

Inductively Coupled Plasma Spectrometry

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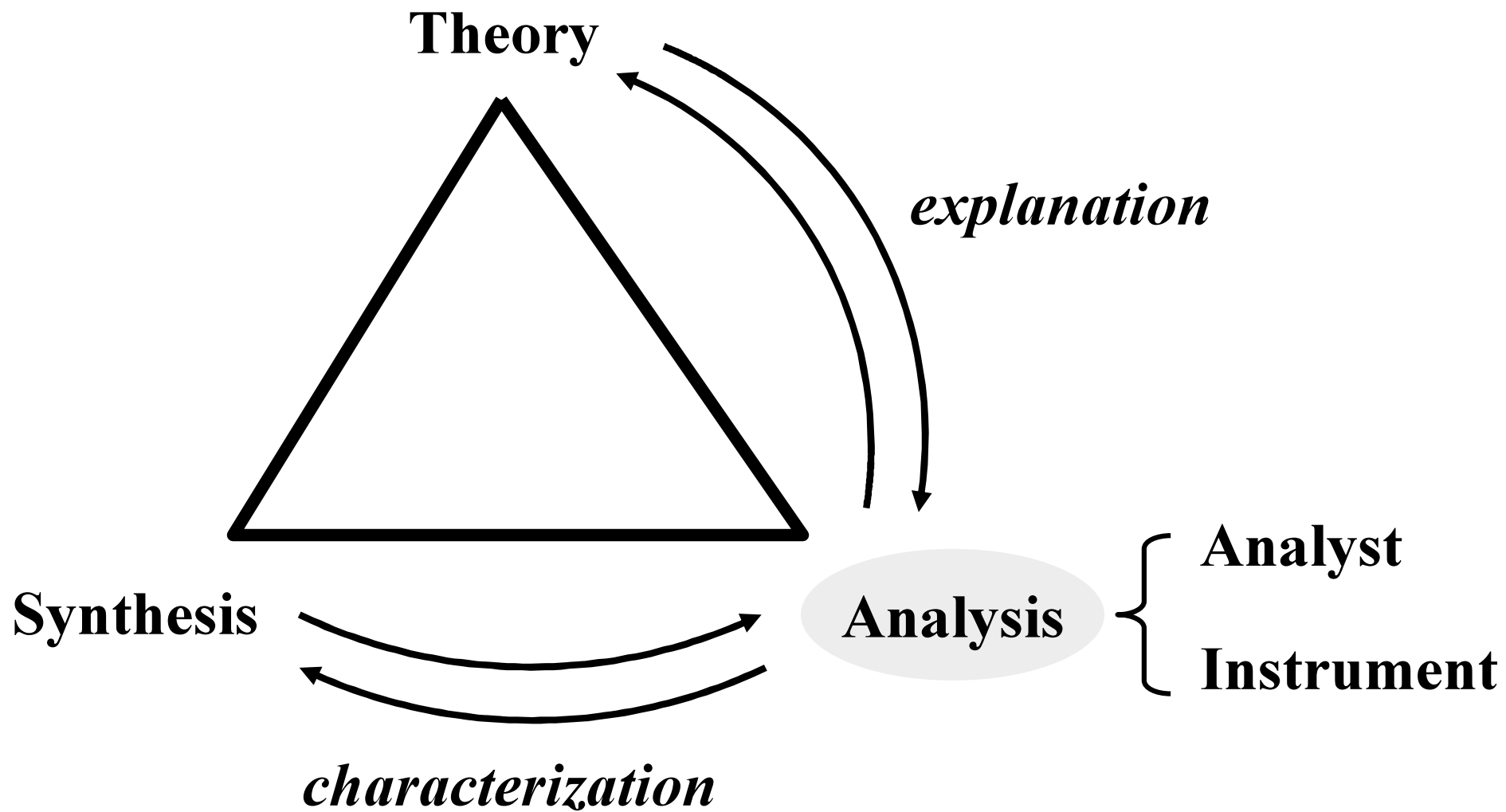
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Chemistry



Methods of chemical analysis

- **Main fields of analytical chemistry:**
 - **separation methods**
 - **spectroscopic methods**
 - **electrochemistry**
- **Classification of spectroscopic methods according to carriers of analytical signal:**
 - **electromagnetic radiation (photons)**
 - **particles (ions, electrons)**

Elemental chemical analysis

○ Elemental analysis makes it possible

↗ to verify the presence of an element (qualitative analysis)

↗ to determine its concentration (quantitative analysis)

↗ to identify a structure in which it is present (structure anal.)

↗ to identify a compound in which it is bound (speciation)

○ WHOWHO analysis

↗ what (qualitative)

↗ how much (quantitative)

↗ where (structure)

↗ how bound (speciation)

○ The aim is to relate the composition to the properties

Photon-based spectroscopic methods used for elemental analysis

- Atomic Emission Spectrometry (AES)**
- Atomic Absorption Spectrometry (AAS)**
- Atomic Fluorescence Spectrometry (AFS)**

Atomic Emission Spectrometry

- ↗ AES is one of the oldest analytical methods**
- ↗ Principles of AES are known since 19th century**
- ↗ AES underwent considerable technological development**
- ↗ Plasmas play a dominant role as radiation sources for AES**

Definition of a plasma

- **A plasma is a neutral gas of charged particles which possess collective behaviour.**
- **Practically, any ionized gas can be considered as a plasma.**
- **Presence of free electrons**



Role of a plasma source in AES

- **Atomization: from compound to free atoms**
 - ▮ **High kinetic temperature**
 - ▮ **Efficient energy transfer**
 - ▮ **Processes of the order of the *ms***
- **Excitation/ionization**
 - ▮ **Energy transfer to higher energy levels**
 - ▮ **Processes of the order of the *ns***

