Allowed and Forbidden Transitions

Lec8

M.Sc Sara Jaleel ahmed

Allowed and Forbidden Transitions

Only a fraction of all possible transitions are observed.

Allowed transitions

-high probability, high intensity, electric dipole interaction

Forbidden transitions

-low probability, weak intensity, non-electric dipole interaction

Selection rules for allowed transitions:

* The parity of the upper and lower level must be different. (The parity is even if Σl_i is even. The parity is odd if Σl_i is odd.)
* $\Delta l = \pm 1$
* $\Delta J = 0$ or ± 1, but $J = 0$ to $J = 0$ is forbidden.

Additional Splitting Effects

- Hyperfine splitting due to magnetic coupling of spin and orbital motion of electrons with the nuclear spin.

- Isotope shift. Sufficient to determine isotope ratios.

- Splitting in an electric field (Stark effect): Relevant for arc and spark techniques.

- Splitting in a magnetic field (Zeeman effect):

  * In absence of a magnetic field, states that differ only by their M_J values are degenerate, i.e., they have equivalent energies.

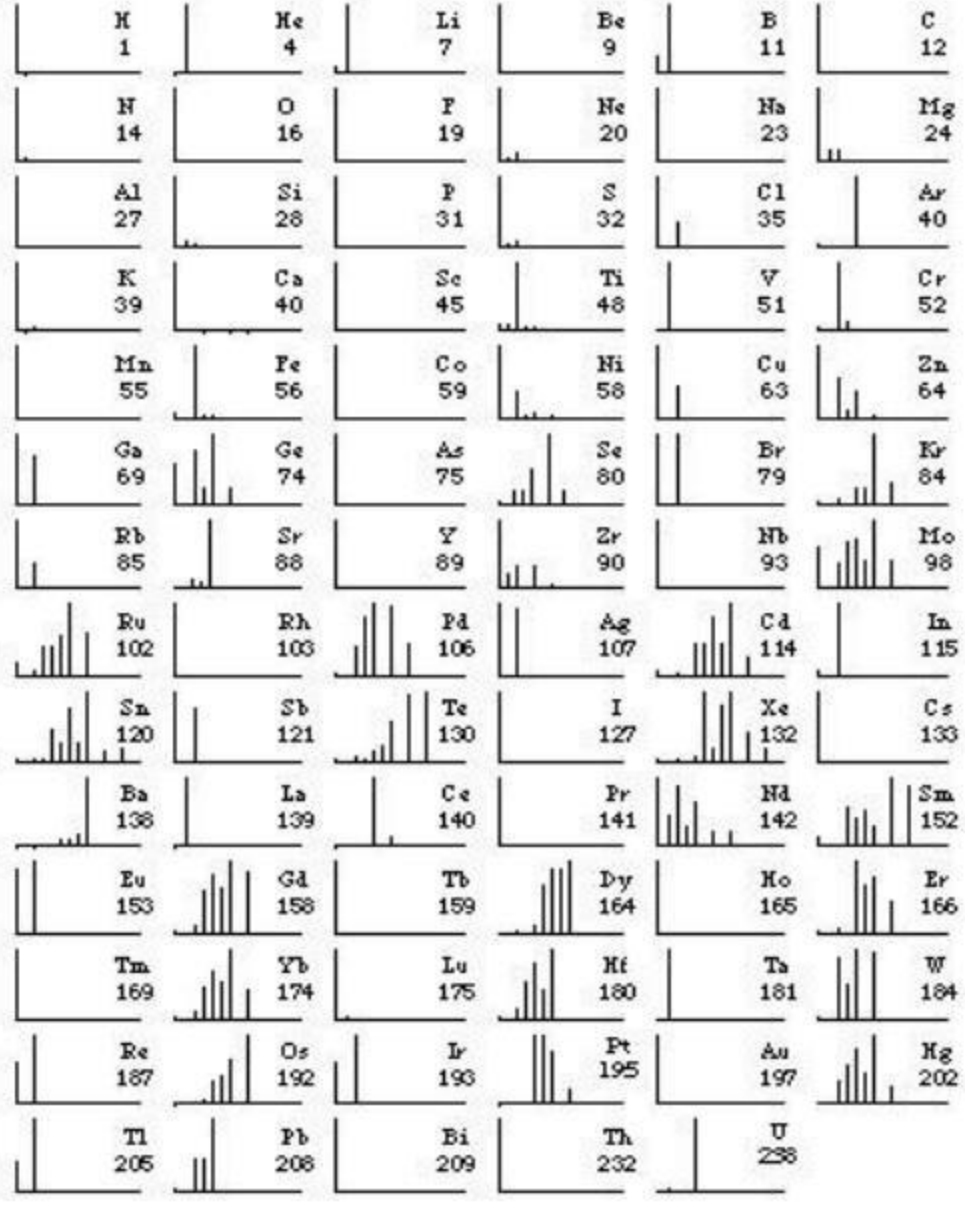
  * In presence of a magnetic field, this is not true anymore.

  * Can be used for background correction.

2.1.2 Properties of Selected Nuclei

Isotope	Natural abundance [%]	Spin quantum number, I	Frequency [MHz] at 2.35 Tesla	Relative sensitivity of nucleus	Relative sensitivity at natural abundance	Electric quadrupole moment [e 10^{-24} cm^2]
^{1}H	99.985	1/2	100.0	1	1	
^{2}H	0.015	1	15.4	$9.6\ 10^{-3}$	$1.5\ 10^{-6}$	$2.8\ 10^{-3}$
^{3}H	0.000	1/2	106.7	1.2	0	
^{10}B	19.58	3	10.7	$2.0\ 10^{-2}$	$3.9\ 10^{-3}$	$7.4\ 10^{-2}$
^{11}B	80.42	3/2	32.1	$1.6\ 10^{-1}$	$1.3\ 10^{-1}$	$3.6\ 10^{-2}$
^{13}C	1.108	1/2	25.1	$1.6\ 10^{-2}$	$1.8\ 10^{-4}$	
^{14}N	99.635	1	7.3	$1.0\ 10^{-3}$	$1.0\ 10^{-3}$	$1.9\ 10^{-2}$
^{15}N	0.365	1/2	10.1	$1.0\ 10^{-3}$	$3.8\ 10^{-6}$	
^{17}O	0.037	5/2	13.6	$2.9\ 10^{-2}$	$1.1\ 10^{-5}$	$-2.6\ 10^{-2}$
^{19}F	100.000	1/2	94.1	$8.3\ 10^{-1}$	$8.3\ 10^{-1}$	
^{31}P	100.000	1/2	40.5	$6.6\ 10^{-2}$	$6.6\ 10^{-2}$	
^{33}S	0.76	3/2	7.6	$2.3\ 10^{-3}$	$1.7\ 10^{-5}$	$-6.4\ 10^{-2}$
^{117}Sn	7.61	1/2	35.6	$4.5\ 10^{-2}$	$3.4\ 10^{-3}$	
^{119}Sn	8.58	1/2	37.3	$5.2\ 10^{-2}$	$4.4\ 10^{-3}$	
^{195}Pt	33.8	1/2	21.5	$9.9\ 10^{-3}$	$3.4\ 10^{-3}$	
^{199}Hg	16.84	1/2	17.8	$5.7\ 10^{-3}$	$9.5\ 10^{-4}$	
^{207}Pb	22.6	1/2	20.9	$9.2\ 10^{-3}$	$2.1\ 10^{-4}$	

