CHE680
Advanced Analytical Chemistry
Lecture 7

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State University of New York

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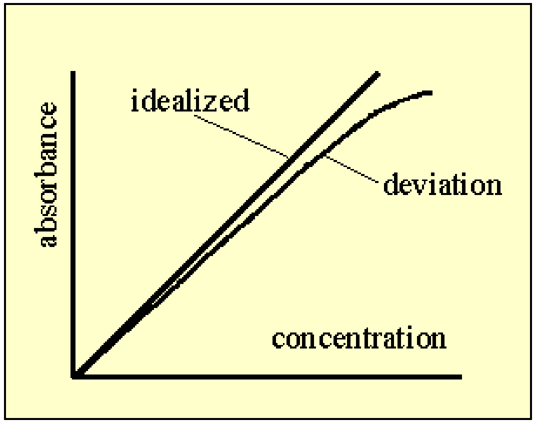
Atomic Absorption/Flame Emission/Atomic Emission Spectroscopy (AAS/FES/AES)



http://elchem.kaist.ac.kr/vt/chem-ed/spec/atomic/aa.htm

Atomic Absorption/Flame Emission/Atomic Emission Spectroscopy (AAS/FES/AES)

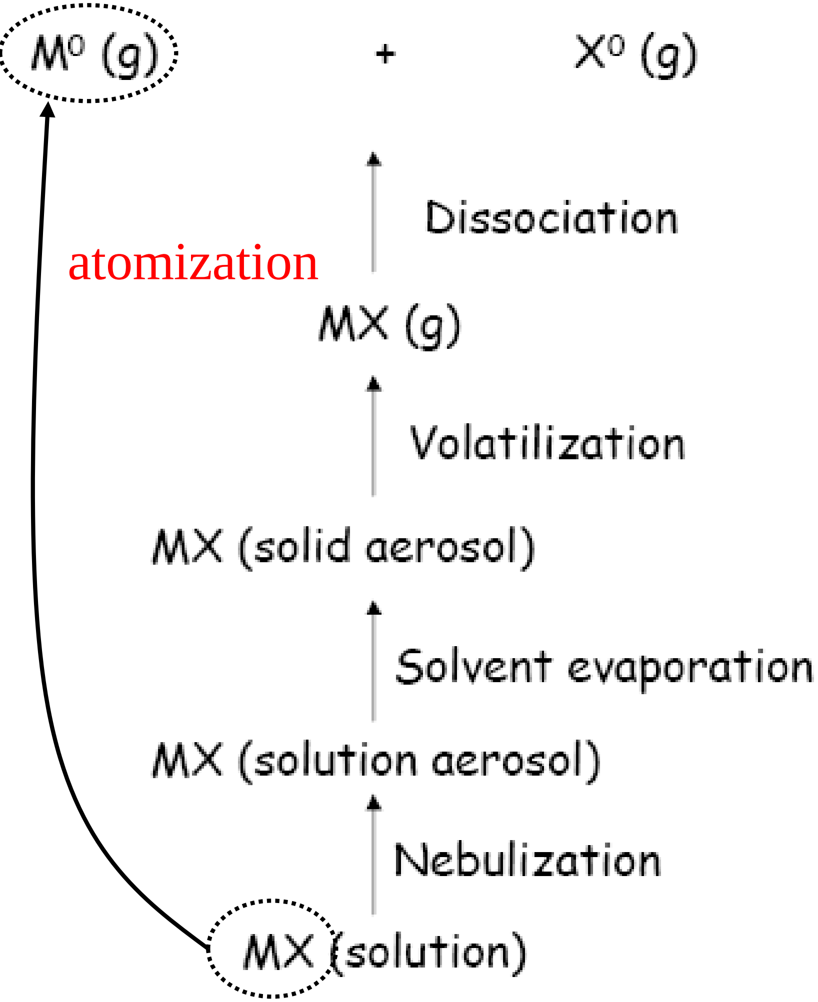
AAS/FES are two methods of *quantitative analysis* that can be used to measure approximately *70 elements (most metals and nonmetals) not compounds*. Although there are close similarities between two techniques, these methods relay on different principles. AES employs high temperature sources to ionize all elements in a sample and contains advanced monochromators (or polychromators) to improve sensitivity and selectivity toward target elements.

In AAS, the optical absorption of atoms from their ground state to excited states is measured when the sample is irradiated with the appropriate source (*best for quantitative analysis*).

In FES, the radiation intensity emitted by a small fraction of atoms from the excited states to ground state is measured (*quantitative analysis for limited elements*).

In AES, the radiation intensity emitted by excited states of ionized *atoms* via high temperature excitation source is measured (*simultaneous and sequential multi-elemental quantitative and qualitative analysis with less sensitivity*).

What's the Atomization and Ionization? (AAS/FES/AES)



M^0 (g) + X^0 (g)

Dissociation

atomization

MX (g)

Volatilization

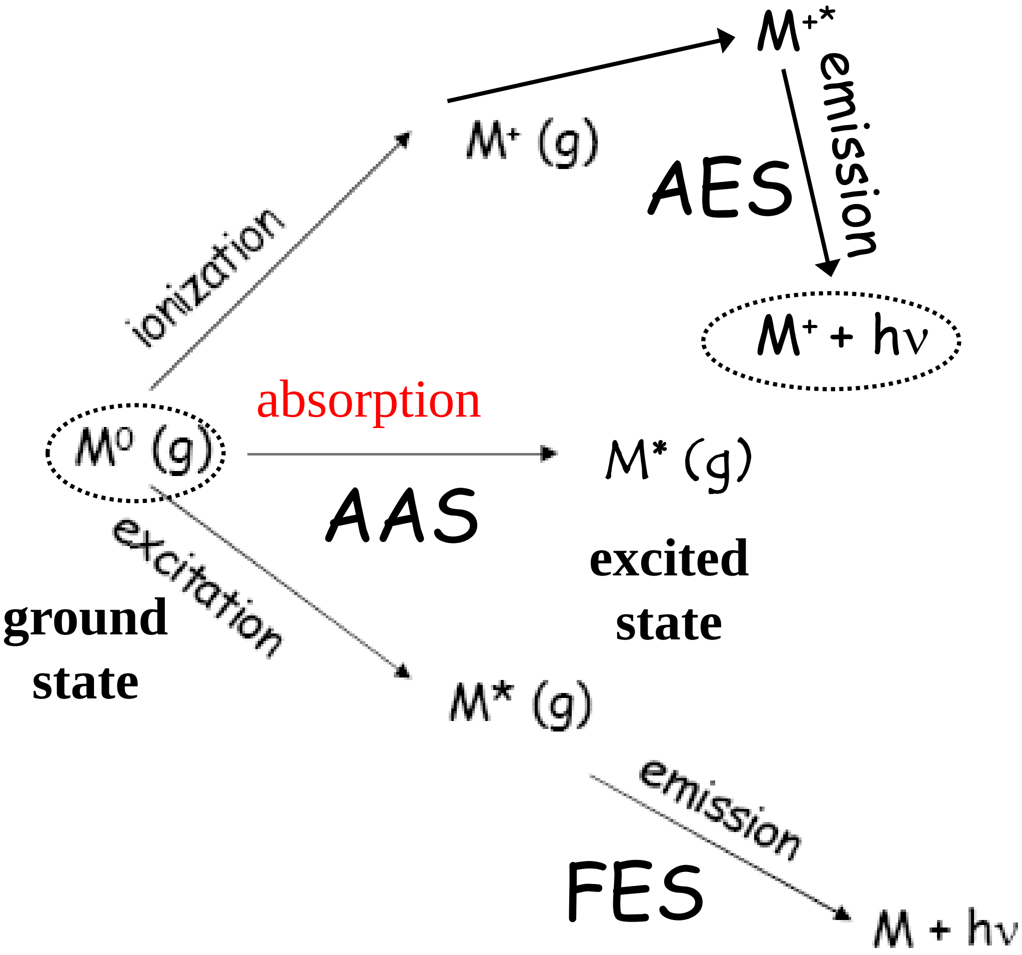
MX (solid aerosol)

Solvent evaporation

MX (solution aerosol)

Nebulization

MX (solution)



M^{+*}

emission

AES

M^+ (g)

ionization

$M^+ + h\nu$

absorption

M^0 (g)

M^* (g)

AAS

excited state

ground state

excitation

M^* (g)