Wavelength and energy

$$E_2 - E_1 = h\nu = \frac{hc}{\lambda}$$

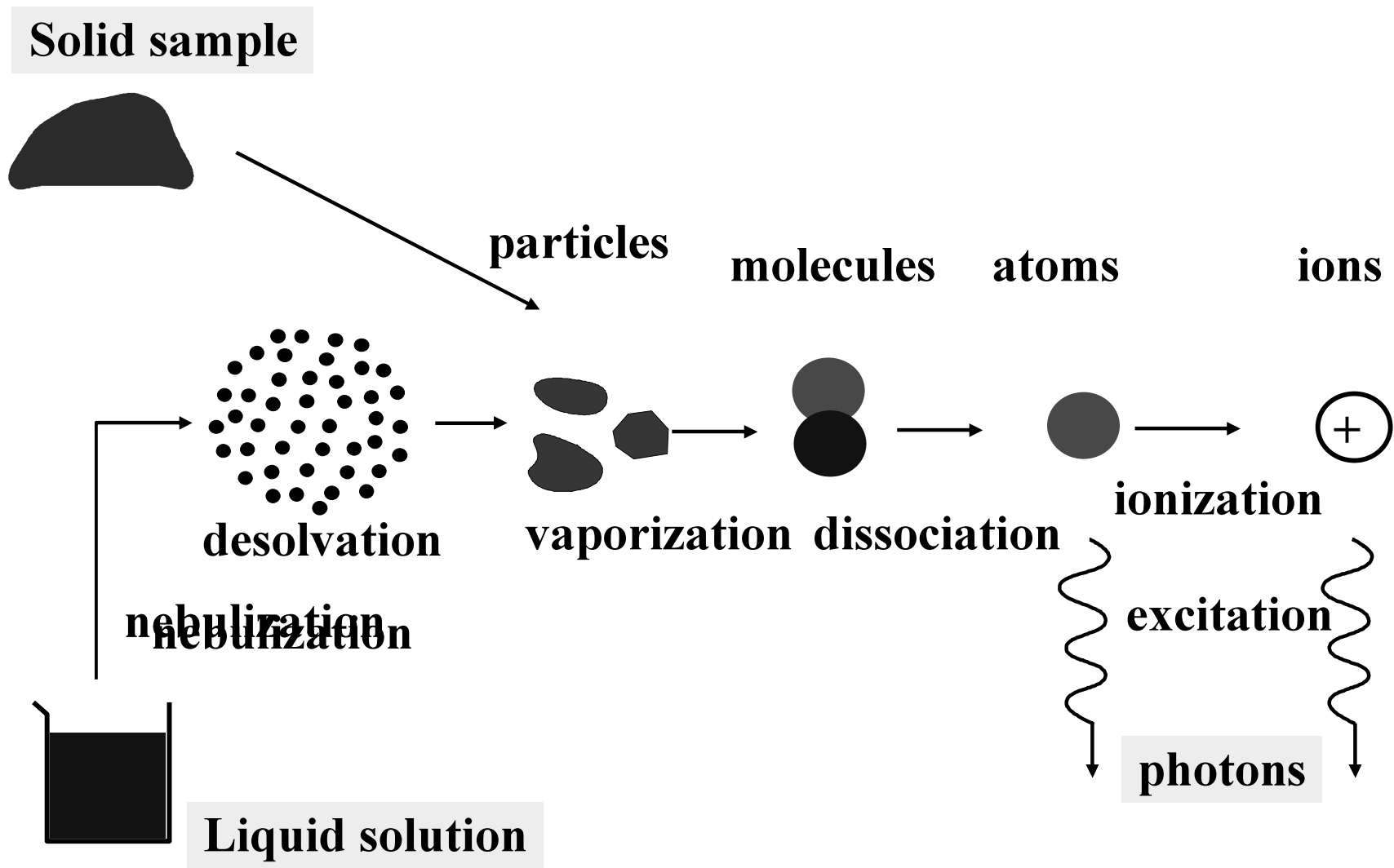
ν : frequency

λ : wavelength

c : light velocity

h : Planck's constant

Generating of analytical signal in AES - from sample to photon



Atomic Emission Spectrometry

- **1666 - Newton, a sunlight dispersion with a prism, particulate nature of light**
- **17thc.-Huygens, wave nature of light**
- **1678 - Johannes Marcus Marci, a rainbow principle**
- **1752 - Melvill, a candle flame through a prism**
- **1802 - Davy, electric arc**
- **1802 - Wollaston, dark lines in the Sun spectrum**
- **1817 - Fraunhofer, transmission diffraction grating**
- **1826 - Talbot, Sr emission in an alcohol flame, recommended for determining of substances**

Atomic Emission Spectrometry

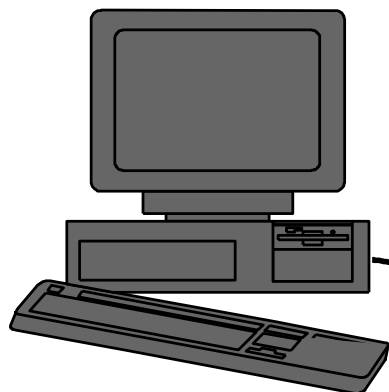
- 1846 - Herschel, Na, K, Ca, Li, Ba, Cu, and Fe could be detected in alcohol flame
- 1859 - Bunsen, Kirchhoff, spectral lines emitted by elements, not compounds, emission/absorption
- 1860 - Foucault, sodium doublet
- 1865 - Balmer, formula for calculating H-wavelengths
- 1869 - Angstrom, reflection diffraction grating
- 1869 - Janssen, quantitative spectroscopy
- 1877 - Gouy, pneumatic nebulizer to introduce liquids into flames
- 1879 - Lockyer, arc and spark spectra

Atomic Emission Spectrometry

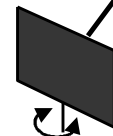
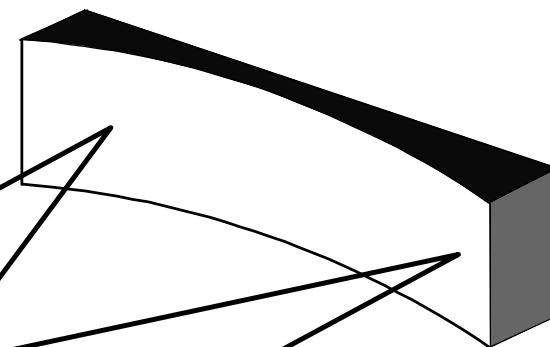
- **1882 - Rowland, concave diffraction grating**
- **20thc.- photographic plate for a light detection**
- **1930 - Gerlach, Schweitzer, internal standard**
- **1930 - AC current arc, HV spark excitation**
- **1935 - Thanheiser, Heyes, first photoelectric detection**
- **1940 - photomultiplier tube, direct-reading analyzers**
- **1950s- grating spectrometers**
- **1960 - DC plasma for analysis of liquids**
- **1965 - Fassel, Greenfield, Inductively Coupled Plasma**
- **1975 - first commercial ICP-AES with polychromator**