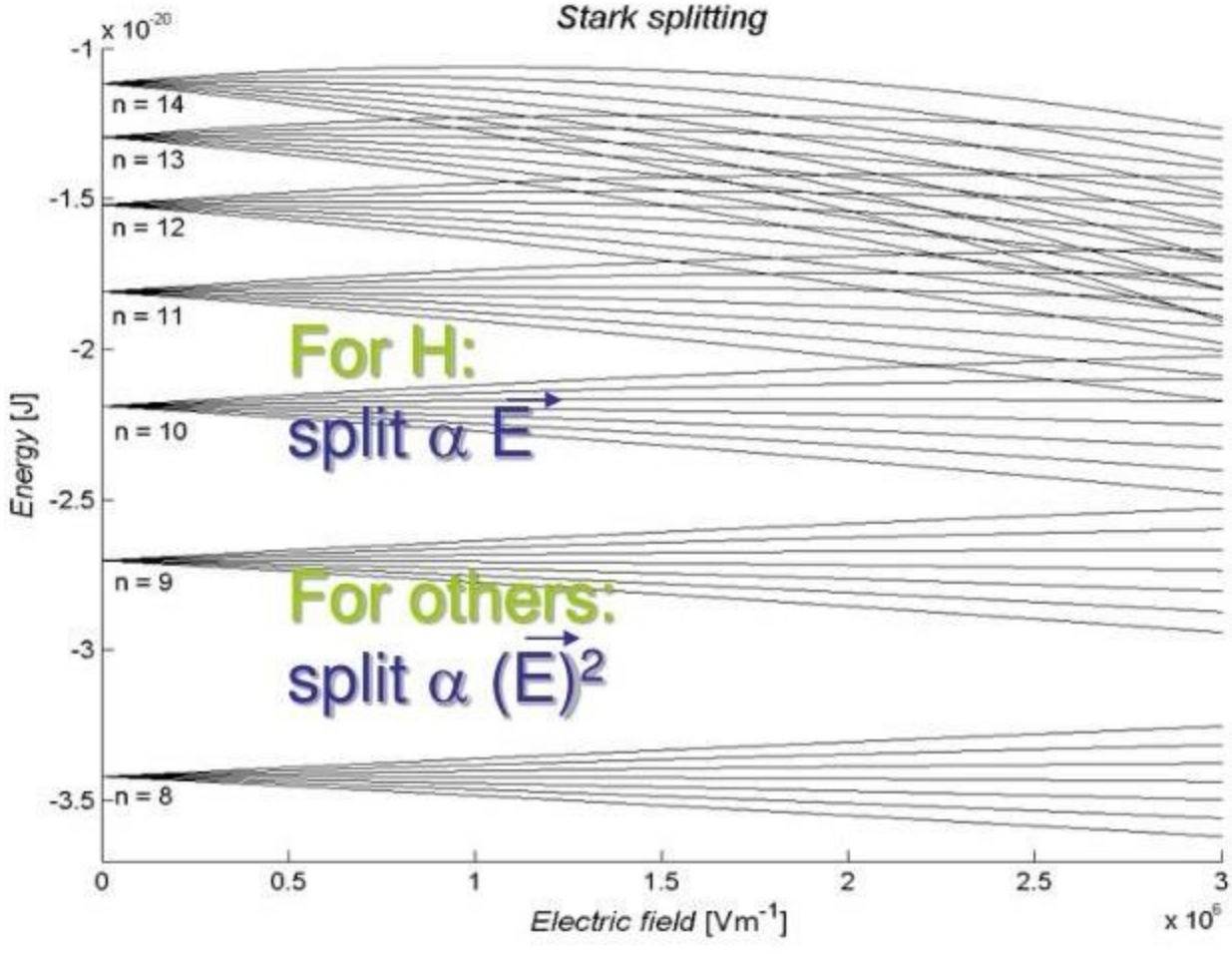
2.5.3
Isotope Patterns of Naturally Occurring Elements



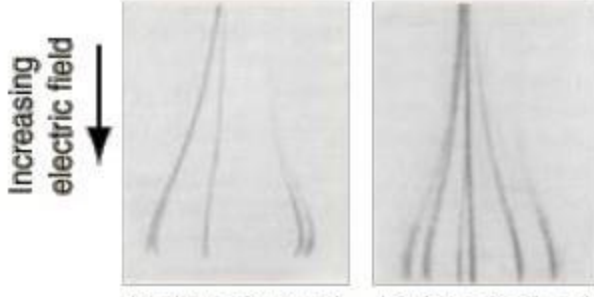
The mass of the most abundant isotope is given under the symbol of the element. The lightest isotope is shown at the left end of the x axis.

Pretsch/Buhlmann/Affolter/Badertscher,
Structure Determination of Organic Compounds

Stark Splitting



Stark effect splitting of the helium transition at 438.8 nm.



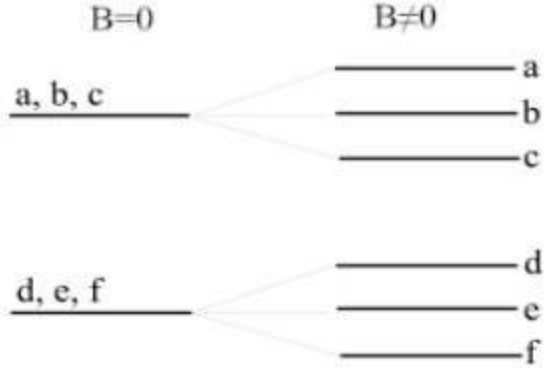
Foster, J. S., J. Frank. Inst. 209, 585, (1930)

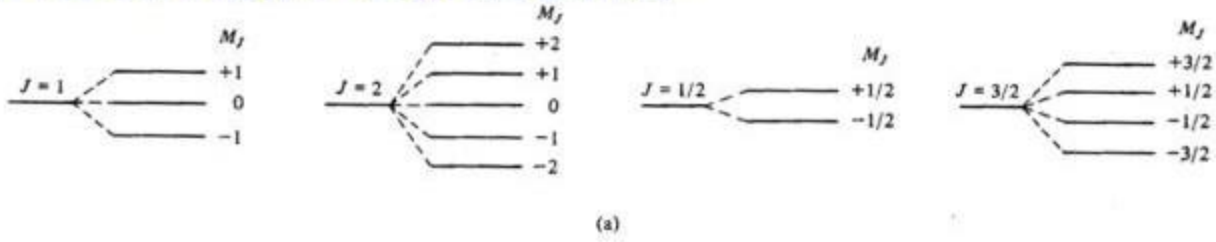
www.wikipedia.org

Zeeman Splitting

M_J – Resultant total magnetic quantum number

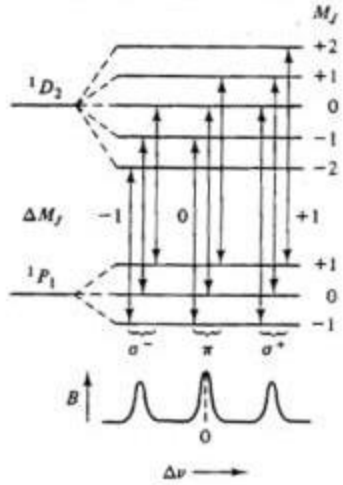
$M_J = J, J-1, \ldots, -J$
$2J + 1$ possible values





