ENVG 60500

FALL 2011

ICP-MS (Inductively Coupled Plasma Mass Spectrometry)

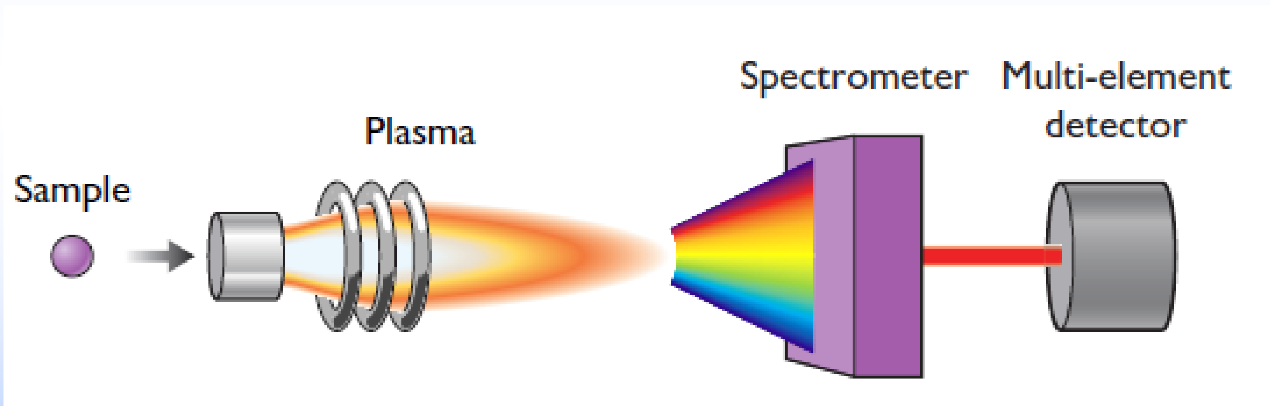
Analytical Techniques

HISTORY

- In the 1940s, arc and high-voltage spark spectrometry became widely utilized for metal analysis
- In the 1950s, flame atomic absorption spectrometry was introduced
- In the 1960s, atomic absorption became more prevalent

HISTORY

- In the 1970s, ICP-AES, -OES (atomic emission spectrometry, optical emission spectrometry)



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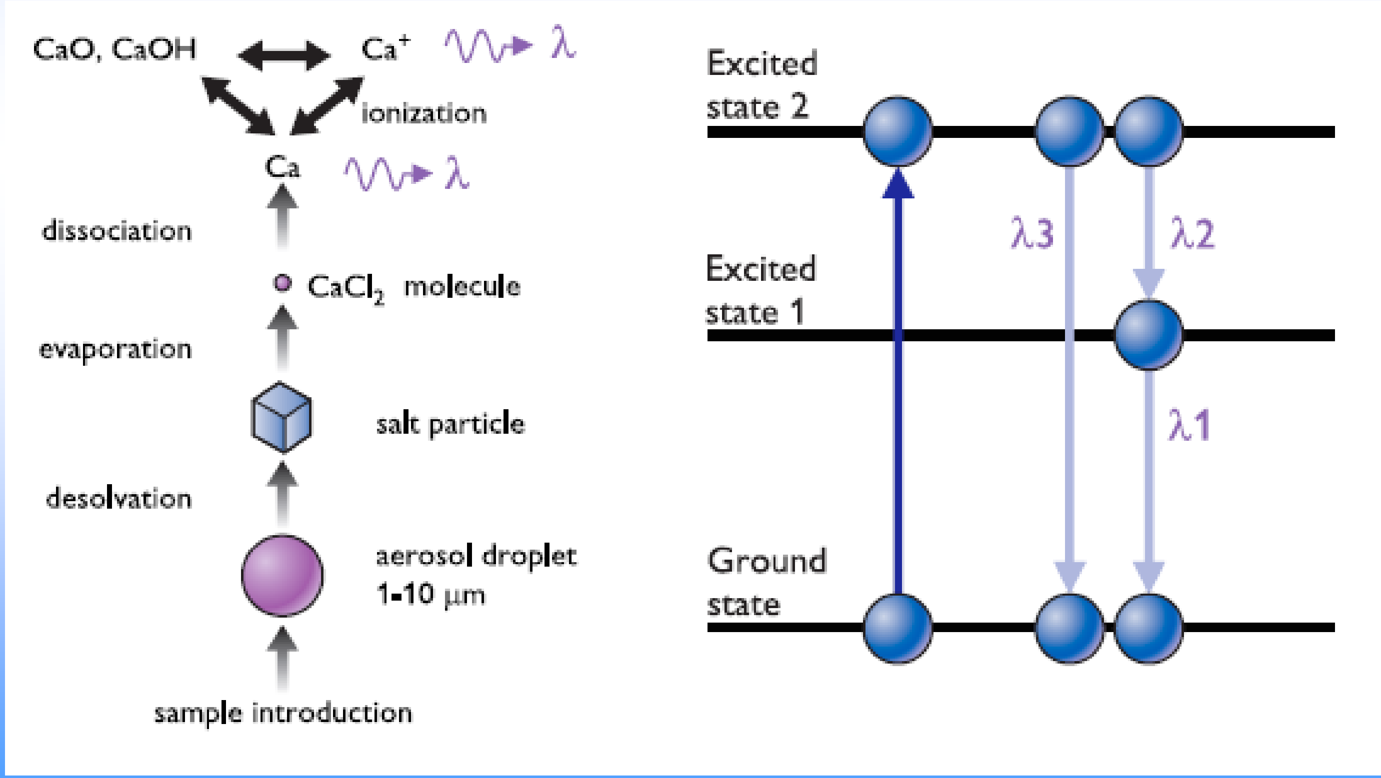