ICP-AES

Data acquisition

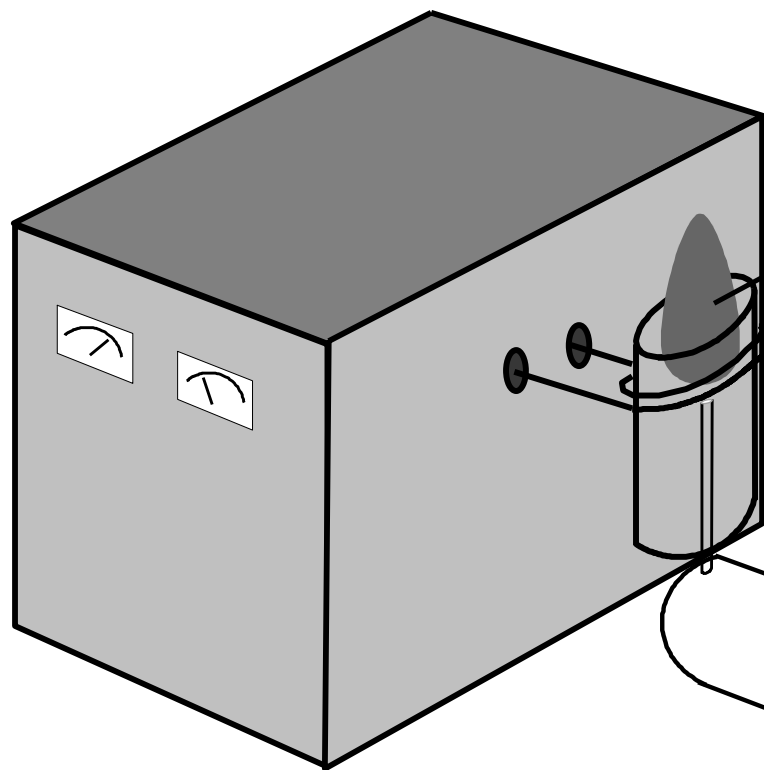


Detector

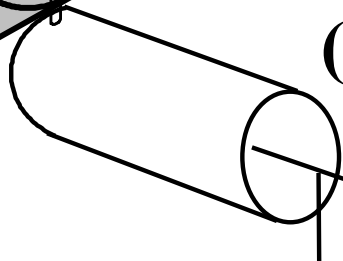


Dispersive system
(spectra isolation)

ICP (signal generation)



Sample introduction system
(pneumatic nebulization)

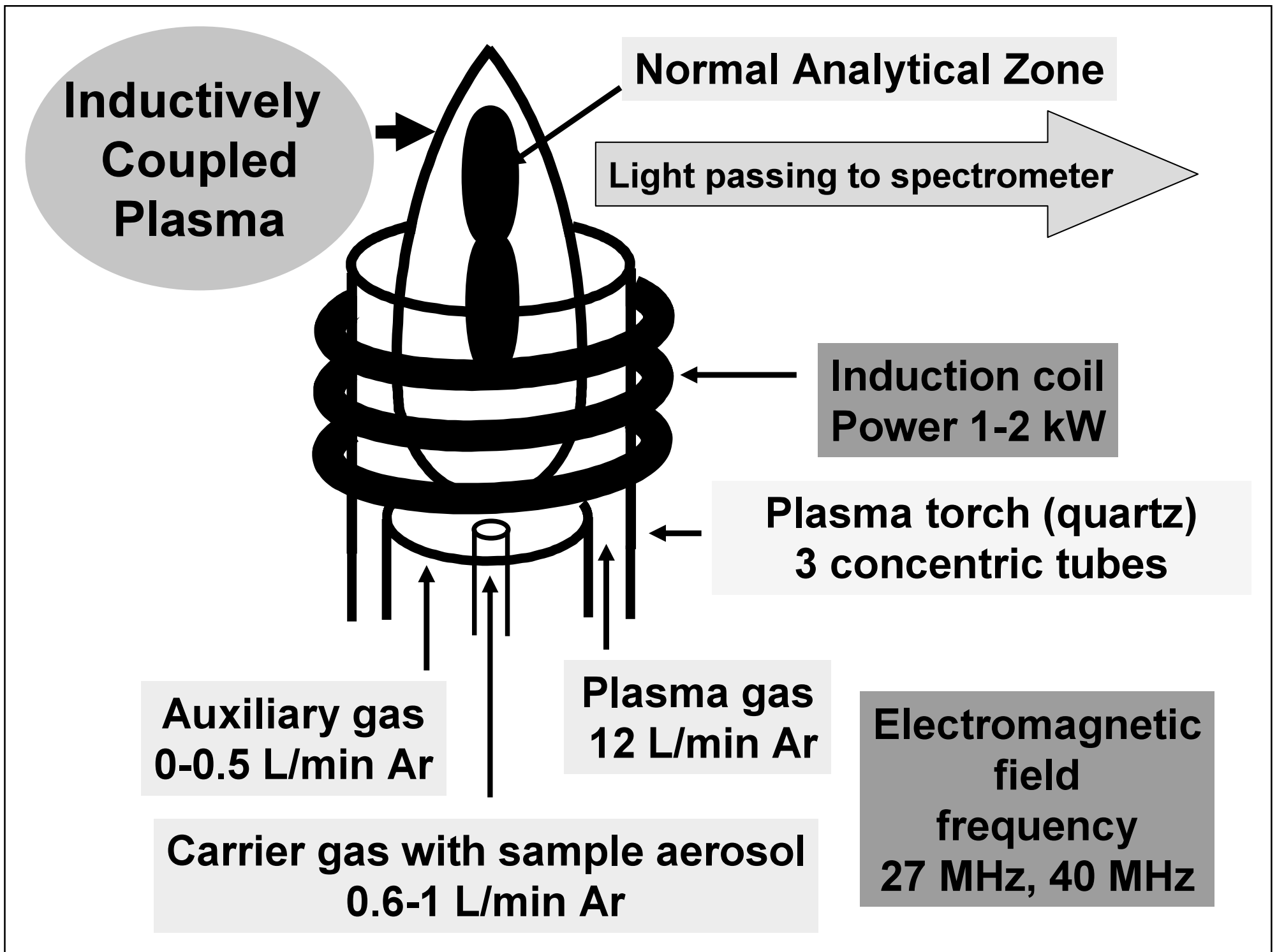


High-frequency generator (energy)