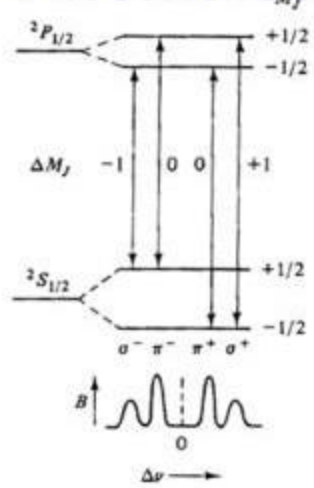
(a)

Normal



(b)

Anomalous



(c)

FIGURE 7-12 Zeeman splitting of spectral lines. In (a) the energy levels corresponding to different M_J values are shown for 4 values of J in the absence (to the left of the dashed lines) and in the presence of a magnetic field (to the right). The normal Zeeman splitting pattern for the Ca 7326-Å line is shown in (b). The upper and lower levels are split by equal amounts in the normal Zeeman effect giving rise to three lines corresponding to the three allowed values of ΔM_J. Components with $\Delta M_J = 0$ are called π components, while those with $\Delta M_J = \pm 1$ are called σ components. The σ^- transition occurs at lower energy than the σ^+ transition. In (c) the anomalous Zeeman effect is illustrated for the Na D_1 line. Here the upper and lower levels are split by different amounts so that the components with the same ΔM_J are no longer of equivalent energy. This gives rise to four lines. The same effect is observed for the Na D_2 line ($^2P_{3/2} \rightarrow {}^2S_{1/2}$).

Ingle and Crouch, *Spectrochemical Analysis*

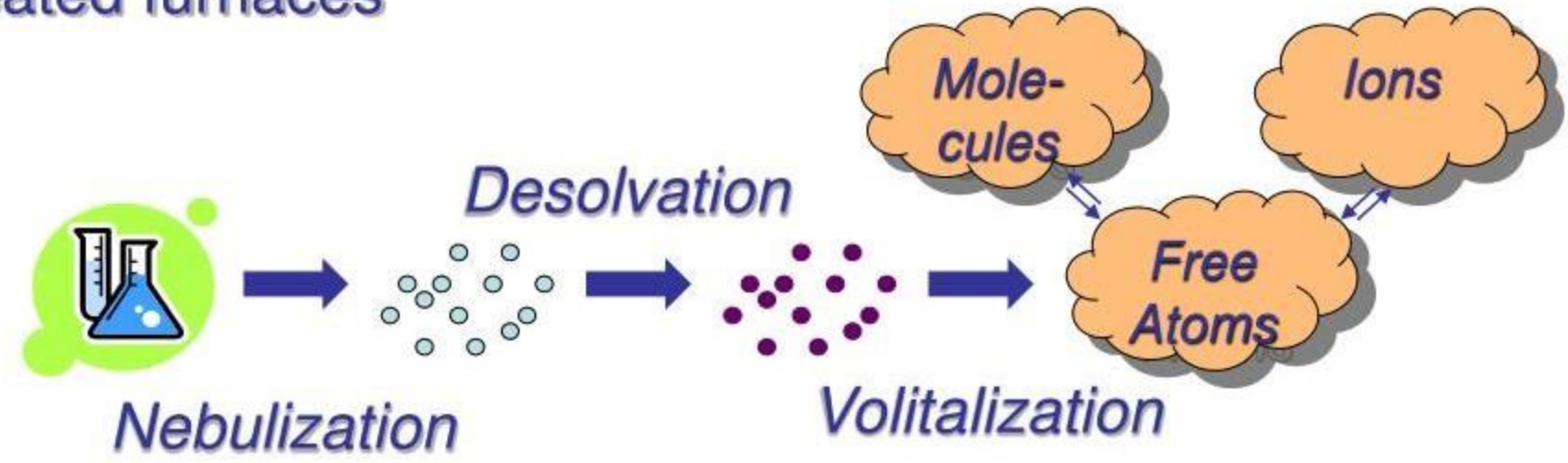
Sample Introduction and Atomization

Atomization:

Convert solution $\xrightarrow{\Delta}$ vapor-phase free atoms

Measurements usually made in hot gas or enclosed furnace:

- flames
- plasmas
- electrical discharges (arcs, sparks)
- heated furnaces



Adapted from Ingle and Crouch

Atomic Emission Spectroscopy (AES)

See also: Fundamental reviews in *Analytical Chemistry*
e.g. Bings, N. H.; Bogaerts, A.; Broekaert, J. A. C. *Anal. Chem.* **2002**, *74*, 2691-2712 ("Atomic Spectroscopy")

•Beginning 19th century: alcohol flame (Brewster, Herschel, Talbot, Foucault)

•mid 1800s: Discovery of Cs, Tl, In, Ga by atomic spectroscopy (Bunsen, Kirchhoff)