HISTORY

- 1980s, ICP-MS became the “hot” technique
- Since then, improvements are constantly being made

Description of an '***ideal***' method of instrumental analysis

- Sample would decompose into its constituent atoms in a controlled fashion (and not a cataclysmic event)

- Each atom would be extracted individually, its position recorded, its oxidation state determined, and its nearest neighbors noted

- The freed atoms would be sorted by size and isotope, and the number of each isotope (for a given element) and corresponding isotopic composition measured

Description of an '***ideal***' method of instrumental analysis

- The detection limit for such an ideal instrument would be at the single-atom (single-isotope) level, matrix interferences would be absent, and precision (of analysis) would be dictated by solely counting statistics

Advantages of an ICP-MS instrument – (not an ***<u>ideal</u>*** instrument), however…..

- **Rapid** analysis (typically within minutes)

- **Higher ionization efficiency** compared to other mass spectrometric techniques (e.g. TIMS – thermal ionization mass spectrometry)

- **Very low detection limits** (i.e. most elements << 1 ppm)

- **Spectral simplicity**
  - Very few interferences, and the overlaps that do occur are predictable; thus these are corrected by evaluating other isotopes of the same element

USE(S)

Elemental abundance determinations (and isotope measurements) in various types of samples

- Environmental
- Biological
- Metallurgical
- Geological
- Industrial
- Agricultural