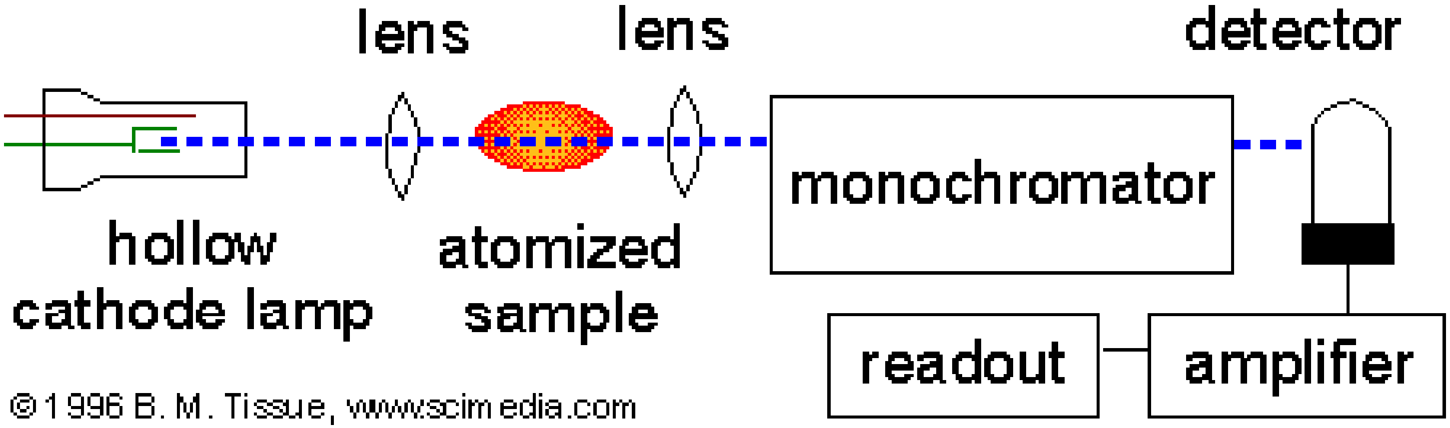
emission

FES

$M + h\nu$

AAS vs. FES (AES)

AAS has a hollow cathode lamp that emits a radiation that will be absorbed by atomized sample



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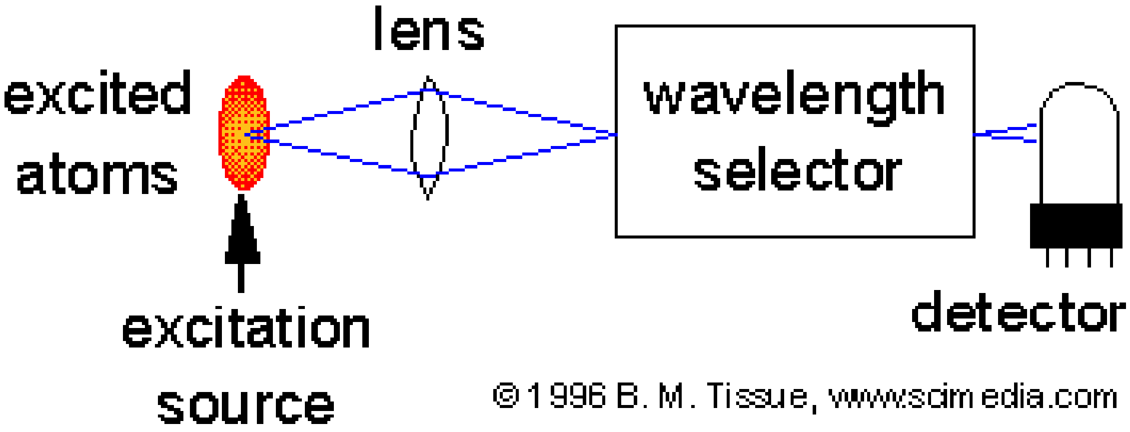
In principle, AES and FES are similar, but AES employs high temperature excitation source and advanced detection system



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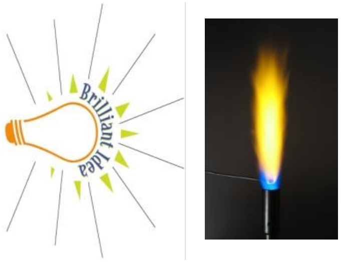
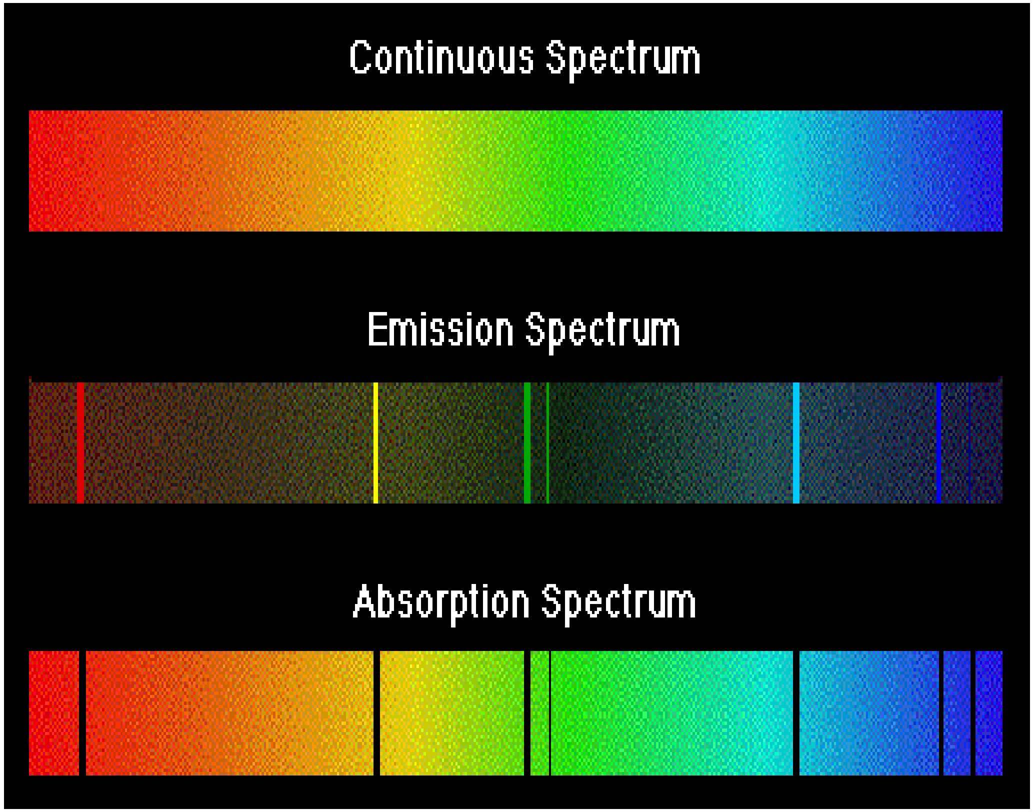
AAS vs. FES (AES)

Light emission from bulb

Light emission from sodium



Light emission from bulb after sodium



AAS vs. FES

Boltzmann Distribution: Relative population of molecules (atoms, electrons, etc), N_1 and N_2, with two energy states, E_1 and E_2, and degeneracy, g_1 and g_2 ($g = g_2/g_1$).

$$\frac{N_2}{N_1} = \frac{g_2 \cdot e^{-E_2/kT}}{g_1 \cdot e^{-E_1/kT}} = g \cdot e^{-\Delta E/kT}$$

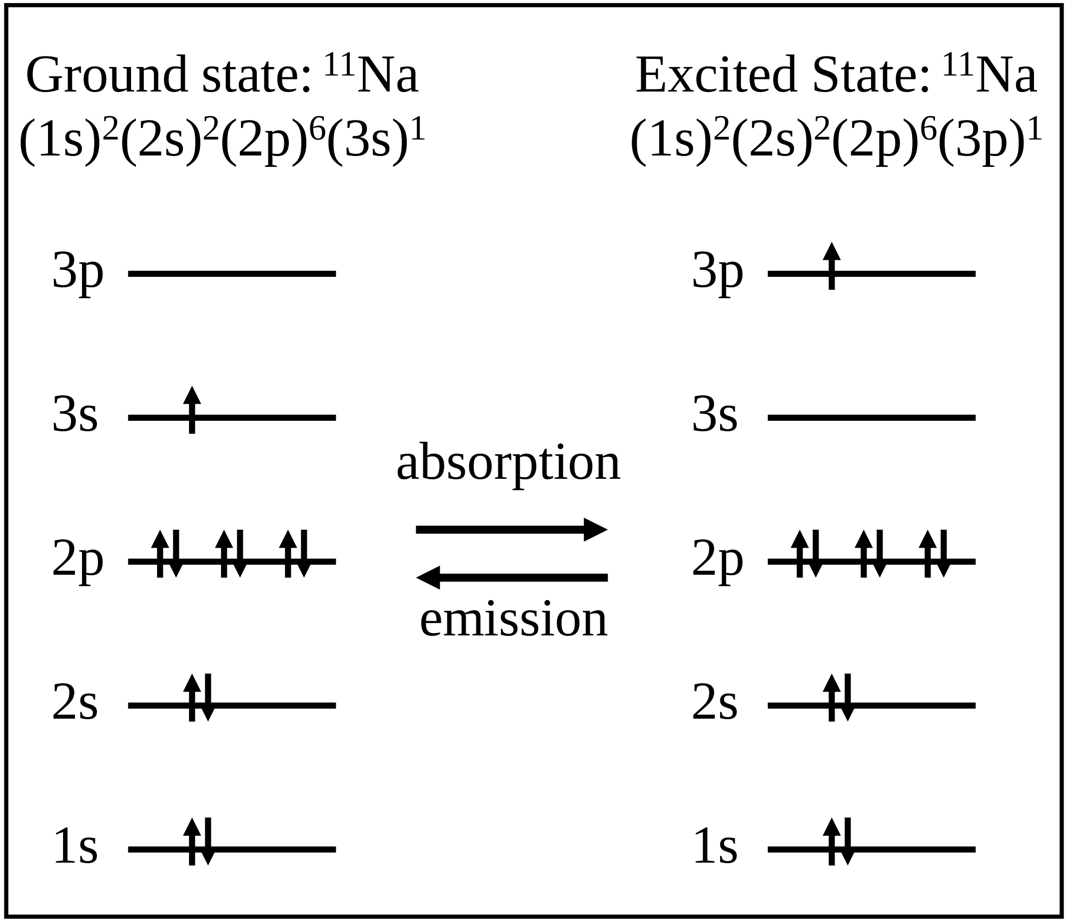
Ratios of N_2/N_1 for certain elements at various temperature