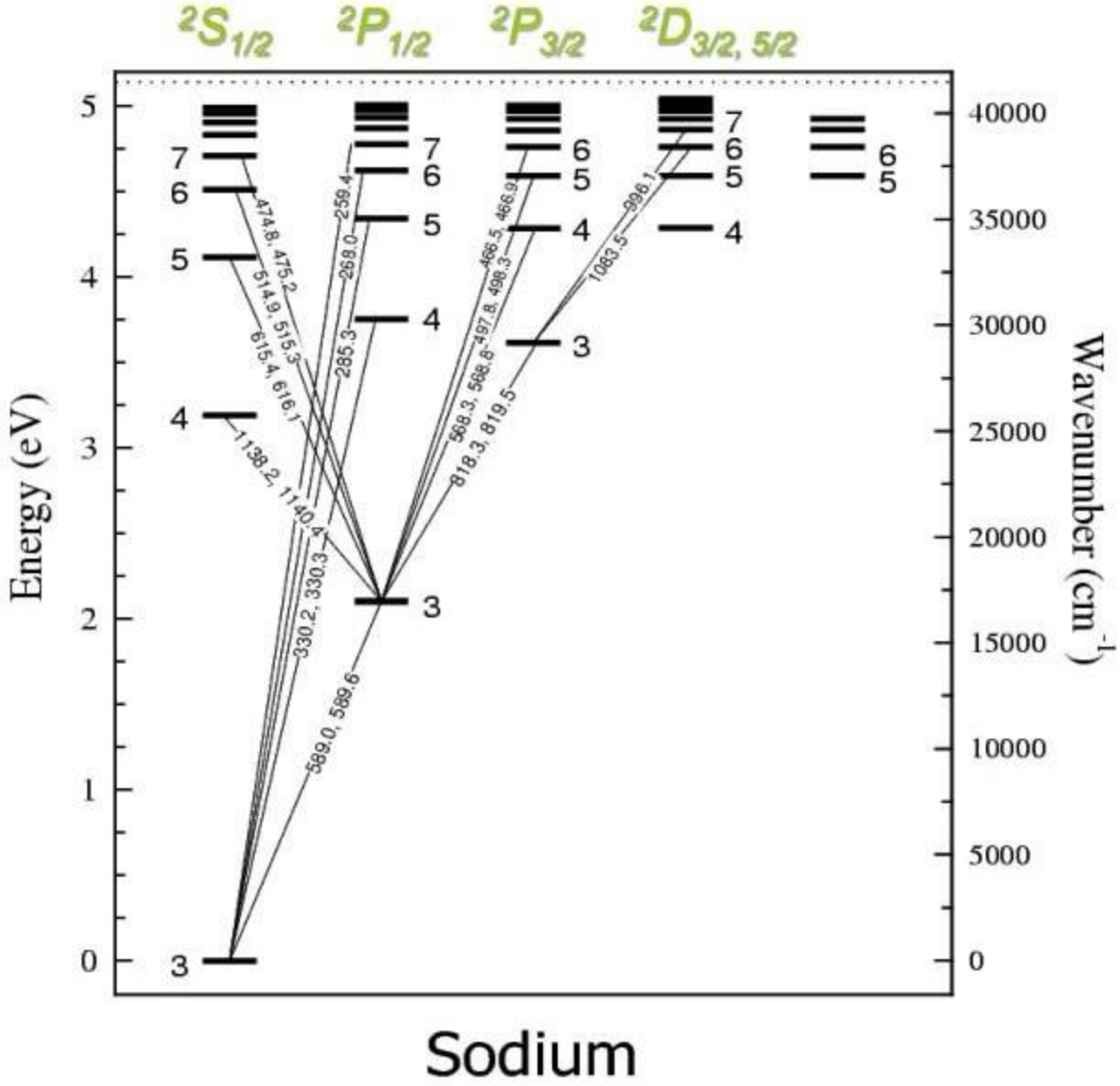
•1877: Gouy designs pneumatic nebulizer

•1920s: Arcs and sparks used for AES

•1930s: First commercial AES spectrometer (Siemens-Zeiss)

•1960s: Plasma sources (commercial in 1970s)

Atomic Emission Spectroscopy (AES)



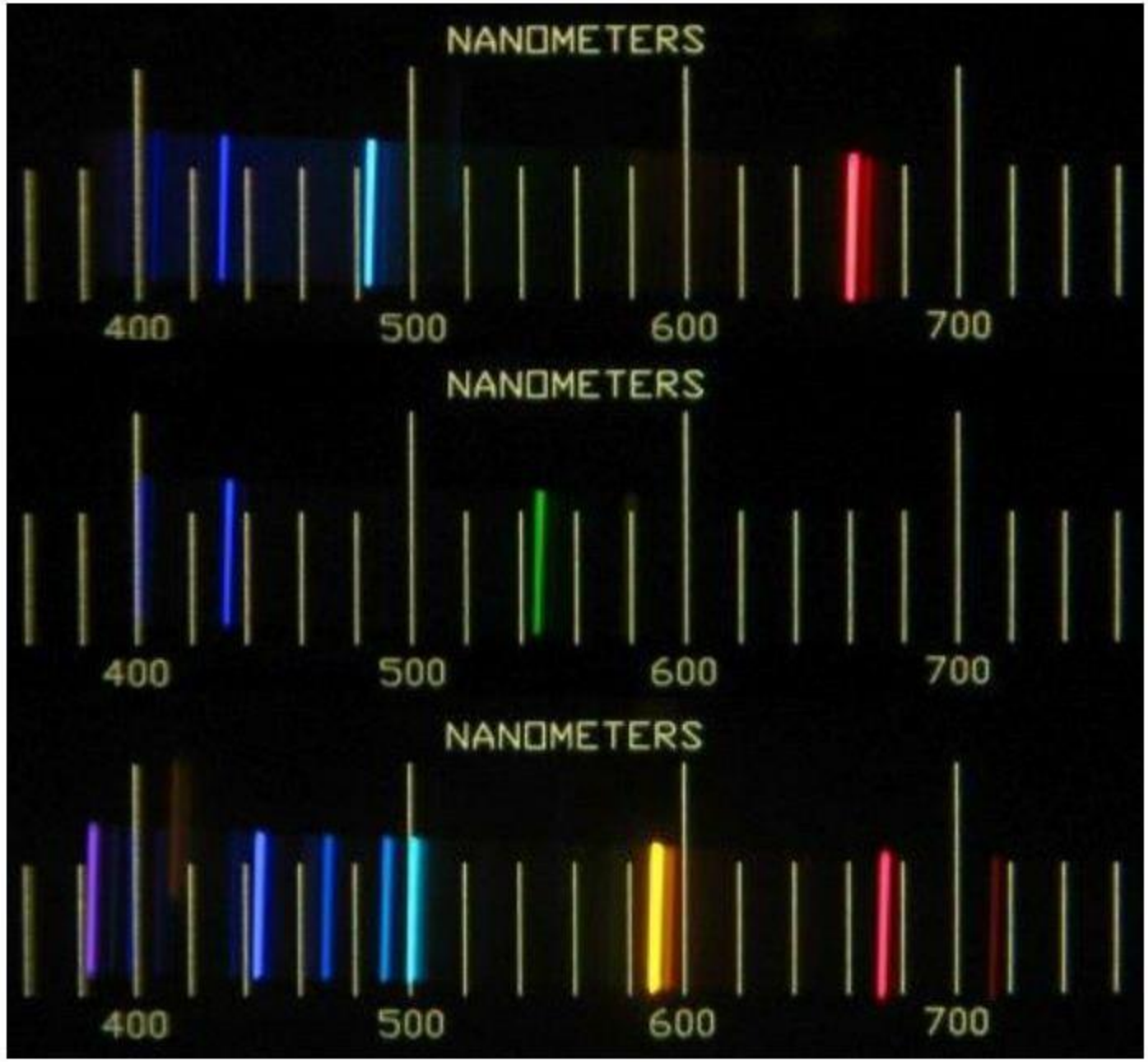
At RT, nearly all electrons in 3s orbital

Excite with flame, electric arc, or spark

Common electronic transitions

http://raptor.physics.wisc.edu/data/e_sodium.gif

Example AE Spectra



H_2

Hg

He

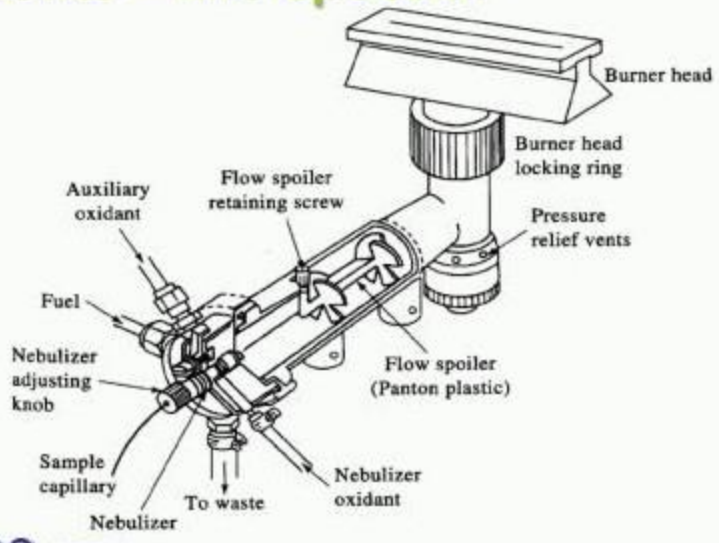
http://www.technology.niagarac.on.ca/lasers/Chapter2.html

An Ideal AES Source

1. complete atomization of all elements
2. controllable excitation energy
3. sufficient excitation energy to excite all elements
4. inert chemical environment
5. no background
6. accepts solutions, gases, or solids
7. tolerant to various solution conditions and solvents
8. simultaneous multi-element analysis
9. reproducible atomization and excitation conditions
10. accurate and precise analytical results
11. inexpensive to maintain
12. ease of operation

Flame AES

- **Background signals due to flame fuel and oxidants – line spectra:**
  - OH^* 281.1, 306.4, 342.8 nm
    from $O + H_2 \Rightarrow H + OH$
    $H + O_2 \Rightarrow O + OH$
  - O_2 250, 400 nm
  - CH 431.5, 390.0, 314.3 nm
  - CO bands between 205 to 245 nm
  - CN, C_2, CH, NH bands between 300 to 700 nm



Unlike bands of atomic origin, these molecular bands are fairly broad.