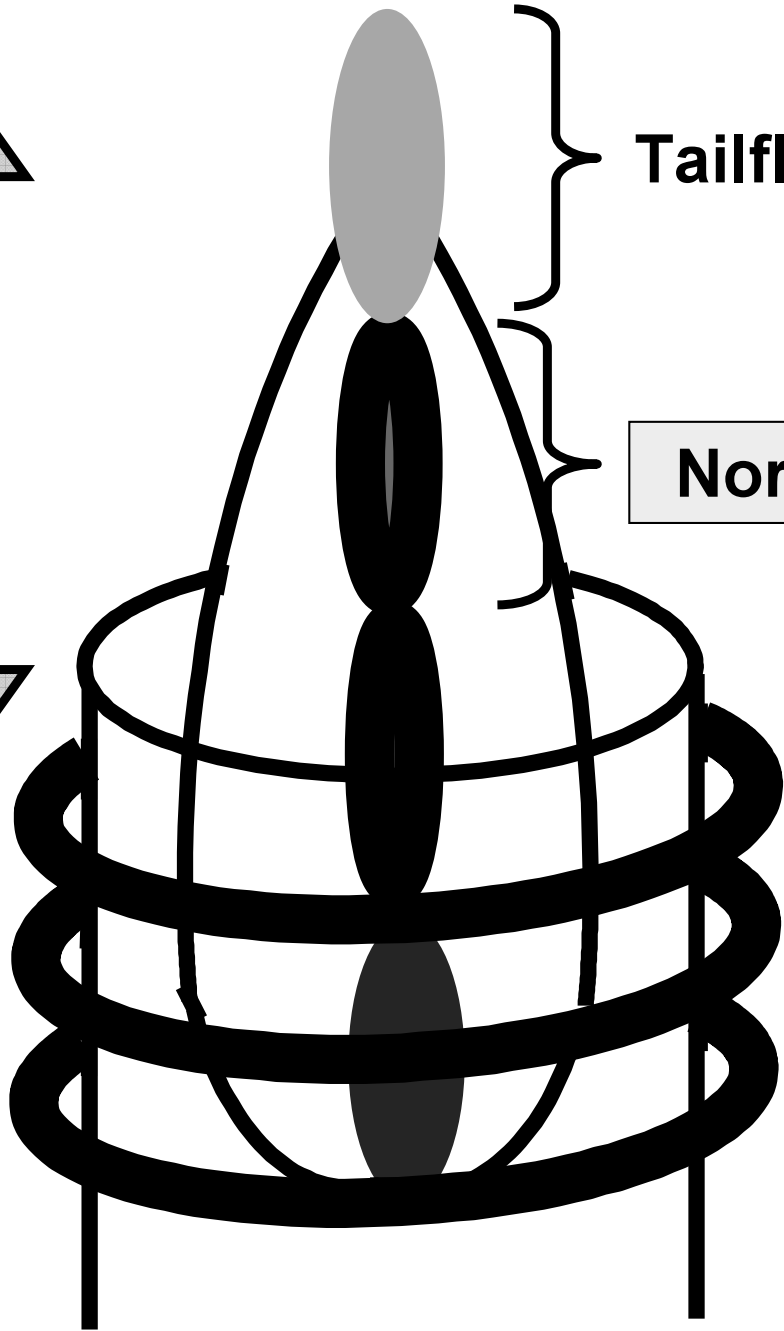
ICP principle

- **High-frequency generator 27 - 64 MHz**
- **Discharge initiation by spark - seed electrons accelerated by electromagnetic field**
- **Avalanche ionization $\text{Ar} + \text{e}^- \rightarrow \text{Ar}^+ + 2 \text{e}^-$**
- **Induction coil, 3-5 turns - primary winding**
- **Electrons in plasma - secondary winding**
- **ICP - plasma gas 12 L/min**
- **Centrally introduced carrier argon with aerosol 0.6 - 1 L/min**