element	λ (nm)	E (eV)	g	2000 K	3000 K	4000 K
Na	589	2.10	2	1.03×10^{-5}	5.95×10^{-4}	4.53×10^{-3}
Ca	423	2.93	3	4.25×10^{-7}	3.60×10^{-5}	6.12×10^{-4}
Cu	325	3.82	2	4.77×10^{-10}	7.69×10^{-7}	3.09×10^{-5}
Zn	214	5.79	3	7.81×10^{-15}	5.68×10^{-10}	1.53×10^{-7}

For reliable measurements, the ratios of N_2/N_1 should be $> 10^{-7}$

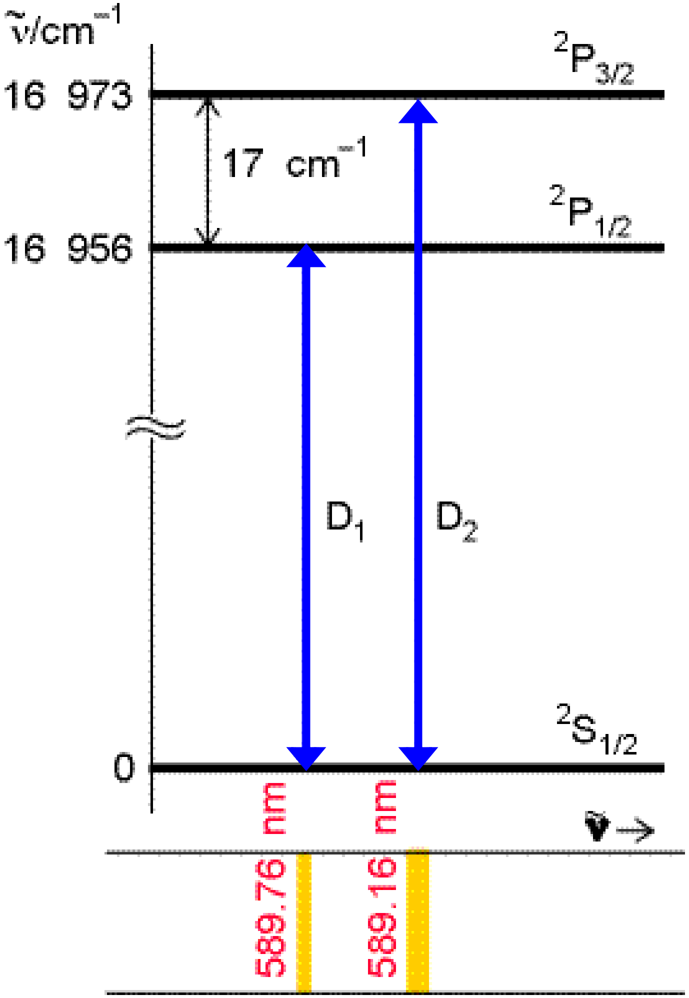
Electronic Transition of Na Atom

Origin of yellow emission from sodium (sodium light)

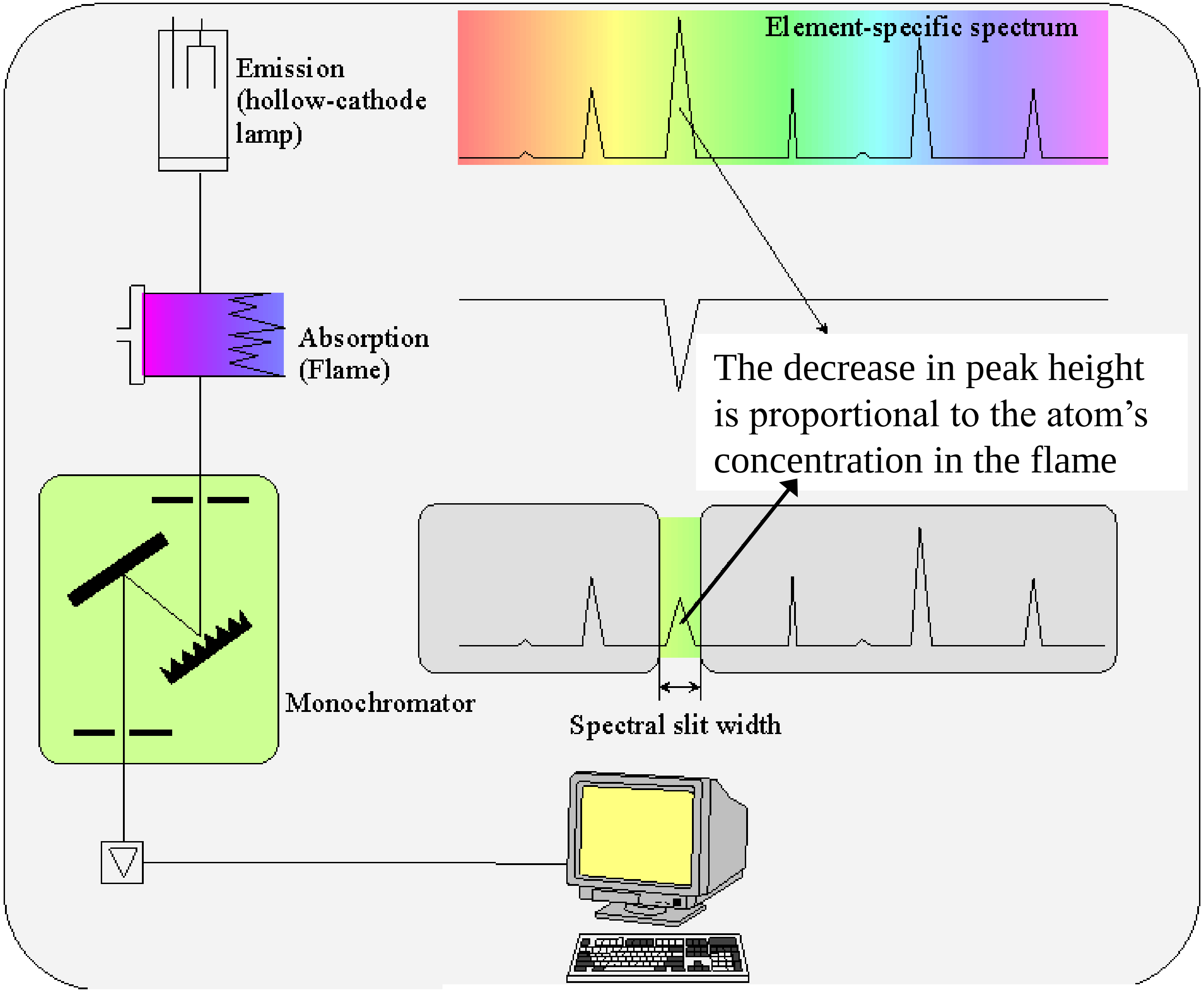


Ground state: ^{11}Na
$(1s)^2(2s)^2(2p)^6(3s)^1$

Excited State: ^{11}Na
$(1s)^2(2s)^2(2p)^6(3p)^1$



Atomic Absorption Spectroscopy (AAS)



The decrease in peak height is proportional to the atom's concentration in the flame

concentration determination by Beer's law

Features of Atomic Absorption Spectroscopy (AAS)

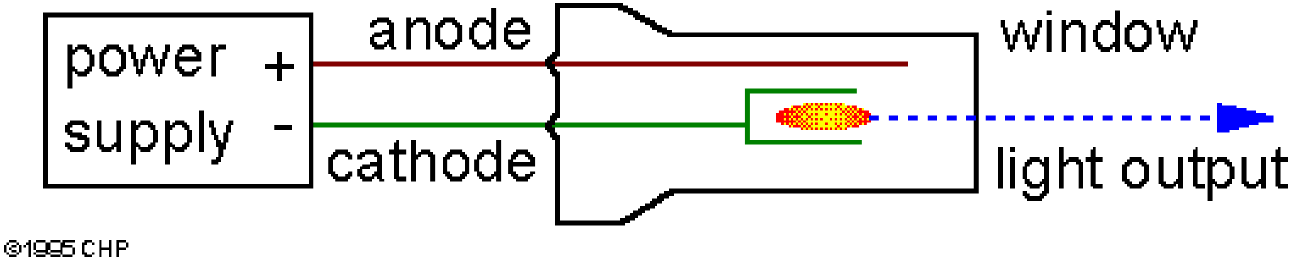
- AAS should be very selective - each element has different set of energy levels and lines very narrow
- BUT for linear calibration curve (Beers' Law) need bandwidth of absorbing species to be broader than that of light source difficult with ordinary monochromator