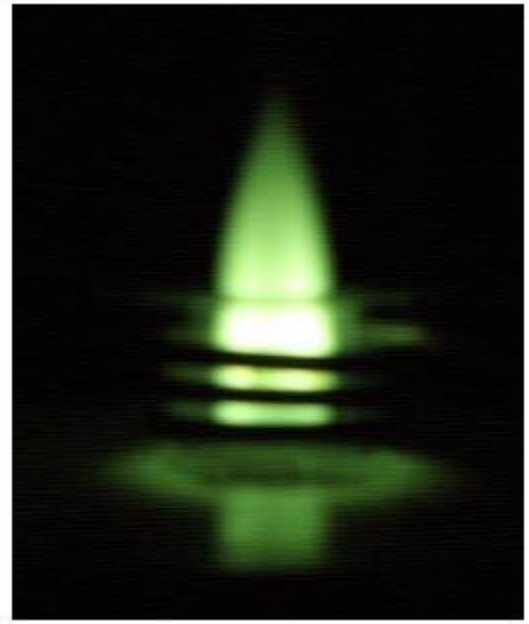
- Continuum emission from recombination reactions
  e.g. $H + OH \Rightarrow H_2O + h\nu$ $\quad\quad$ $CO + O \Rightarrow CO_2 + h\nu$

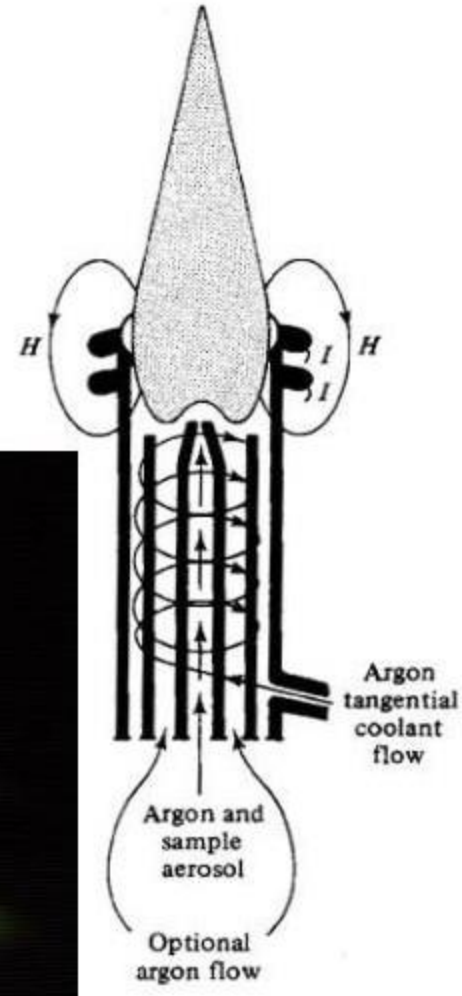
$\Rightarrow \Rightarrow$ Flames used in AES nowadays only for few elements. Cheap but limited. {Flame AES often replaced by flame AAS.}

Ingle and Crouch

Inductively Coupled Plasma AES

- Spectral interference more likely for plasma than for flame due to larger population of energetically higher states.
- Modern ICP power: 1–5 kW (4 to 50 MHz)
- 4000 to 10,000 K: Very few molecules
- Long residence time (2–3 ms) results in high desolvation and volatilization rate
- High electron density suppresses ionization interference effects
- Background: Ar atomic lines and, in hottest plasma region, Bremsstrahlung (continuum radiation from slowing of charged particles)
- Price > $ 50 k
- Operating cost relatively high due to Ar cost (10–15 mL/min) and training.

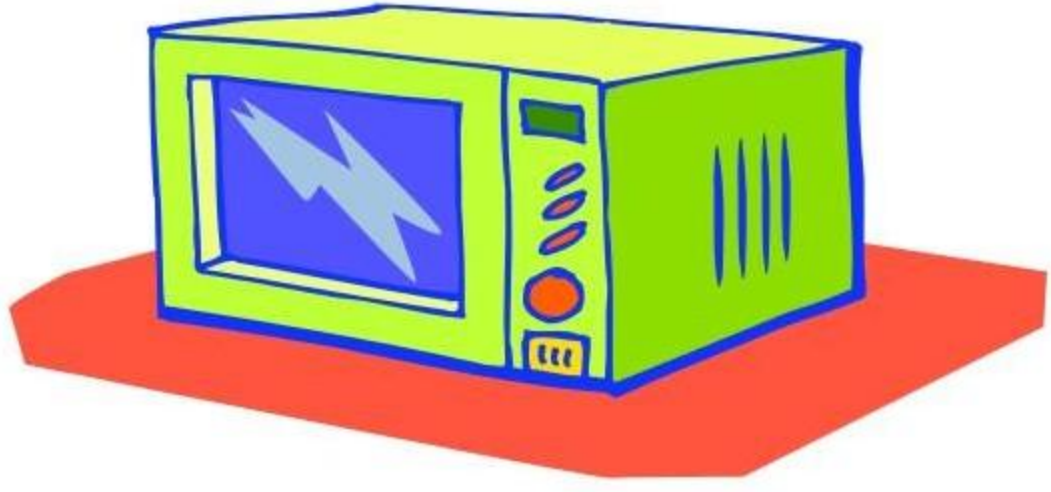




www.wikipedia.org, Ingle and Crouch

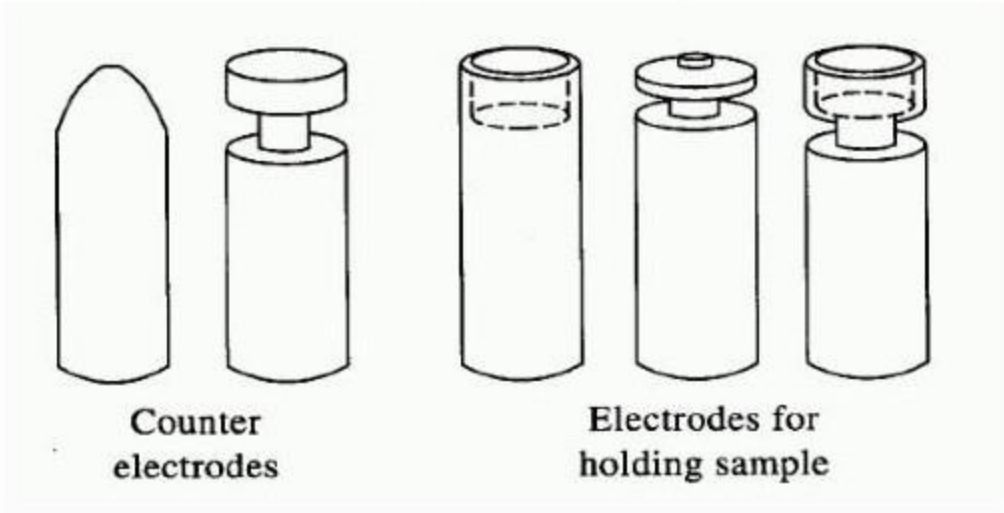
Microwave Plasma AES

- **Power 25 to 1000 W** (ICP 1000–2000 W)
- **Frequency 2450 MHz** (ICP 4 to 50 MHz)
- **Argon, helium or nitrogen**
- Temperature estimated to be 2000 - 3000 K
- **Low temperature causes problems with liquids**
- **Useful for gases:** GC–microwave plasma AES