ICP-MS
MAIN COMPONENTS

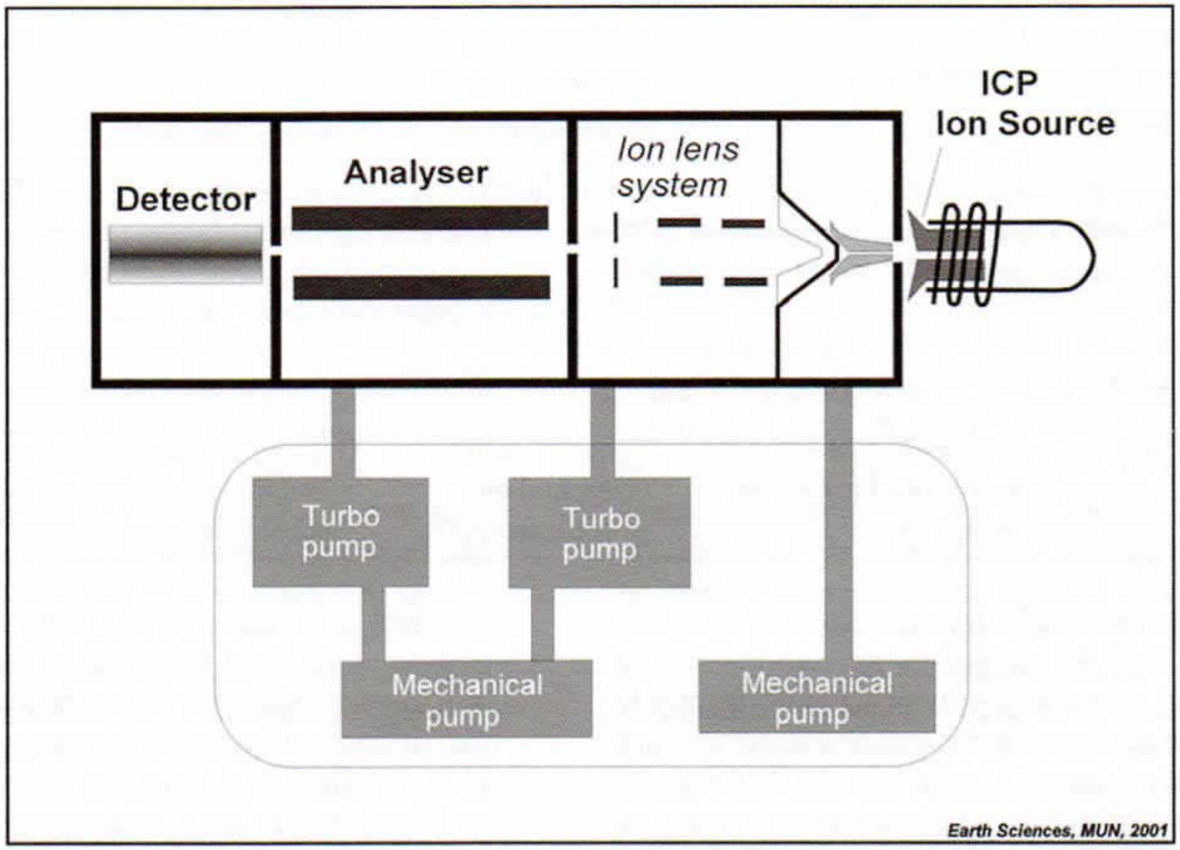