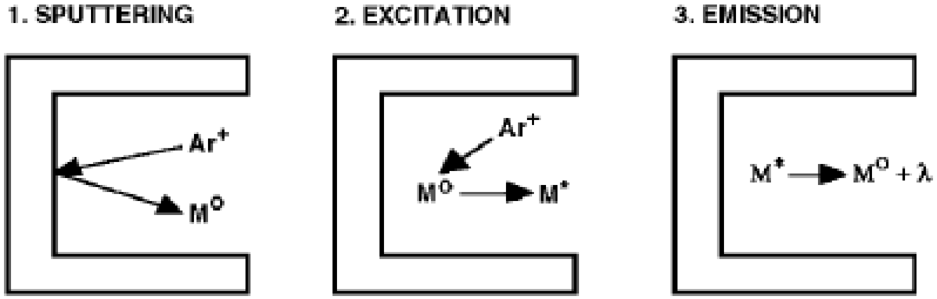
Solved by using very narrow line radiation sources (HCL)

- minimize Doppler broadening
- pressure broadening
- lower P and T than atomizer and using resonant absorption

Hollow-Cathode Lamps

Hollow-cathode lamps produce radiation sources specific for elements under investigation. They are a type of discharge lamp that produces narrow emission from atomic species. They get their name from the cup-shaped cathode, which is made from *the element of interest and restricts multi-elements detection*. The electric discharge ionizes rare gas atoms, which are accelerated into the cathode and sputter metal atoms into the gas phase. Collisions with gas atoms or electrons excite the metal atoms to higher energy levels, which decay to lower levels by emitting light.





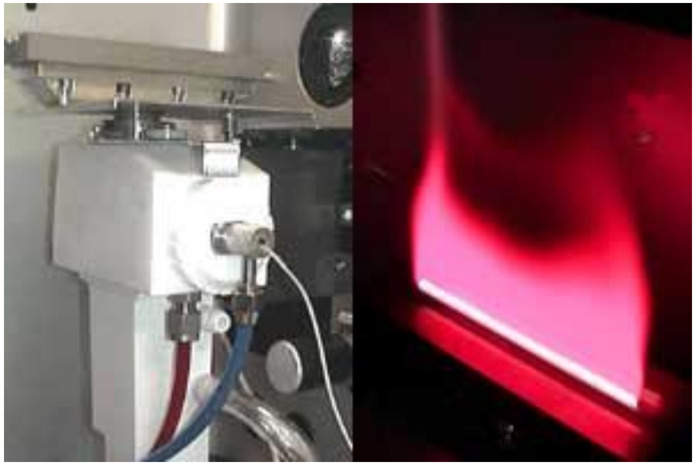
Radiation source ⟹

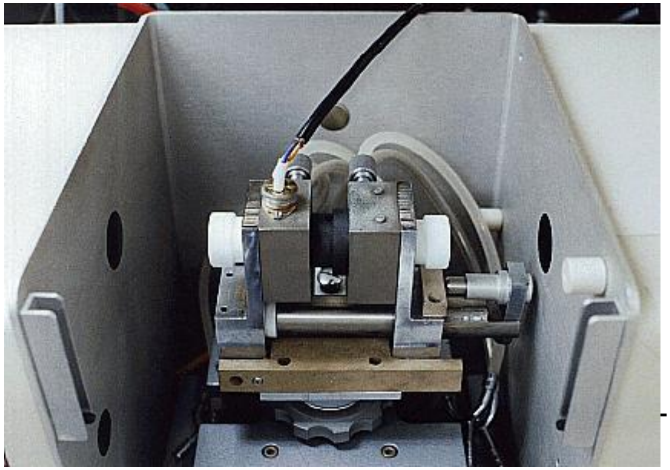
Atomizer

The atoms or ions in the sample be in the gas phase via dissolution and vaporization in a high-temperature source such as a flame or graphite furnace.

- Flame AA can only analyze solutions (2000 – 4000 k)
- A simple and slot-type burner to increase the path length and the total absorbance
- Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame.

- A small amount of samples (solutions, slurries, or solid).
- Provides a reducing environment for easily oxidized elements.
- Samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the atoms in the sample.

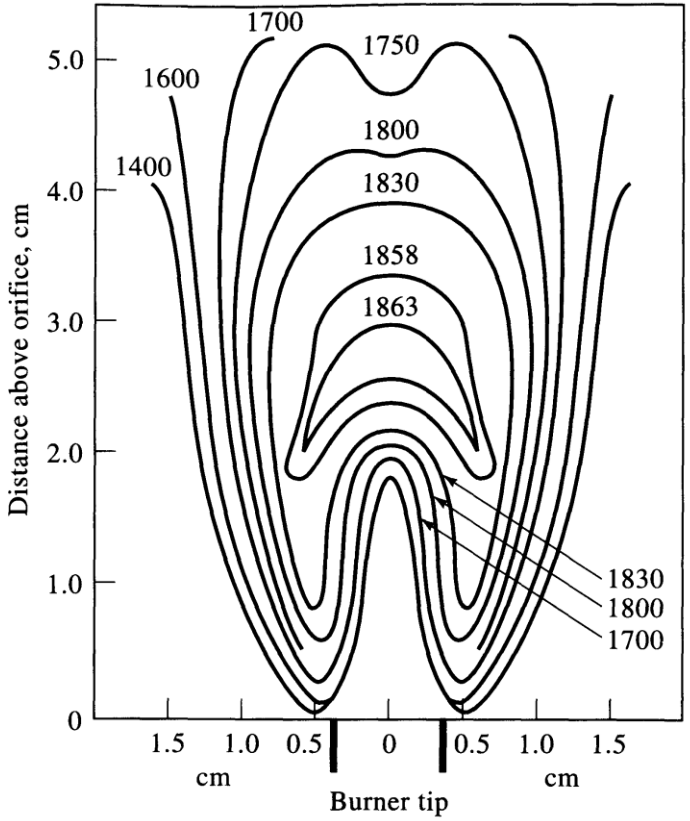


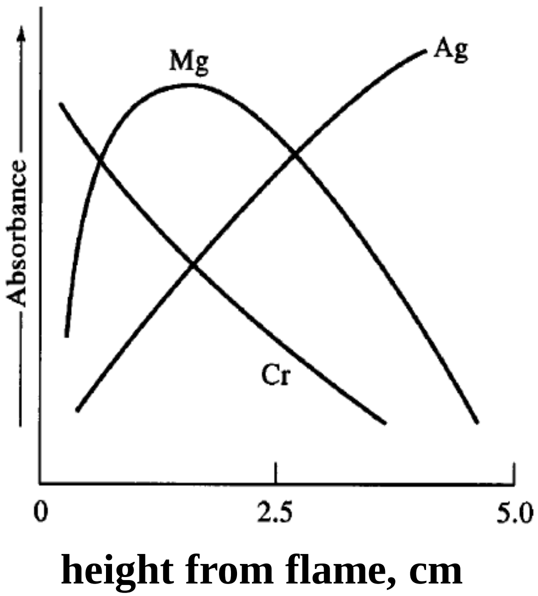


Flame AAS

- laminar flow burner - stable "sheet" of flame
- flame atomization best for reproducibility (precision, <1%)
- relatively insensitive - incomplete volatilization, short time in beam

Fuel	Oxidant	Temperature
Gas	Air	~1800 °C
H_2	O_2	~2600 °C
Acetylene	O_2	~3000 °C