Arcs and Sparks

- Arc = An electrical discharge between two or more conducting electrodes (1-30 A)
- Spark = An intermittent high-voltage discharge (few μsec)



- Limited to qualitative and semi-quantitative use (arc flicker)
- Particularly useful for solid samples (pressed into electrode)
- The burn takes > 20 sec (need multichannel detector)

AES: Figures of Merit

- Linearity over 4 to 5 concentration decades

Reasons for deviations from linearity:

- Self-absorption
- Extent of ionization affected by sample
- Flow rate
- Atomization efficiency

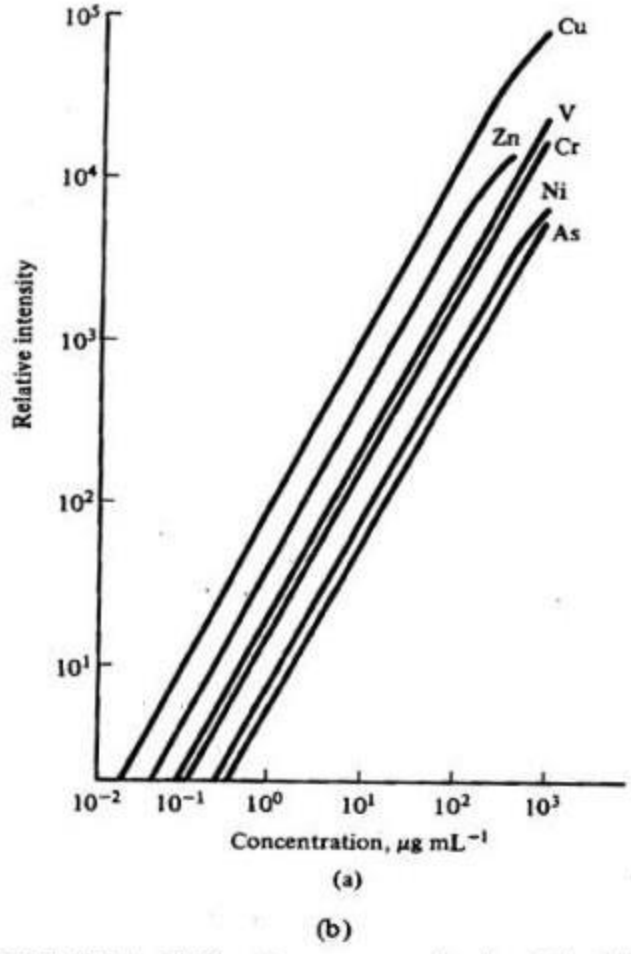


FIGURE 8-15 Calibration curves obtained by ICP atomic emission spectrometry. In (a), working curves for 6 elements are shown. For most elements such curves are linear over a concentration range that covers four to six orders of magnitude. In (b), the lack of interelement effects is shown. For the calibration curves, some solutions were prepared in deionized water, while in other cases tap water and high-salt-concentration matrices were used. A yttrium line at 242.2 nm

Ingle and Crouch

AES: Figures of Merit

- Linearity over 4 to 5 concentration decades
- Precision: Typically a few % (lower in calibration solutions)

  Limited by stability of source and random electrical noise
- Accuracy: An optimized spectrometer should be capable of precision-limited accuracy

  Limited in ICP AES by spectral overlap
- Applicability: 3/4 of all elements (ICP)
- Limitations in detection limits: * Major transitions in UV
  * Temperature too high for alkali metals (ion emission in UV as they have fully occupied electron shells)

Detection Limits for Flame AES

Some flame emission detection limits

Element	Wavelength (nm)	Flame[a]	DL (μg mL^{-1})
Ag	328.1	N/A	0.02
Al	396.2	N/A	0.005
Au	267.6	N/A	0.5
Ba	553.6	O/A	0.002
Bi	223.1	O/A	2
Ca	422.7	N/A	0.0001
Cd	326.1	N/A	2
Co	345.4	N/A	0.05
Cr	425.4	N/A	0.005
Cs	852.1	O/A	0.008
Cu	327.4	N/A	0.01
Fe	372.0	N/A	0.05
Ga	417.2	N/A	0.01
In	451.1	N/A	0.2
K	766.5	O/A	0.003
Li	670.8	N/A	0.000003
Mg	285.2	N/A	0.005
Mo	390.3	N/A	0.1
Na	589.0	O/A	0.0001
Ni	341.5	N/A	0.6
Pb	405.8	N/A	0.2
Rb	780.0	O/A	0.002
Sn	284.0	N/A	0.3
Sr	460.7	N/A	0.0002
Ti	399.9	N/A	0.2
Tl	377.6	N/A	0.02
V	437.9	N/A	0.2
Zn	213.8	O/A	50

[a]N/A, Nitrous oxide–acetylene; O/A, oxygen–acetylene.

Ingle and Crouch,
Spectrochemical Analysis

Detection Limits for ICP AES

Some flame emission detection limits

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Ag	328.1	N/A	0.02
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Ca	422.7	N/A	0.0001
Cd	326.1	N/A	2
Co	345.4	N/A	0.05
Cr	425.4	N/A	0.005
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[a]N/A, Nitrous oxide–acetylene; O/A, oxygen–acetylene.

Ingle and Crouch,
Spectrochemical Analysis

ICP detection limits

Element	ICP (ng mL^{-1})
Ag	0.2
Al	0.2
As	2
Au	0.9
B	0.1
Ba	0.01
Be	0.003
Bi	10
Ca	0.0001
Cd	0.07
Co	0.1
Cr	0.08
Cu	0.04
Er	1
Eu	0.06
Fe	0.09
Ga	0.6
Ge	0.5
In	0.4
La	0.1
Mg	0.003
Mn	0.01
Mo	0.2
Na	0.1
Ni	0.2
P	15
Pb	1
Pt	0.9
Sb	10
Sc	0.4
Si	2
Sr	0.002
Te	15
Th	3
Ti	0.03
V	0.06
W	0.8
Zn	0.1
Zr	0.06

