumption
- μL samples
- long residence time (sec)
- low sample throughput
- picogram det. limits

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Sources

■ Need a narrow line source Why?

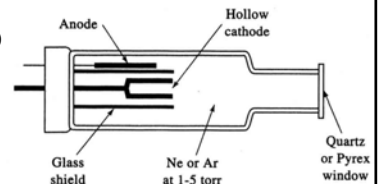
- Atomic spectral features are very narrow (linewidths typically < 10⁻² Å)
- Continuum source necessitates monochromator with Δλ_{eff} < 10⁻³ Å . . . not easily done!
- So, need a source which can provide emission at discrete wavelengths with linewidths less than those found in flame or graphite furnace atom cells

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Hollow Cathode Lamps

■ The ideal source for AAS!

- Electric discharge (200-400 volts, 5-15 mA)
- Negatively charged cathode made out of element of interest
- Fill gas ions sputter atoms from cathode
- Collisions with e⁻ excite atoms



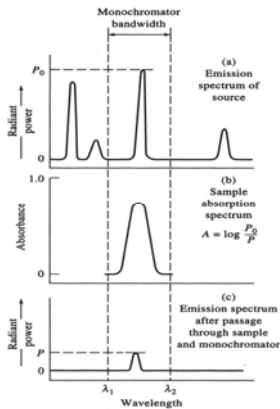
Gives intense narrow line spectrum of cathode material

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Absorbance Measurement

• Hollow cathode lamp (HCL) source linewidth is much less than absorption linewidth in flame or graphite furnace

• Gives best sensitivity
• Follows Beer's Law



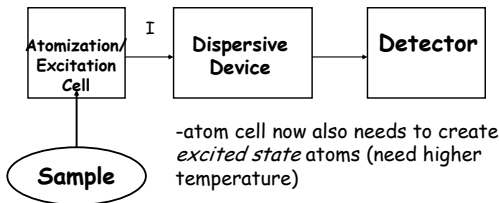
Spectrometers for AAS

- **Low-to-moderate resolution with PMT detector**
 - Selectivity accomplished with HCL
 - Want maximum light throughput
 - No scanning (cannot obtain an absorbance spectrum)
- **Background Correction?**
 - use a *continuum source* (D₂ lamp) to obtain absorbance due to non-atomic species within $\Delta\lambda_{eff}$
 - subtract to obtain net atomic absorption

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Instrumentation for AES

- Simple! Get rid of source and change the atom cell:



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Atomization/Excitation Sources for AES

- **Flames**
 - *need high temperatures*
(4500 °C possible with O₂/(CN)₂ flame)
 - *need a short pathlength*
(eliminates problems with *self-absorption*)
 - *use a total consumption burner*
(noisy, small, inefficient)
 - *complementary with Flame AAS*
(ppm - ppb detn limits)

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Plasma Sources for Atomization/Excitation

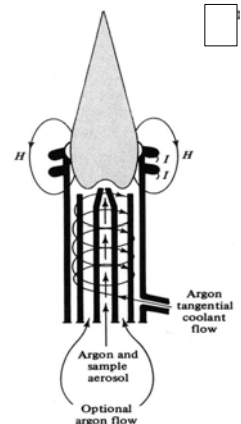
Plasmas: hot, ionized gas

- **Arcs and Sparks**
 - electrical (directly coupled) ionization
 - useful for solid samples
- **Laser-Induced Plasmas**
 - optical ionization/atomization
 - micro-atomization
- **The Inductively Coupled Plasma (ICP)**
 - electrical (inductively coupled) ionization
 - most common AES source for solution samples

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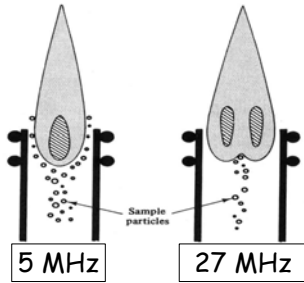
ICP Sources