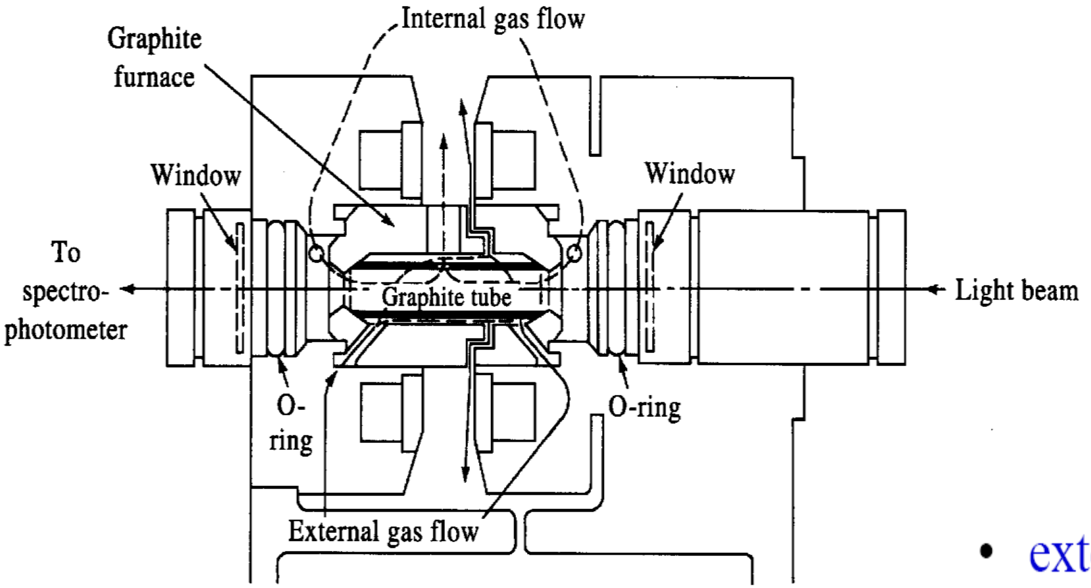




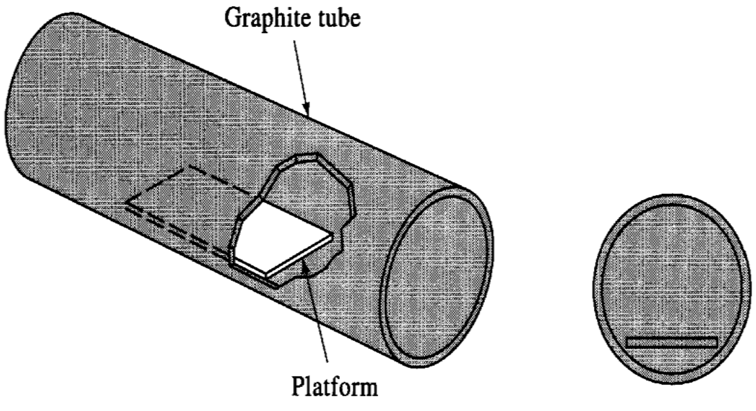
most sensitive part of flame for AAS varies with analyte
sensitivity varies with element
must maximize burner position
makes multielement detection difficult

Graphite AAS

- entire sample atomized short time (2000 – 3000 °C)
- sample spends up to 1 s in analysis volume
- superior sensitivity ($10^{-10} – 10^{-13}$ g analyte)
- less reproducible (5 – 10 %)



(a)

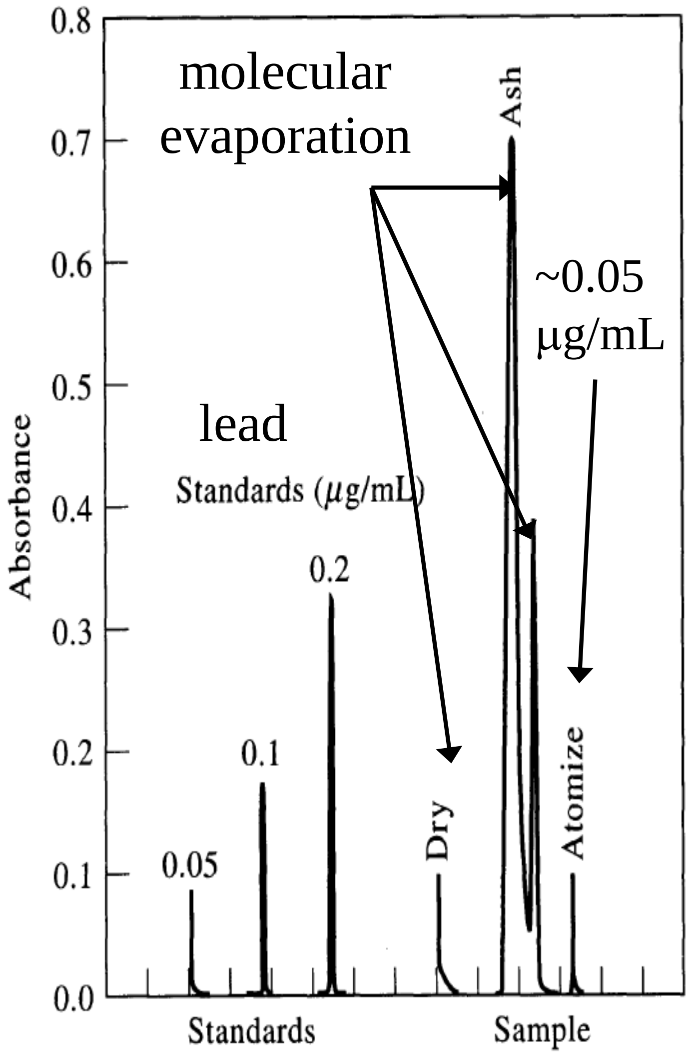


(b)

- external Ar gas prevents tube destruction
- internal Ar gas circulates gaseous analyte

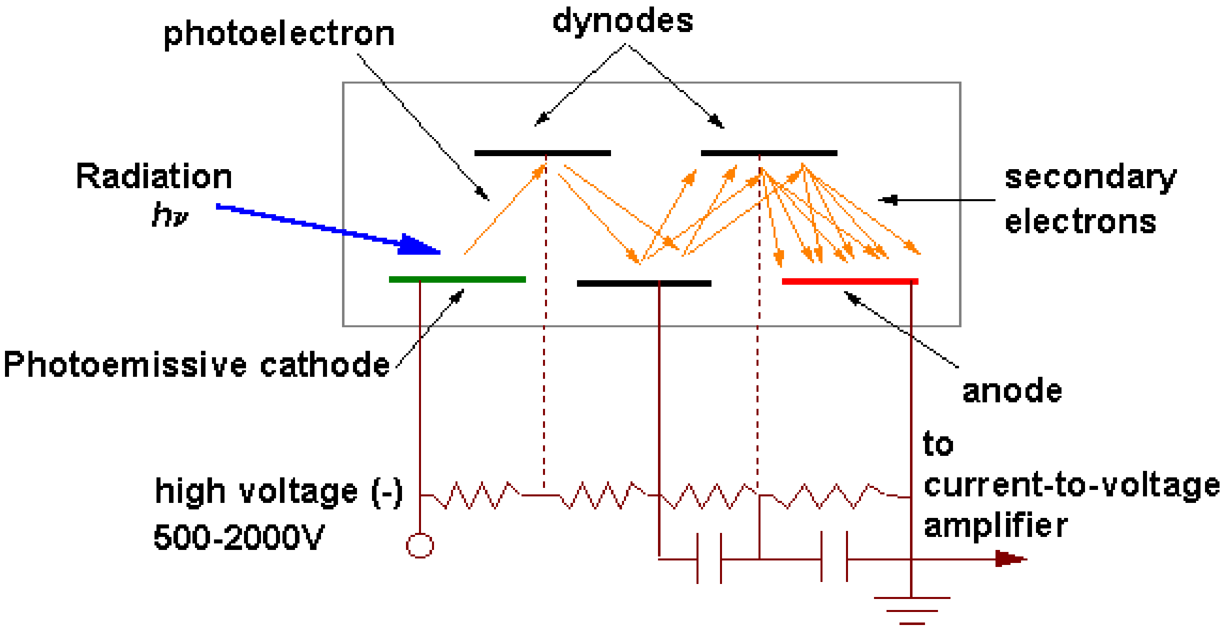
Three Step Sample Preparation for Graphite Furnace AAS

1. Dry - evaporation of solvents (10 – 100 s)
2. Ash - removal of volatile hydroxides, sulfates, carbonates (10 – 100 s)
3. Fire/Atomize - atomization of remaining analyte (1 s)



PMT Detector for AAS and AES

The collected electrons are accelerated towards a series of additional electrodes called dynodes. These electrodes are each maintained at a more positive potential. Additional electrons are generated at each dynode. This cascading effect creates 10^5 to 10^7 electrons for each photon hitting the first cathode depending on the number of dynodes and the accelerating voltage. This amplified signal is finally collected at the anode where it can be measured.



Atomic Emission Spectroscopy (AES)

- Qualitative analysis is done using AES in the same manner in which it is done using FES.
- The spectrum of the analyte is obtained and compared with the atomic and ionic spectra of possible elements in the analyte.
- Generally an element is considered to be in the analyte if at least three intense lines can be matched with those from the spectrum of a known element.
- Quantitative analysis with a plasma can be done using either an atomic or an ionic line.
- Ionic lines are chosen for most analyses because they are usually more intense at the temperatures of plasmas than are the atomic lines.