AES: Instrumental Aspects

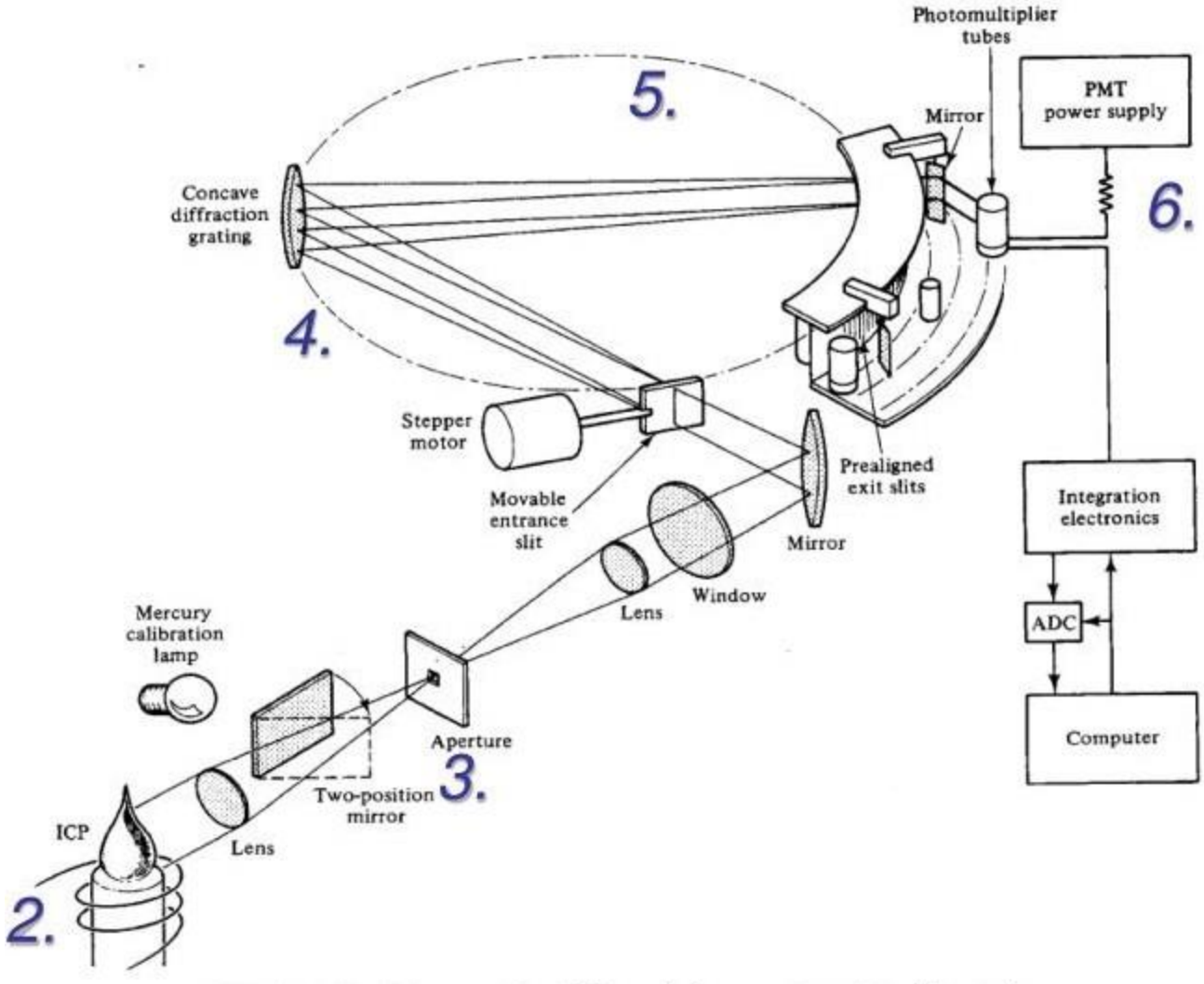


FIGURE 8-13 Direct-reading ICP emission spectrometer. The polychromator is of the Paschen–Runge design. It uses a concave diffraction grating and produces a spectrum in focus around a Rowland circle. Separate exit slits isolate each spectral line, and a separate photomultiplier tube converts the optical information into electrical signals.

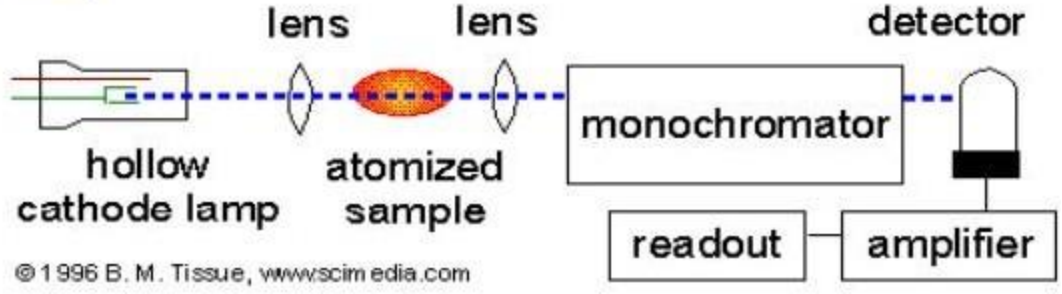
Ingle and Crouch, *Spectrochemical Analysis*

Atomic Absorption Spectroscopy (AAS)

See also: Fundamental reviews in *Analytical Chemistry*
e.g. Bings, N. H.; Bogaerts, A.; Broekaert, J. A. C. *Anal. Chem.* **2002**, *74*, 2691-2712 ("Atomic Spectroscopy")

- 1802 Wollaston observes absorption lines in solar spectrum
- 1914 Hollow cathode lamp
- 1955 Walsh describes analytical AAS
- 1959 1st Commercial Flame AAS
- 1960s L'vov and Massman describe graphite furnace (commercial in 1970s)

Recall: $A \equiv -\log_{10}(T)$



Hollow Cathode Lamp

- Typical primary source of radiation: Hollow cathode lamp
  - * Typically one lamp per element
  - * Different intensities for different elements
  - * Multielement lamps for multielement analysis

- Continuum sources (e.g. Xe arc lamp) only for multielement analysis

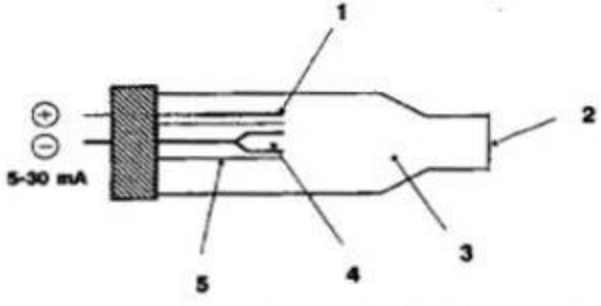


Fig. 8.2-3. Principle of a hollow cathode lamp. 1: anode, 2: silica window, 3: gas (Ar or Ne), 4: hollow cathode, 5: glass envelope

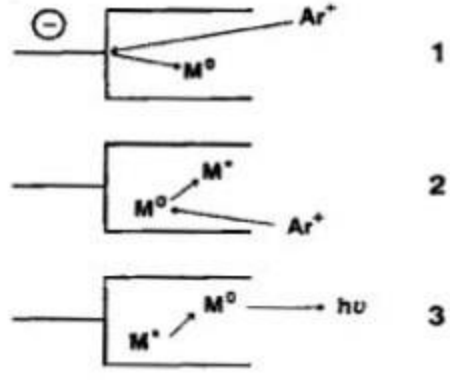


Fig. 8.2-4. Mechanisms in the hollow cathode lamp. 1: sputtering of the atoms, 2: excitation of the atoms by the ions of the filing gas, 3: radiative de-excitation of the excited atoms