Lateral viewing

Observation height



Tailflame



ionic lines

Normal Analytical Zone

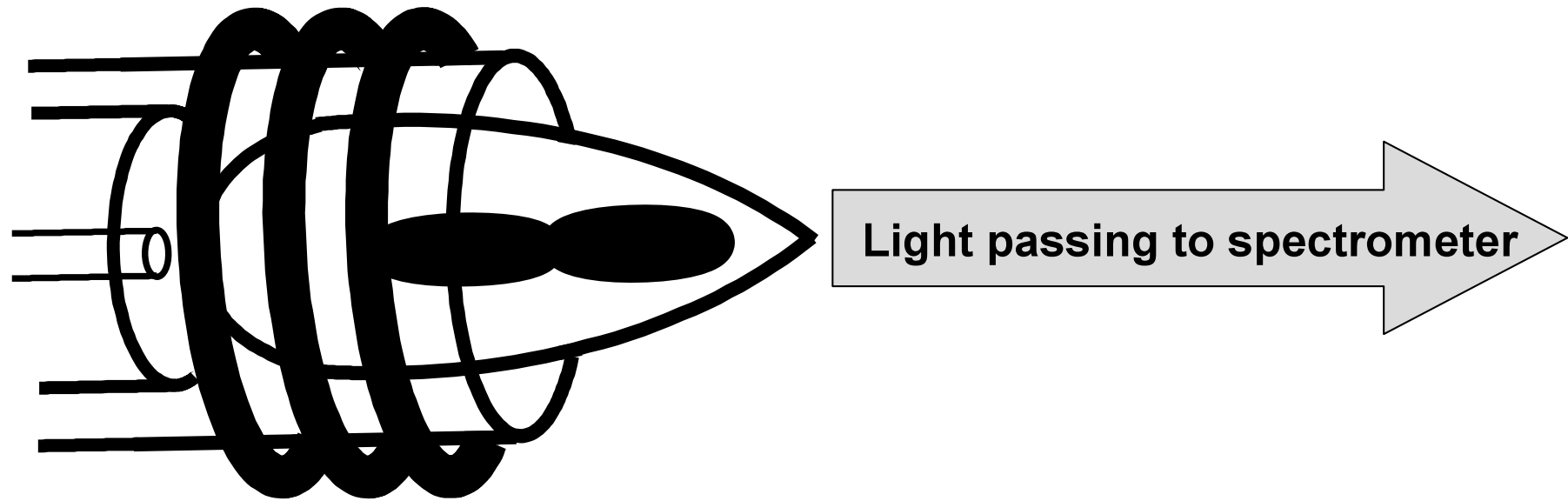


atomic lines

Initial Radiation Zone

Preheating Zone

Axial viewing



Longer optical path



3-10x better limits of detection

ICP features

- **Annular (toroidal) plasma**
- **Induction region (10 000 K), skin-effect**
- **Central analytical channel (5000-6000 K)**
- **High temperature and sufficient residence time (3 ms) \Rightarrow efficient atomization**
- **High concentration of Ar^+ , Ar^* , Ar^m
efficient ionization / excitation ($E_{\text{ion}} = 15.8 \text{ eV}$)**
- **High concentration of electrons 10^{20} - 10^{21} m^{-3}
(0.1% ionization of Ar) \gg in flame (10^{14} - 10^{17} m^{-3})
 \Rightarrow low influence of matrix ionization on shift of ionization equilibria \Rightarrow no typical ionization interferences**

ICP features

Hot annular plasma encloses cooler central channel containing a sample



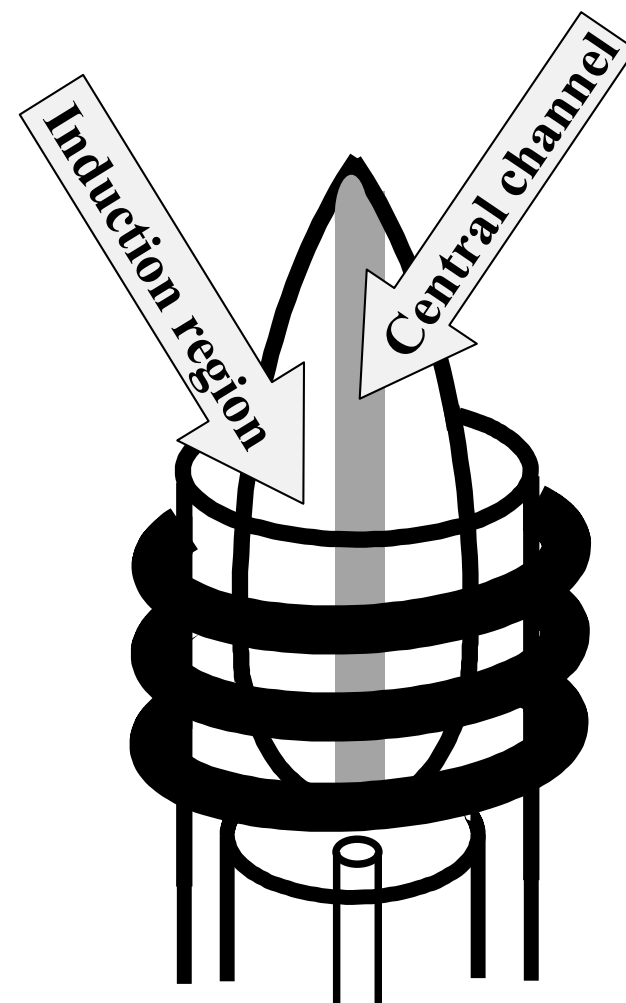
excited analyte atoms in the channel are not surrounded with analyte atoms in lower energy states



there is no or only minimum self-absorption in the induction region



linearity of calibration extends over 4 to 5 orders of magnitude.



ICP excitation

- $\text{Ar}^+ + \text{X} \rightarrow \text{Ar} + \text{X}^{+*} \pm \Delta \text{E}$ Charge transfer
- $\text{Ar}^m + \text{X} \rightarrow \text{Ar} + \text{X}^{+*}$ Penning effects
- $\text{e}^- + \text{X} \rightarrow \text{e}^- + \text{e}^- + \text{X}^+$ Collisional ionization
- $\text{e}^- + \text{X} \rightarrow \text{e}^- + \text{X}^*$ Collisional excitation
(X - atom of analyte)

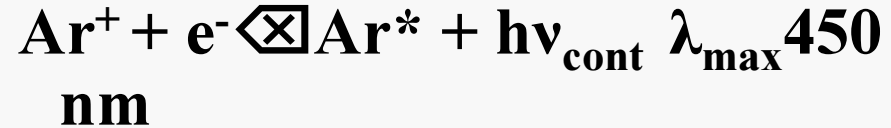
suprathermal concentrations of X^{+*} and X^+



preferential excitation of ionic spectral lines

ICP background and line emission

 **Recombination
continua** 



Ca⁺/Ca^{*}: > 302 nm, 202 nm;

Mg⁺/Mg^{*}: 257-274 nm, <255nm,


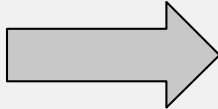
 **Molecular
bands emission** 

Stable oxides above/below NAZ;

OH (281-355nm); NH 336 nm;

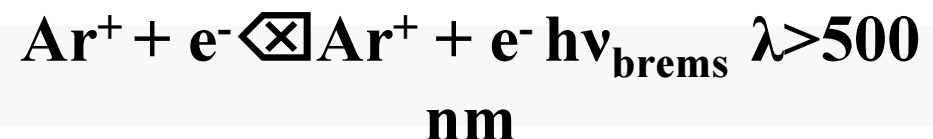
NO (200-280 nm); C₂, CN, CO,

PO, SO

 **Line (I, II)
emission** 

**205 Ar lines 207-600 nm, mostly
by 430 nm, no at 200-300 nm**

 **Bremsstrahlung**



Spatial distribution of emission in ICP

Energy (J) emitted by excited atoms or ions at a transition from upper p to lower q energy level per unit of time (s) from unit volume (m^3) to unit solid angle (sr) is emissivity ($\text{Wsr}^{-1}\text{m}^{-3}$)

$$J_{pq} = \frac{h\nu_{pq}}{4\pi} A_{pq} n_p = \frac{hc}{4\pi} A_{pq} n_p$$

where ν_{pq} and λ_{pq} are radiation frequency and wavelength, 4π is total solid angle, A_{pq} is probability of spontaneous emission $p \rightarrow q$ (number of transitions per sec), n_p is concentration of atoms or ions on level p (m^{-3}), h is Planck's constant and c is velocity of light.