Advantages and Disadvantages of AES

Advantages

1. analyze ionic emission lines (rich spectra with more lines)
2. no refractory compounds (high temperature source)
3. self absorbance is not observed (less ground state atoms)
4. optimum condition is less sensitive to flame height (unlike AAS/FES)
5. optimum height in the flame similar among elements
6. extended linear range in calibration
    - typically 5 to 6 orders of magnitude (2 orders for AAS/FES at best)
    - reason: no ionization interference, no self absorption (self reversal)
7. favorable excitation source for multi-element analysis

Disadvantages

1. spectral interference is more common (too many lines)
    - more emission lines present for ions and atoms under the high temperature
2. more powerful monochromator or equivalent detection systems
3. expensive to purchase and operate
    - $100K to $300K
    - cost of argon ($100/day) + electricity

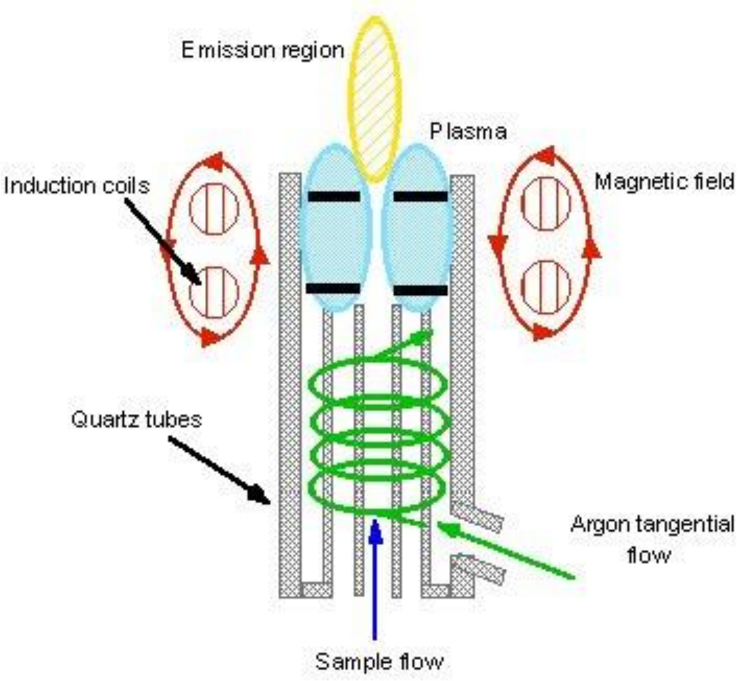
AES: Three Types of High-Temperature Plasmas

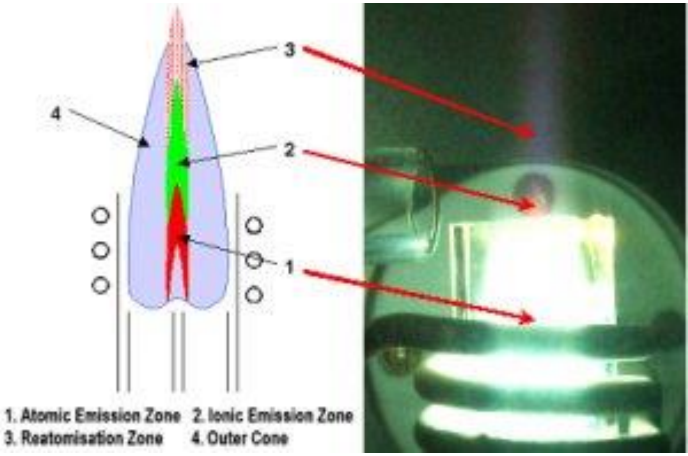
- The inductively coupled plasma (ICP).
- The direct current plasma (DCP).
- The microwave induced plasma (MIP).
- The most important of these plasmas is the inductively coupled plasma (ICP).

http://www.plasmas.org/basics.htm
http://en.wikipedia.org/wiki/Plasma_%28physics%29

Inductively Coupled Plasma (ICP)

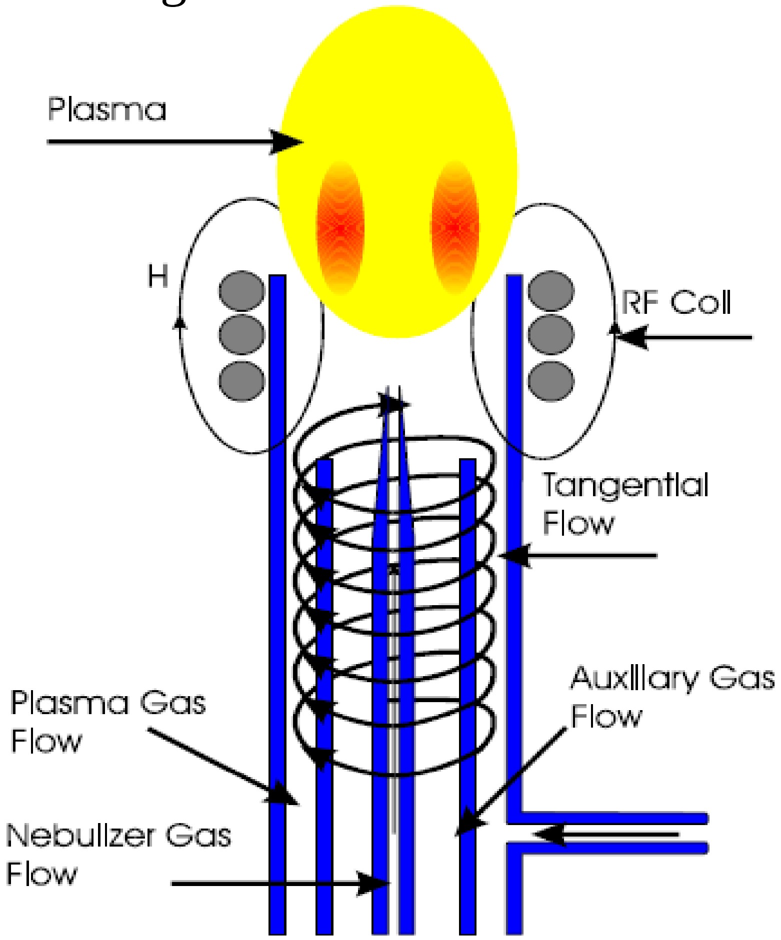
- The sample is nebulized and entrained in the flow of plasma support gas, which is typically Ar.
- The plasma torch consists of concentric quartz tubes.
- The inner tube contains the sample aerosol and Ar support gas and the outer tube contains flowing gas to keep the tubes cool.
- A radiofrequency (RF) generator (typically 1-5 kW @ 27 MHz) produces an oscillating current in an induction coil that wraps around the tubes.
- The induction coil creates an oscillating magnetic field.
- The magnetic field in turn sets up an oscillating current in the ions and electrons of the support gas (argon) as the ions and electrons collide with other atoms in the support gas.

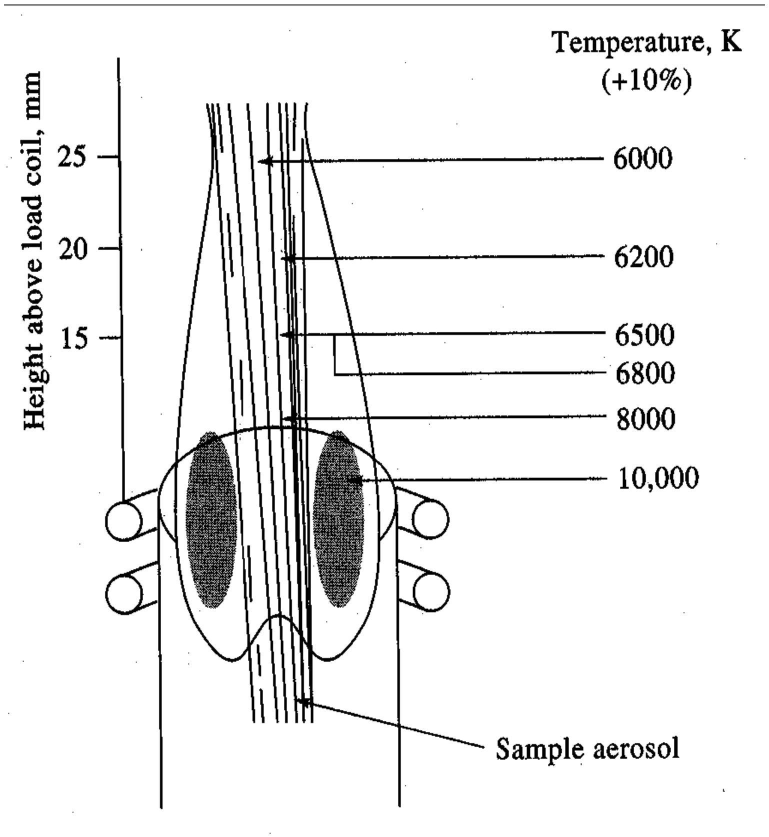




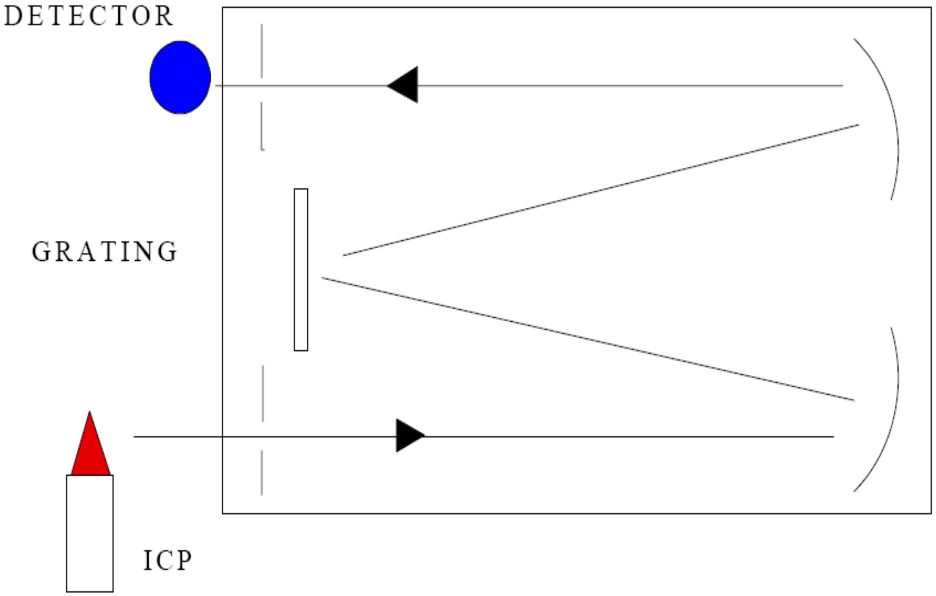
Inductively Coupled Plasma (ICP)

A "spark" of electrons from the tesla coil ignites the plasma by causing collisions between the electrons and Ar atoms induced by the magnetic field, resulting in creation of Ar+ and more electrons and so the process becomes self-sustaining.