Kellner et al.,
Analytical Chemistry

Flame AAS

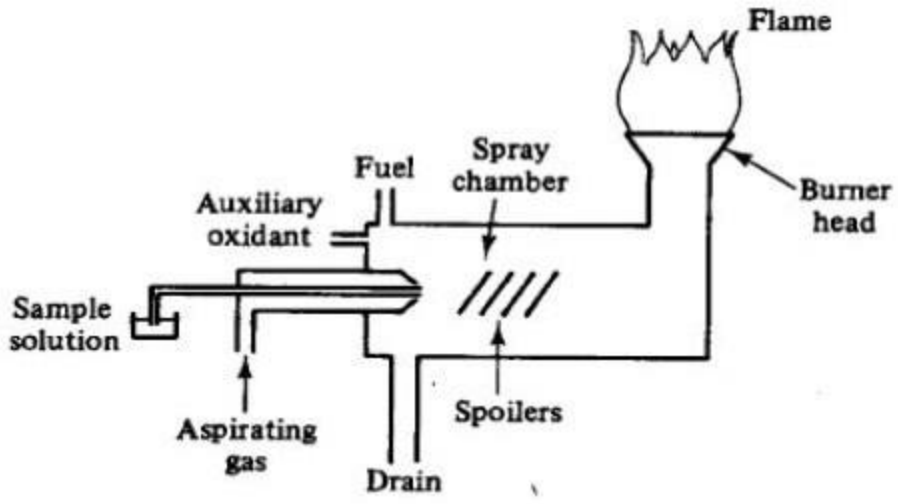


FIGURE 8-3 Premixed, spray chamber nebulizer/burner. The sample is aspirated and nebulized into the spray chamber by a concentric nebulizer with oxidant as the nebulizing gas. Often aerosol modifiers (spoilers) are used to break up larger droplets. All but the finest spray particles condense and are drained away (see Chapter 7). The sample spray is mixed in the spray chamber with the fuel and additional oxidant gas to control the fuel-to-oxidant ratio. Only the small (5–20 μm)-diameter particles enter the flame. Typical solution flow rates are 2 to 5 mL min^{-1}.

Ingle and Crouch, *Spectrochemical Analysis*

At <5000 K most atoms are predominantly in their electronic ground state.

Slot burners with 5-10 cm path lengths.

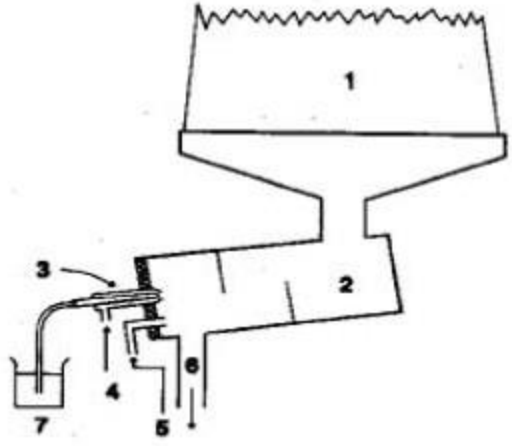
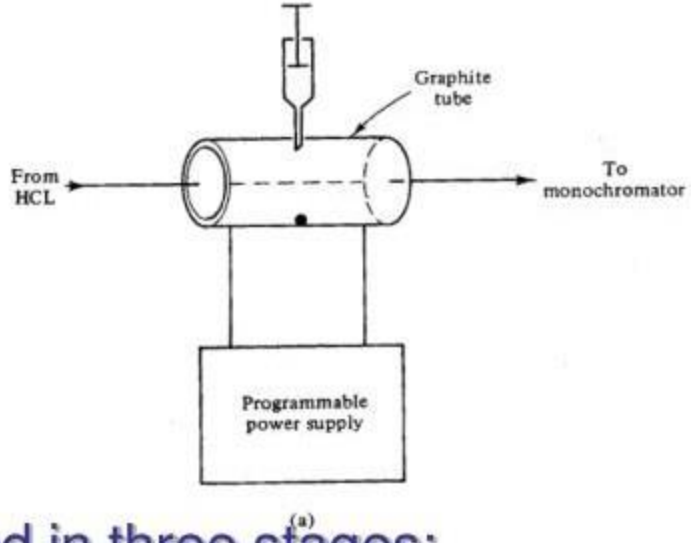


Fig. 8.2-6. Principle of flame-AAS. 1: flame, 2: burner, 3: nebulizer, 4: oxidant gas, 5: fuel gas, 6: drain, 7: liquid sample

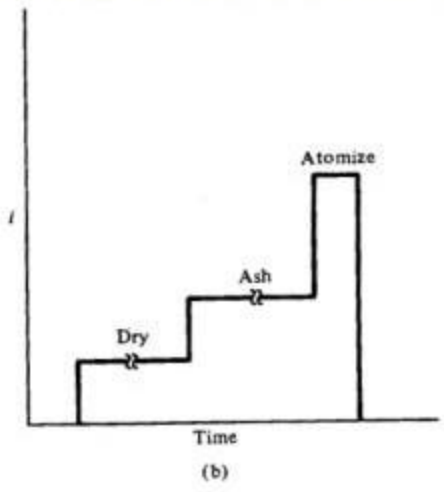
Kellner et al., *Analytical Chemistry*

Electrothermal Atomization



- Heating current of several hundred A
- Heating rates of up to 1000 °C/s
- LOD 100 times lower than flame AAS

Heated in three stages:



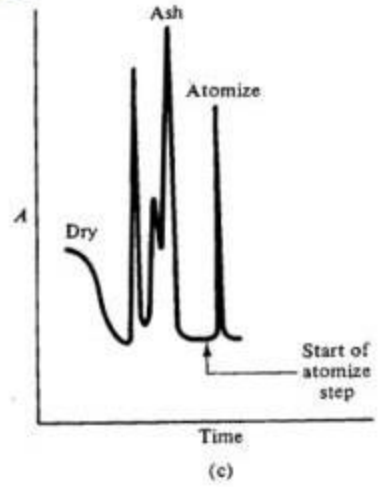


FIGURE 10-2 Design and use of electrothermal atomizers. In (a) an electrothermal atomizer system is shown to be a small furnace tube heated by passing current through it from a programmable power supply. The sample is deposited into the tube with a syringe or injector and then the tube is heated in stages as shown in (b). The dry and ash steps remove water and organic or volatile inorganic matter, respectively. The atomization step produces a pulse of atomic vapor that is probed by the radiation beam from the HCL as shown in (c). Many instruments sense and hold the peak absorbance value for readout.

Ingle and Crouch, *Spectrochemical Analysis*

Electrothermal Atomization

- **Typical furnace material: Graphite**

  ⇒ Graphite Furnace AAS

  *Graphite tube 18-28 mm

  *Samples 5-100 uL

  *200 to 1000 cycles

  *Temperature up to 3000 °C to avoid graphite decomposition

  *Carbon may be reducing agent for metal ions

  *Argon flow avoids oxidation

- **Other furnace materials: Ta, W, Pt**

  *High melting point required

  *Should not emit brightly at high temperature (disadvantage for W and Ta)

Are you getting the concept?

Is ICP a good source for AAS?