- **RF Power Source**
(1-2 kW @ 27 MHz)
- **Three Argon Flows**
 1. **Plasma Gas** (10-20 L/min)
 2. **Nebulizer Gas** (~1 L/min)
 3. **Auxilliary Gas** (~0.5 L/min)
- **High Temperature** (~8000 K)
- **Heated from Outside-In**
 - *Skin-depth effect*



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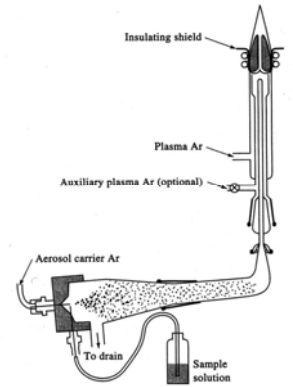
Effect of Frequency



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More on ICPs

- Sample Introduction
 - Nebulization (aqueous)
- High temperature gives:
 - Efficient atomization
 - Efficient excitation
- ppb detection limits
- No self-absorption
 - 6 decades LDR



Spectrometers for AES

- Highest possible resolution gives best L/B, so invest in instrument with *high dispersion*
- For simultaneous multi-element determinations: use multichannel spectrometer (direct reader or echelle)
- With AES, you obtain a spectrum
 - qualitative analysis possible
 - easy background correction

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Applications

- ✓ Qualitative Analysis
 - AES only (no spectrum with AAS)
- ✓ Quantitative Analysis
 - Calibration Curves
 - AAS: 1-2 decades LDR (limited by stray light)
 - AES: 6-7 decades LDR (with ICP)
 - Deviations at *high concentrations* due to self-absorption
 - Deviations at *low concentrations* due to ionization (%-ionization greatest at low conc, so atom line emission depressed more at low concentrations)

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Interferences

■ Ionization

- signal will vary with %-ionization (a function of e^- number density):



- *easily ionizable elements* (e.g., Na, K, Li, etc.) will be more significantly ionized than other elements

- the presence of an *EIE* in a sample will affect the electron density, shifting the ionization equilibrium of the *analyte* and affecting the resulting signal, leading to an: *Easily Ionizable Element Interference Observation*

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EIEIO

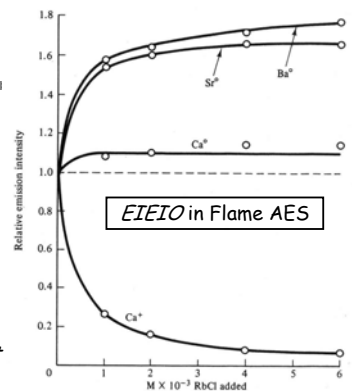
So, it's the *variability* of the e^- density that is problematic

Solution:

- *flood* system with an EIE to give a large, constant e^- density

- Flames: add *ionization suppressant*

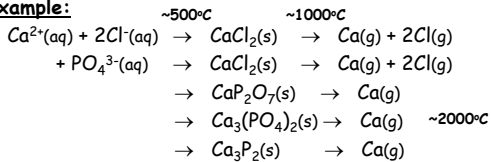
- ICP: *no EIEIO!*



Atomization Interferences

- Cooler sources are *high-temperature reaction cells*
-sample matrix can provide species which react with analyte to reduce signal

Example:



-also a problem with other matrix elements
(e.g., SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, Al, etc.)

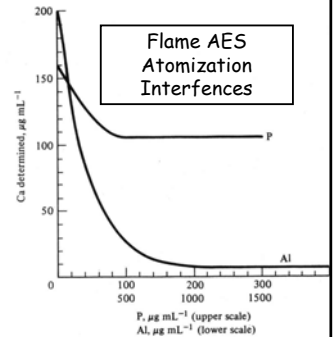
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Atomization Interferences

Again, the *variability* of the interferent is the problem

Solutions:

1. Chemistry
-Add a *releasing agent*
-Add a *complexing agent*
2. Higher Temperature
-hotter flame
-*ICP*



AES versus AAS

GF-AAS

- low cost
- single element
- low sample throughput
- atomization interferences

ICP-AES

- moderate-high cost
- multielement
- high sample throughput
- spectral interferences

Complementary Techniques

- *together*, can get *low-to-sub-ppb* det. limits for ~70 elements

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