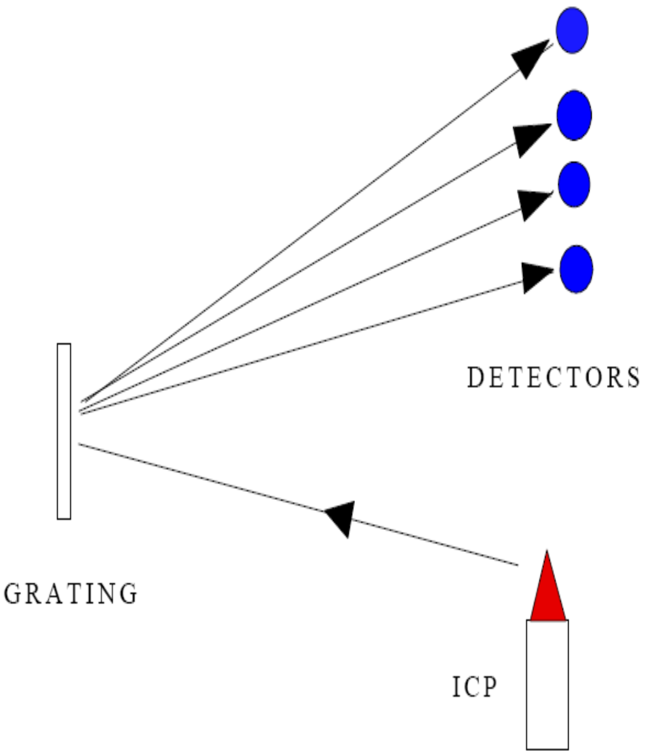


A Monochromator for Sequential Analysis of Radiation.



1. Sequential systems utilize a prism or grating and a PMT.
2. Sequential systems allow for the analysis of only one analytical line at a time, which is time consuming.
3. To scan an entire region of the electromagnetic spectrum with a sequential system, the detector is held at a fixed position and the grating is turned sequentially.

A Polychromator for Simultaneous Analysis of Radiation (Similar to DAD).

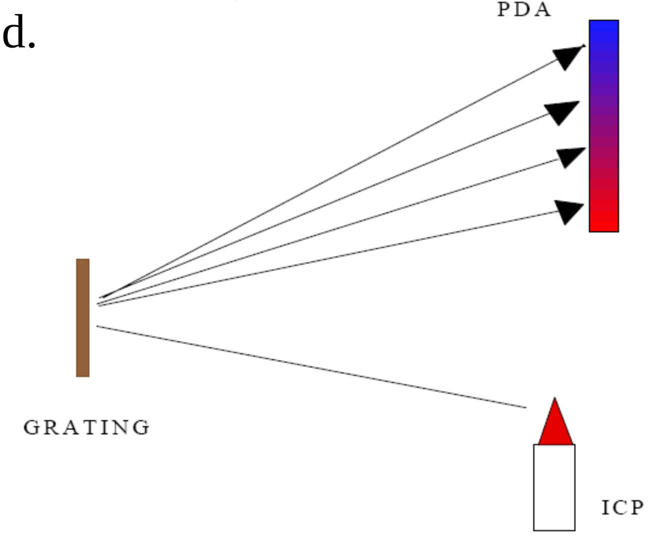


1. More efficient systems measure specific wavelengths at multiple positions simultaneously.
2. The ability of these so-called polychromators to measure more than one analytical line at a time, is a distinct advantage over monochromators.
3. But polychromators suffer from a lack of flexibility.
4. Thus, once the dispersion and detection systems are set, only certain analytical lines and elements may be measured.

A Polychromator for Simultaneous Analysis of Radiation.

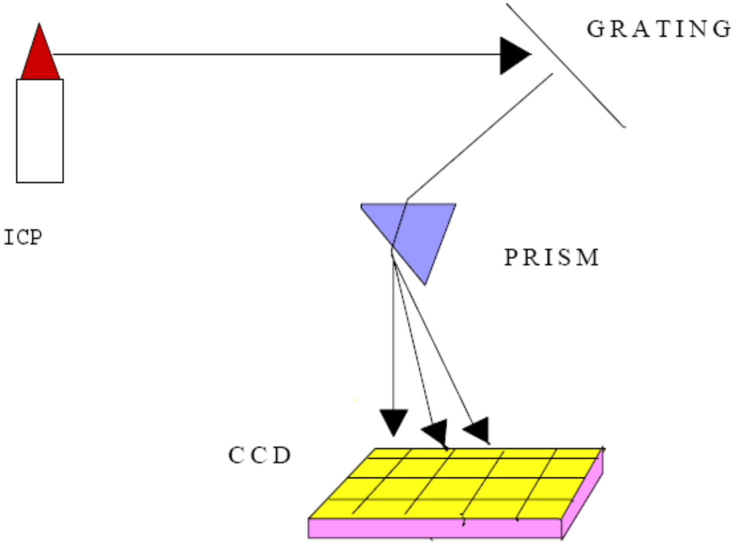
A photodiode array (PDA) is similar to a PMT in that the detectors are in a fixed position, but the PDA detectors are smaller and less expensive. As a result, more detectors can be incorporated into a single instrument.

A typical PDA will hold 1,024 miniature detectors that measure energy simultaneously in a two- to three-inch space. This allows for spectral windows in the 50–100 nm range to be simultaneously measured.