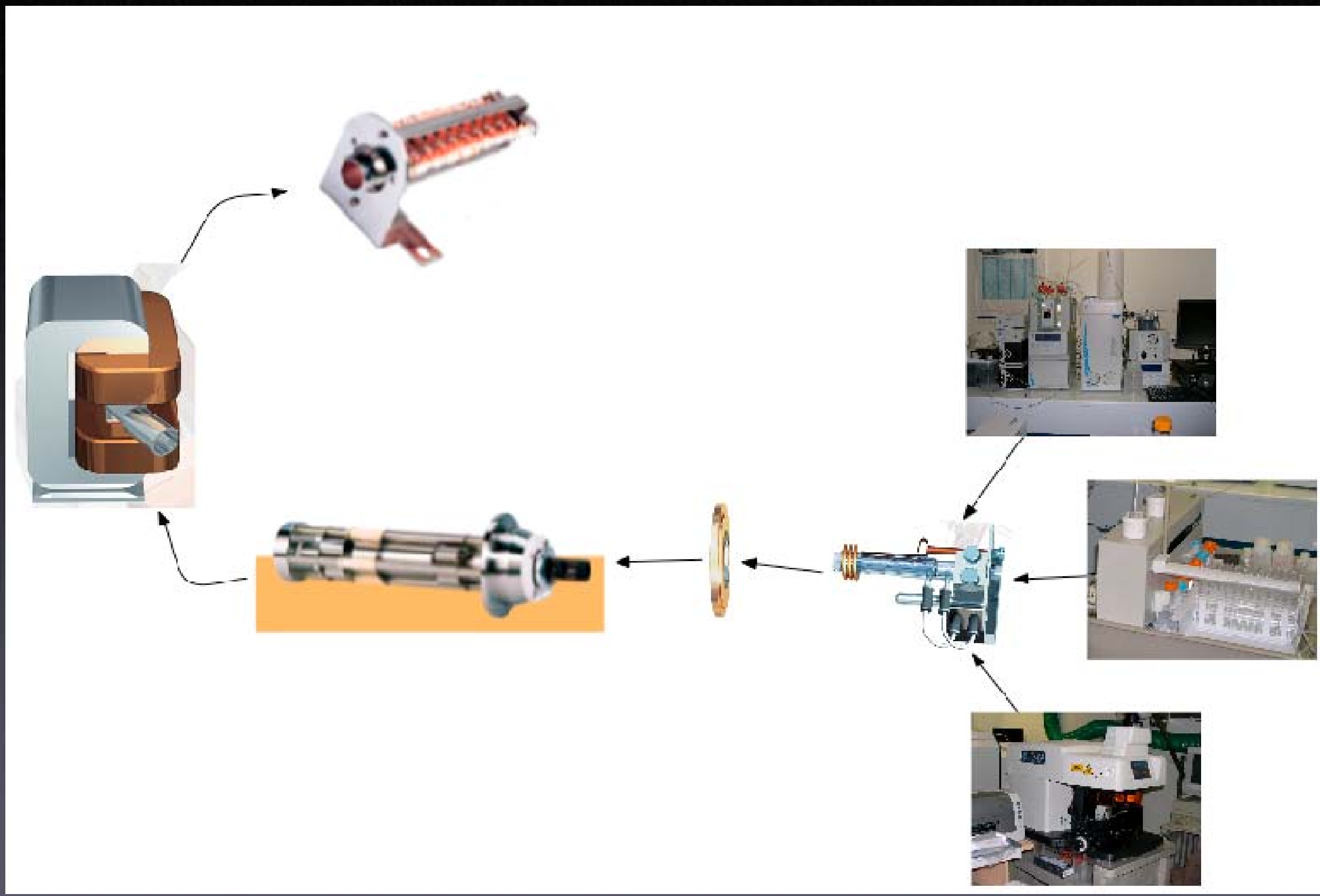