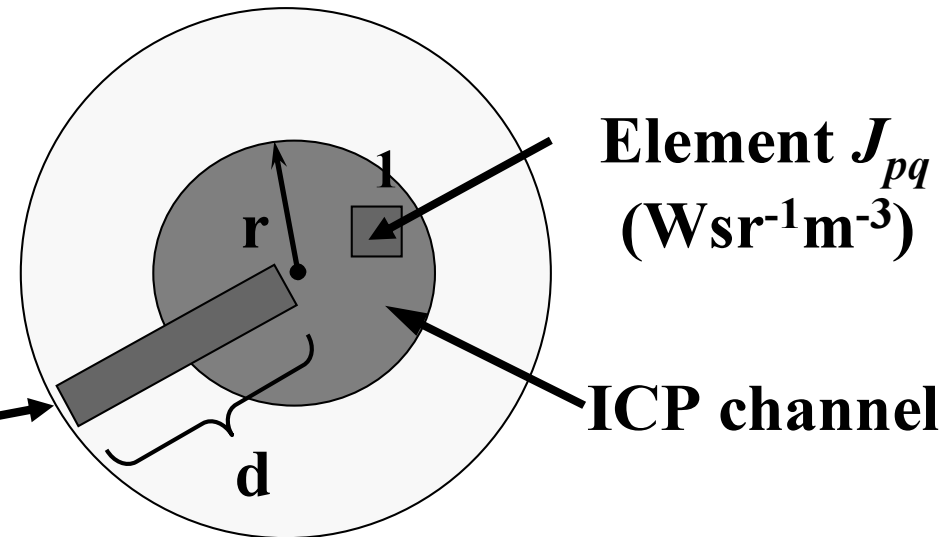
Spatial distribution of emission in ICP

Emissivity J_{pq} corresponds to radial intensity distribution

$$I_{pq} = J_{pq} * d$$

d - plasma layer
thickness (m^{-1})

Radiant intensity I_{pq}
($\text{Wsr}^{-1}\text{m}^{-2}$)

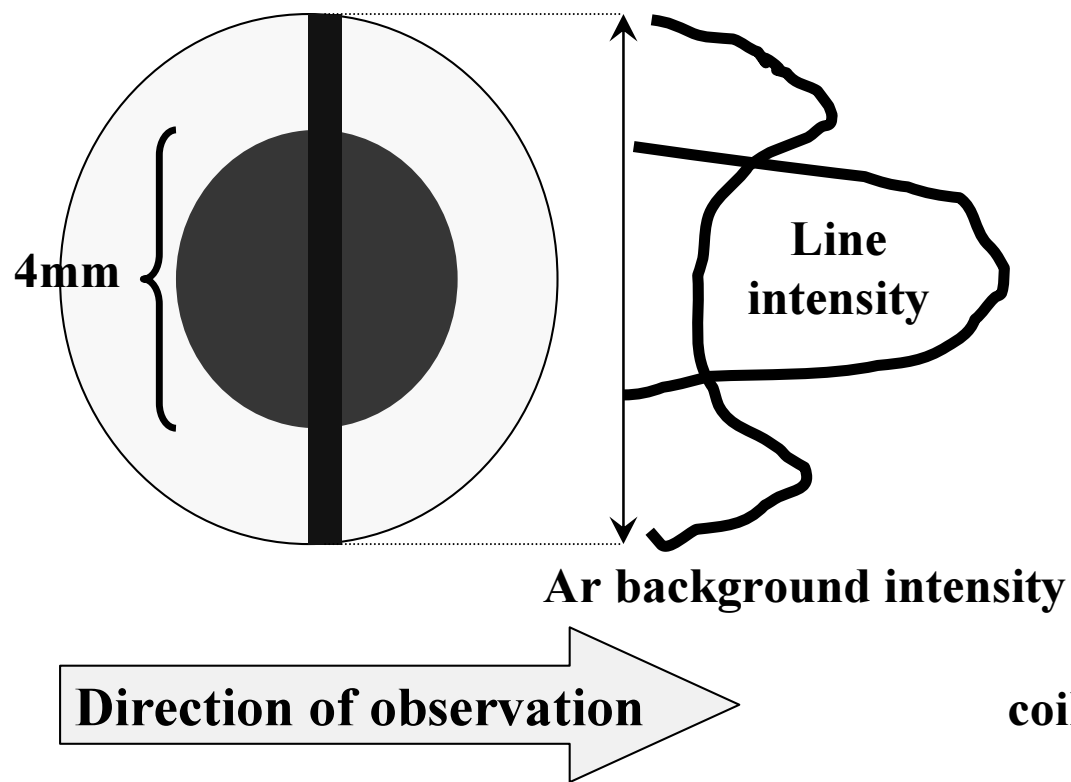


Radiant intensity I_{pq} is energy emitted per unit time into unit solid angle by unit area of plasma layer of thickness d , i.e. power per unit area per unit solid angle ($\text{Wsr}^{-1}\text{m}^{-2}$). This relates to axial and lateral intensity distribution.