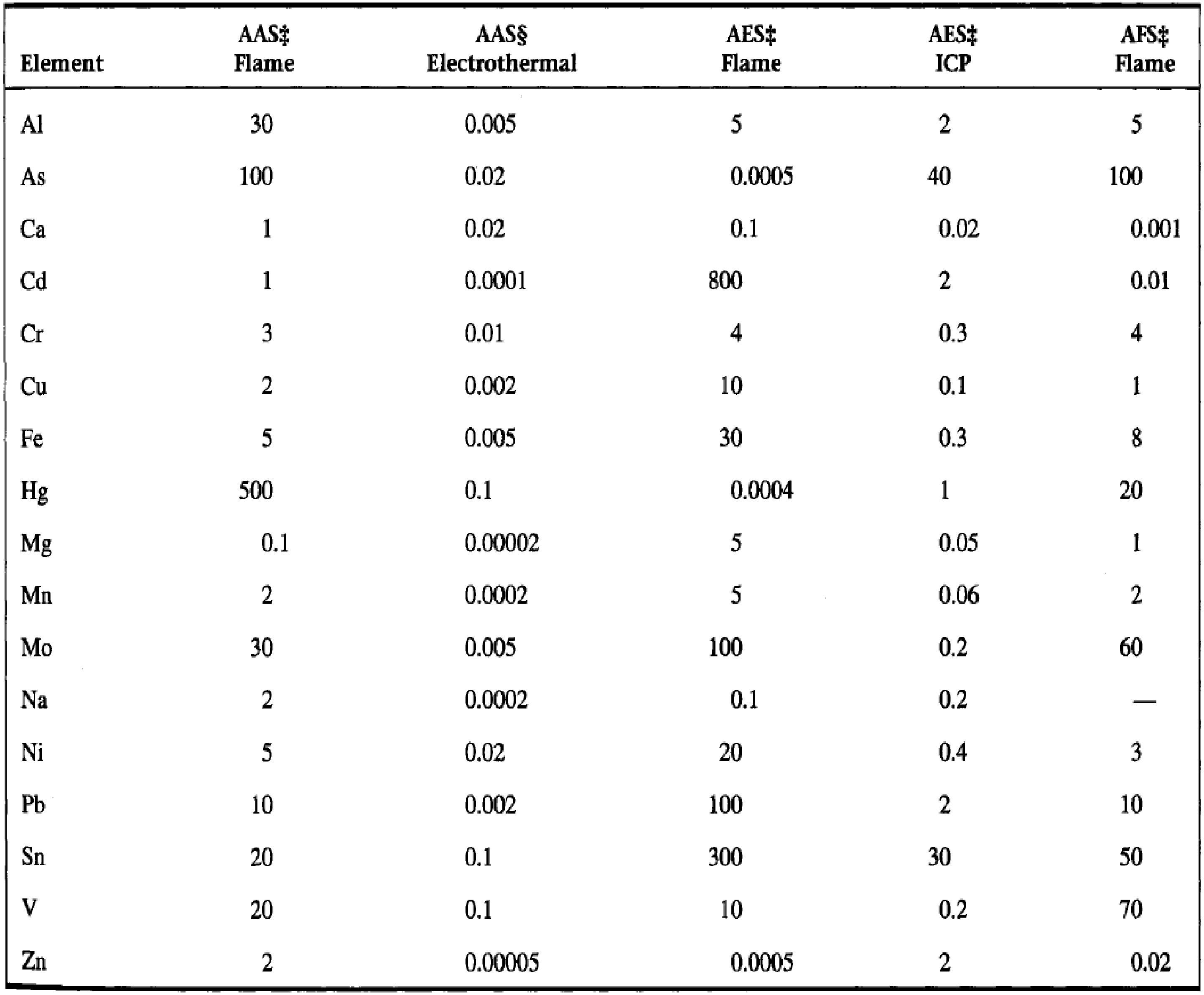


A charge coupled device (CCD) is an extension of solid state detector technology into two dimensions (e.g., 300 by 500 pixels) and allows for multielement analysis.

Each pixel in CCD discharges a current proportional to the energy striking it. CCDs commonly use a grating in conjunction with a prism to disperse the spectral radiance as a function of energy.

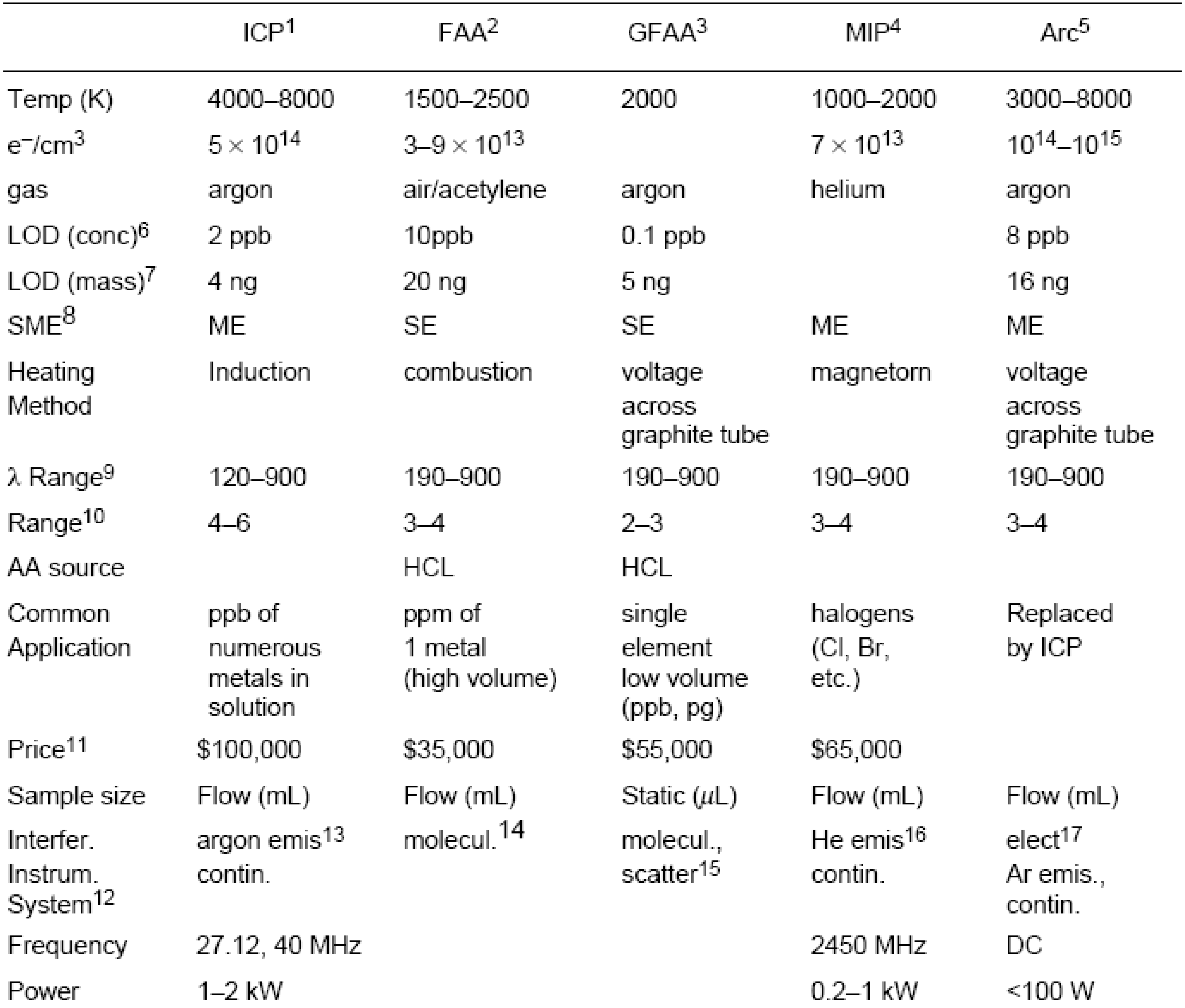


Detection Limits of AAS, FES, and AES



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
Ca	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

Comparison of AAS, FES, and AES 1



	ICP[1]	FAA[2]	GFAA[3]	MIP[4]	Arc[5]
Temp (K)	4000–8000	1500–2500	2000	1000–2000	3000–8000
e^-/cm^3	5×10^{14}	$3–9 \times 10^{13}$		7×10^{13}	$10^{14}–10^{15}$
gas	argon	air/acetylene	argon	helium	argon
LOD (conc)[6]	2 ppb	10ppb	0.1 ppb		8 ppb
LOD (mass)[7]	4 ng	20 ng	5 ng		16 ng
SME[8]	ME	SE	SE	ME	ME
Heating Method	Induction	combustion	voltage across graphite tube	magnetorn	voltage across graphite tube
λ Range[9]	120–900	190–900	190–900	190–900	190–900
Range[10]	4–6	3–4	2–3	3–4	3–4
AA source		HCL	HCL		
Common Application	ppb of numerous metals in solution	ppm of 1 metal (high volume)	single element low volume (ppb, pg)	halogens (Cl, Br, etc.)	Replaced by ICP
Price[11]	$100,000	$35,000	$55,000	$65,000	
Sample size	Flow (mL)	Flow (mL)	Static (μL)	Flow (mL)	Flow (mL)
Interfer. Instrum. System[12]	argon emis[13] contin.	molecul.[14]	molecul., scatter[15]	He emis[16] contin.	elect[17] Ar emis., contin.
Frequency	27.12, 40 MHz			2450 MHz	DC
Power	1–2 kW			0.2–1 kW	<100 W

Comparison of AAS and AES 2

Maturity:
Flame AA well established
Furnace AA well established
DCP superseded by ICP
ICP established and growing
ICP-MS new and growing

Speed:
Flame AA fast (single-element)
Furnace AA slow (single-element)
DCP fast (multi-element)
ICP fast (multi-element)
ICP-MS fast (multi-element)

Sensitivity:
Flame AA moderate; poor for refractories
Furnace AA excellent; limited for refractories
DCP moderate; very good for refractories
ICP moderate; excellent for refractories
ICP-MS excellent

Interferences:
Flame AA few; well understood
Furnace AA many; controlled with STPF
DCP many
ICP spectral
ICP-MS moderate, mass overlap

Relative Cost:
Flame AA low to moderate
Furnace AA moderate to high
DCP moderate to high
ICP moderate to very high
ICP-MS very high

Acronyms and more

1. Inductively Coupled Plasma-Atomic Emission Spectrometer.
2. Flame Atomic Absorption.
3. Graphite Furnace Atomic Absorption.
4. Microwave Induced Plasma.
5. DC plasma arc.
6. The limit of detection for iron by concentration (MIP-AES is used primarily for nonmetals).
7. The limit of detection for iron by absolute mass (for ICP, FAA, DCP assumes 2 mL volume, GFAA assumes 50 uL).
8. Single or multielement analysis possible on a single sample. For example, a commercial ICP can simultaneously detect 20 elements but a graphite furnace atomic absorption system is only capable of single element detection with a single "shot."
9. The linear dynamic range (orders of magnitude).
10. The wavelength range of the technique. These values can vary with sources, dispersing element, and detector chosen.
11. Varies with vendor, model, accessories, etc.
12. 1Interferences from instrumental system.
13. Ar emission; continuum background.
14. Molecular emission; absorbance from gas species (e.g., C2, N2, CO, etc).
15. Scattering from particulate matter.
16. Helium emission.
17. Electrode degradation (e.g., W, WC, emission etc).