FIG 1-1. Schematic diagram of an inductively coupled plasma mass spectrometer showing the 4 main parts, as discussed in this chapter: the vacuum system; the ion source or ICP; the analyzer; and the detector.

ICP-MS
MAIN COMPONENTS



ICP-MS
MAIN COMPONENTS

- **<u>VACUUM SYSTEM</u>**

  – Ions will not get very far in the presence of atmospheric pressure

  – “Mean free path” length of an ion has > 1 meter in order for the mass spectrometer to be useful

  – “Mean free path” is the mean or average distance which an ion can move before it hits another particle

Table 1.2. Units of pressure measurement.

	Bar	psi	Torr	Pascal
1Bar	1	14.5	750	100 000
1 psi	0.068 9	1	51.7	6 895
1 Torr	0.001 33	0.019 3	1	133
1 Pascal	0.000 01	0.000 145	0.007 5	1

from CRC, 2000.

Table 1.1 Mean free path distances as a function of the system pressure

Pressure (torr)	Mean Free Path
760 (1 atm)	0.0000001 m (0.1 μm)
1	0.00005 m (0.05 mm)
0.05	0.001 m (1 mm)
10^{-5}	5 m
10^{-6}	50 m
10^{-7}	500 m
10^{-8}	5,000 m

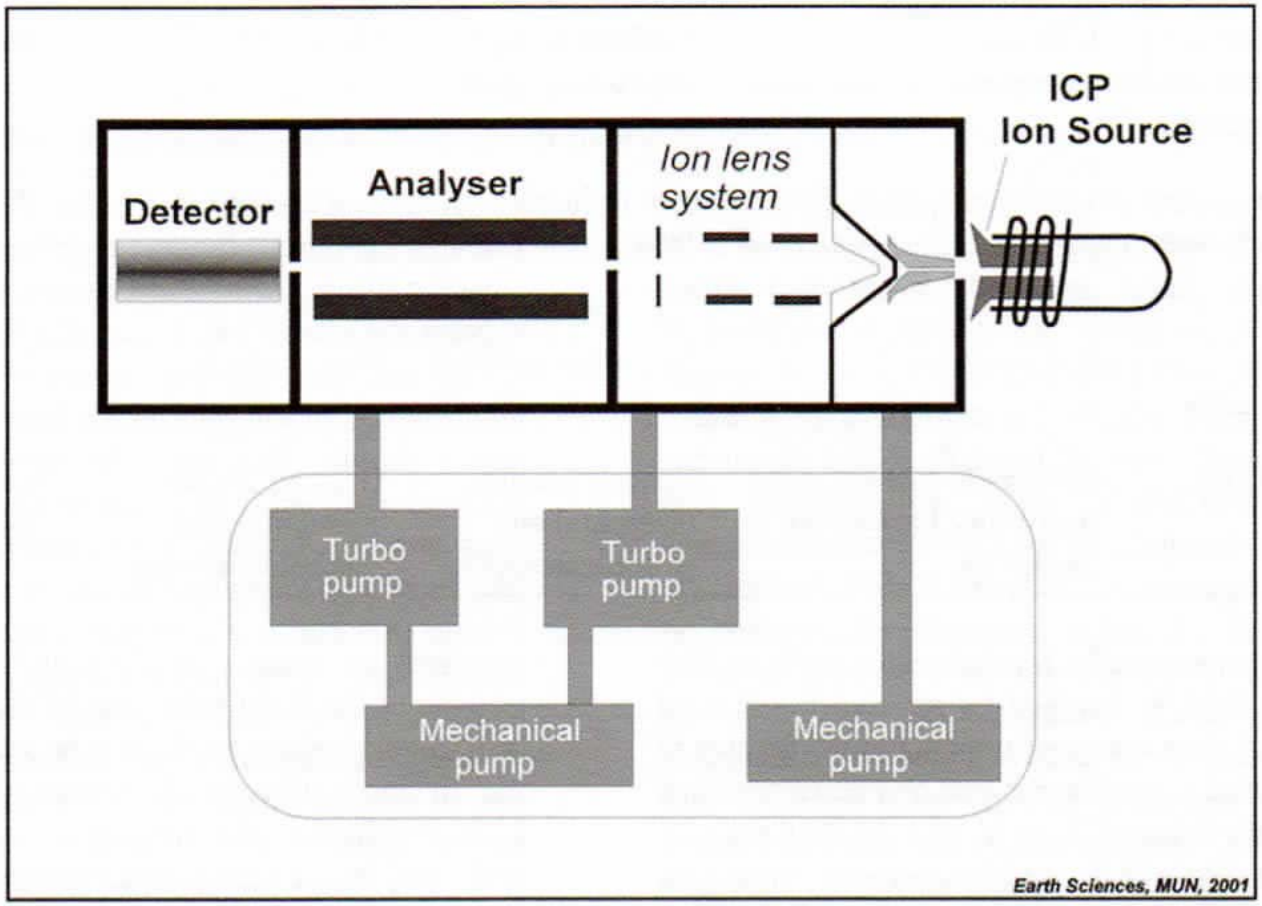


FIG 1-1. Schematic diagram of an inductively coupled plasma mass spectrometer showing the 4 main parts, as discussed in this chapter: the vacuum system; the ion source or ICP; the analyzer; and the detector.

Vacuum System

- **Mechanical (Rotary) Pumps**
  - First line pumps
  - Range from atmosphere to less than one torr (approx. <1 millibar)
  - Use to back Turbo pumps

- **Turbo Molecular Pumps**
  - Consists of 10 to 20 “fan” blades (similar to jet engine turbine blades) turning at 100,000 RPM!
  - As residual gas molecules get close to a blade, they are hit by the blade and forced towards the next blade, etc.