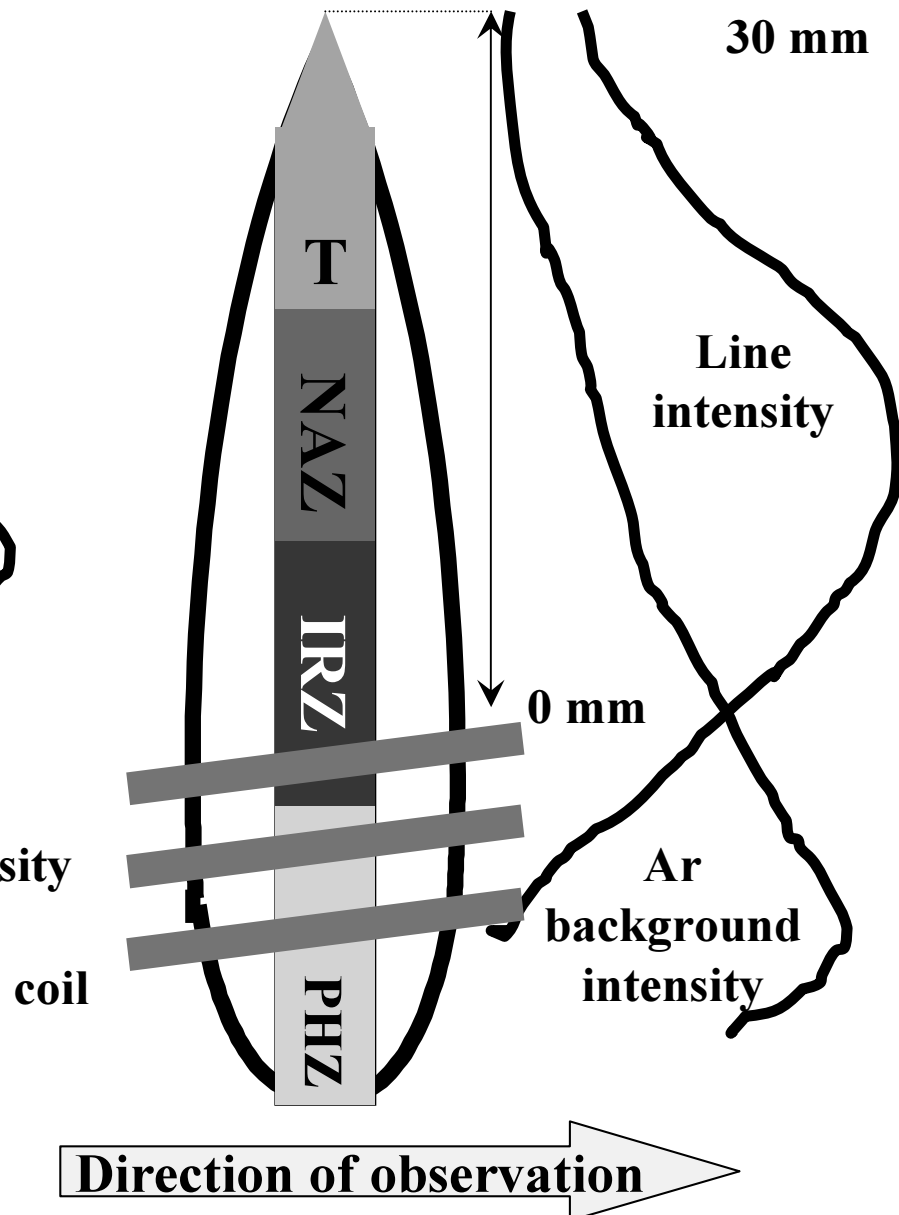
Spatial distribution of emission in ICP

LATERAL OBSERVATION

Lateral intensity distribution

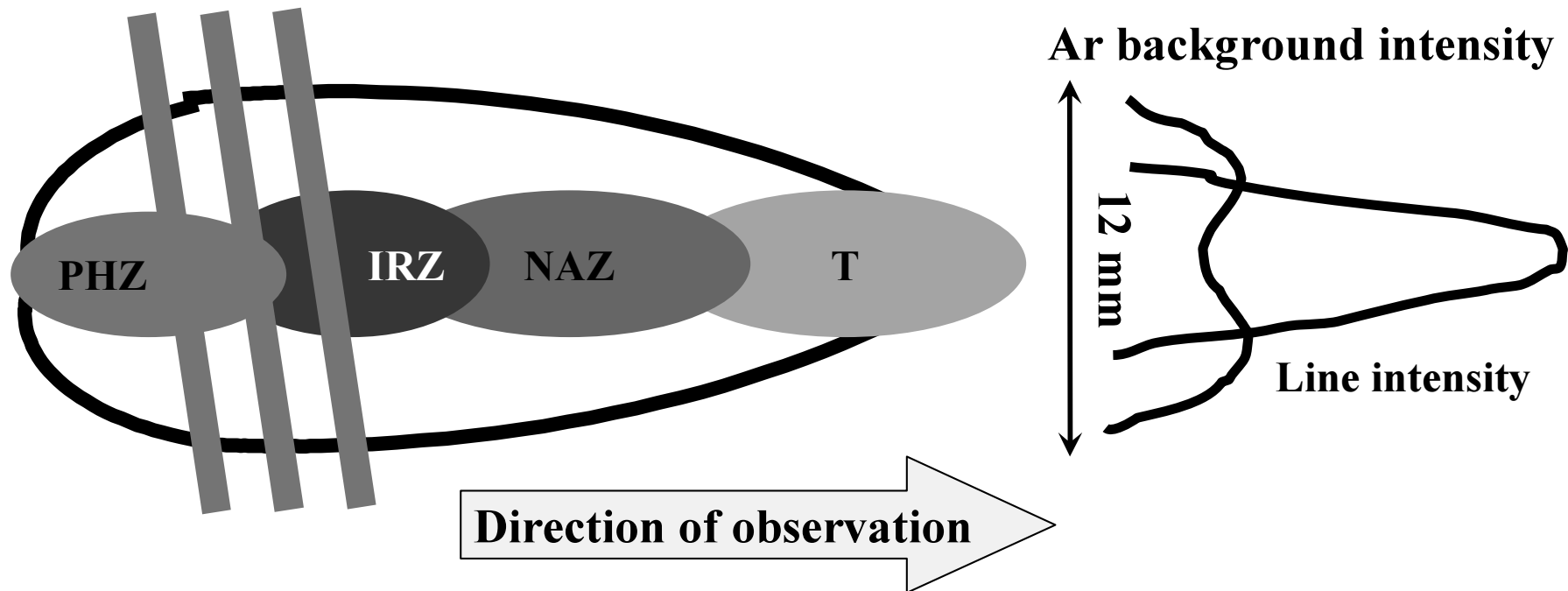


Axial intensity distribution



Spatial distribution of emission in ICP

AXIAL OBSERVATION



Spatial distribution of emission in ICP

- **Preheating Zone - PHZ:**

- ☞ aerosol desolvation

- ☞ vaporization of solid particles

- ☞ atomization of molecules and radicals

- **Initial Radiation Zone - IRZ:**

- ☞ excitation of atomic lines of low to medium 1st ionization energies which exhibits here maxima of their axial intensity distributions

- ☞ less intensive ionic (II) emission and low values of their signal-to-background ratios S/B

- ☞ non-spectral (matrix) interferences - enhancement of both atomic and ionic emission in the presence of excess of easily ionisable elements - excitation interferences

Spatial distribution of emission in ICP

- **Normal Analytical Zone - NAZ:**
 - ☞ higher concentration of electrons and temperature \times IRZ
 - ☞ excitation of ionic lines exhibiting here maxima of their axial intensity distributions and maximum S/B
 - ☞ sufficient intensity of atomic lines with low to medium 1st ionization energies, higher S/B in comparison to IRZ
 - ☞ minimum matrix interferences - combination of effects at nebulization and aerosol transport with interferences in plasma, mostly non-specific depression $< 5\%$ under optimum conditions
- **Tailflame T:**
 - ☞ lower temperature and electron density than in NAZ
 - ☞ recombination reactions, ionization interferences, alkali metals intensive emission

Spatial distribution of emission in ICP

- Power emitted by a certain surface area of an ICP is measured for a time period (integrated).
- Signal intensity is corresponding electrical quantity (photoelectric current, voltage, charge).
- Frequency of ICP oscillator influences electron density and excitation temperature. For a certain ICP generator the signal intensity depends on:
 - ☞ geometry of plasma torch
 - ☞ power input to plasma, P
 - ☞ gas flow rates (outer F_p , intermediate F_a , carrier F_c)
 - ☞ observation mode (axial, lateral - observation height)
 - ☞ ionization E_i , E_{i+1} and excitation energies E_{exc} of elements and transitions
 - ☞ amount and composition of sample transported into ICP

Axial distribution of emission in ICP

- Axial intensity distribution exhibits maximum at a certain observation height h depending of electron density and concentration of argon species Ar^+ , Ar^* and Ar^m , and E_i , E_{i+1} and E_{exc} at which “norm temperature” of the line is achieved. For stable compounds, dissociation energies are also important.
- Number density of atoms n_{ap} excited on the level p is related to total number density n_a of atoms by Boltzmann relation (g_p^a being statistical weight, Z_a partition function, E_p^a excitation energy considered form the fundamental state of atom $E=0$).

$$n_{ap} = n_a \left(\frac{g_p^a}{Z_a} \right) \exp \left(- \frac{E_p^a}{kT} \right)$$

Axial distribution of emission in ICP

where partition function (sum over k states) reads

$$Z_a = \sum_k g_k^a \exp\left(-\frac{E_k^a}{kT}\right)$$

Atomic line emission intensity
is then

$$I_{pq} = \left(\frac{hc}{4\pi\lambda_{pq}}\right) A_{pq} n_a \left(\frac{g_p^a}{Z_a}\right) \exp\left(-\frac{E_p^a}{kT}\right)$$

Axial distribution of emission in ICP

- Ionization equilibrium is described by Saha equation

$$\frac{n_i n_e}{n_a} = \left(\frac{2\pi m_e k T_{ion}}{h^3} \right)^{3/2} 2 \frac{Z_i}{Z_a} \exp\left(-\frac{E_i}{k T_{ion}} \right)$$

where Z_a and Z_i are partition functions of atomic and ionic states, n_i , n_e and n_a are ion, electron and neutral atom number densities, m_e - electron mass, T_{ion} is ionization temperature and E_i ionization energy. Saha equation can be taken into account for evaluation of atomic emission by means of the degree of ionization

$$\alpha = \frac{n_i}{n_a + n_i}$$

Axial distribution of emission in ICP

- Consequently, for atomic line emission intensity yields

$$I_{pq} = \left(\frac{hc}{4\pi\lambda_{pq}} \right) A_{pq} n_0 (1 - \alpha) \left(\frac{g_p^a}{Z_a} \right) \exp\left(-\frac{E_p^a}{kT} \right)$$

where $n_0 = n_a + n_i$ is total concentration of particles (atoms and ions) of a certain element. As a result, atomic line intensity increases with temperature in Boltzmann exponential term, however, at the same time the concentration of atoms decreases according to Saha equation due to ionization. The Intensity - Temperature dependence reaches maximum at a norm temperature.

Axial distribution of emission in ICP

- Ionic line emission intensity is described by relation

$$I_{pq} = K \left(\frac{g_p^i A_{pq} n_i}{\lambda_{pq} Z_i} \right) \cdot \exp \left(- \frac{E_i + E_{exc}}{kT} \right)$$

- The most significant constituent of the background of Ar ICP is Ar recombination continuum

$$I_{\nu < \nu_L} = K \frac{n_e n_i}{\sqrt{kT_e}} \quad I_{\nu > \nu_L} = K \frac{n_e n_i}{\sqrt{kT_e}} \exp \left(\frac{h(\nu_L - \nu)}{kT_e} \right)$$

Axial distribution of emission in ICP

- As it is approximately $n_i = n_{Ar^+} = n_e$

it means that the intensity of recombination continuum background rises with the second power of concentration of electrons, which again increases with temperature, i.e. with power input. Usually the Ar-background rises more steeply than line intensity with power.

- Different spatial distribution of emission and different behaviour of lines led to the following classification:

☞ Hard lines – atomic lines of elements with high 1st ionization energies and most of ionic lines





☞ Soft lines – at. lines with low and medium 1st ioniz. energies

☞ Between these 2 groups are ionic lines with low and medium 2nd ionization energies (Ba II 455.403 nm, La II 408.672 nm).

Inductively Coupled Plasma Atomic Emission Spectrometry

- ☞ Determination of 73 elements (P, S, Cl, Br, J)**
- ☞ Simultaneous and fast sequential measurement**
- ☞ High selectivity**
- ☞ Low limits of detection (0.1-10 ng/mL)**
- ☞ Linear dynamic range (5-7 orders of magnitude)**
- ☞ Minimum matrix effects ($\pm 10\%$ rel.)**
- ☞ Introduction of liquid, solid, gaseous samples**
- ☞ Conventional flows of liquids (mL/min) or microsamples ($\mu\text{L}/\text{min}$)**

Inductively Coupled Plasma Atomic Emission Spectrometry

-  **Acceptable precision (0.5 - 2 % rel.)**
-  **Acceptable accuracy (~ 1 % rel.)**
-  **High sample throughput ~ routinely 10^2 - 10^3
determinations per hour**
-  **Automation of operation**