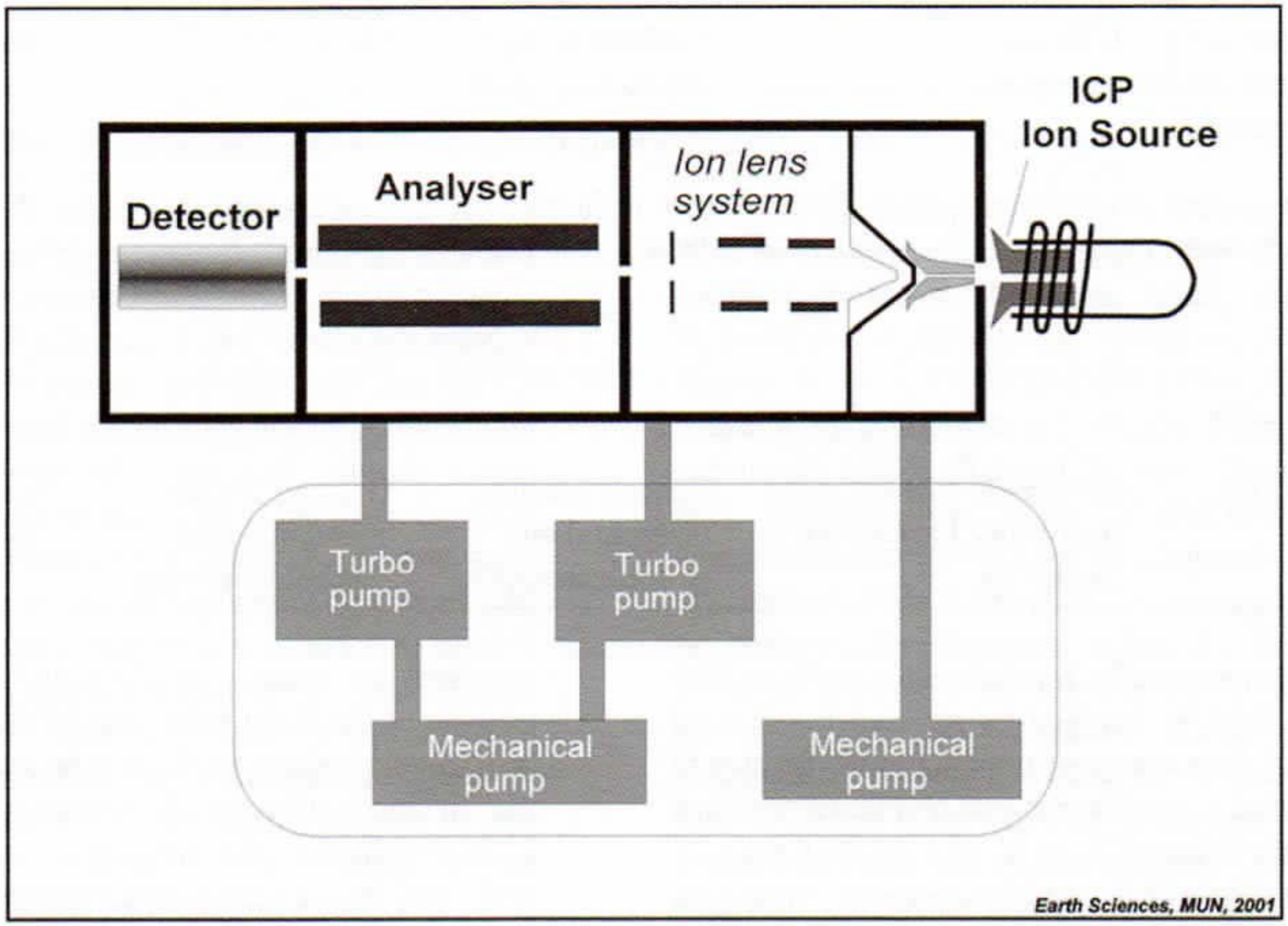


FIG 1-1. Schematic diagram of an inductively coupled plasma mass spectrometer showing the 4 main parts, as discussed in this chapter: the vacuum system; the ion source or ICP; the analyzer; and the detector.

Ion Source

- Ion source is the place and means in which ions are created, accelerated in the desired direction, and focused to increase the ion beam current
  - ***ICP*** is the ion source of interest

ICP- Ion Source

- **"Good" source of ions**
  - Temperature of ICP ~6000 -8000 K, or close to the apparent temperature of the surface of the sun (most familiar type of plasma)
- **Main problem initially**
  - How to get ions from atmospheric pressure plasma into a suitable low pressure vacuum system containing a mass spectrometer

ICP- Ion Source

- **ION**
  - an atom carrying a + or – electric charge due to the loss or gain of one or more electrons

ICP- Ion Source

- **IONIZATION** (as related to ICPs)
  - Addition of external energy can remove an electron to create + charged ions

ICP- Ion Source

- How much energy?
  - **Ionization potential**

    ↑ more energy required

    ↓ less energy required
  - Each element is characterized by a specific ionization potential

Ionization Potentials

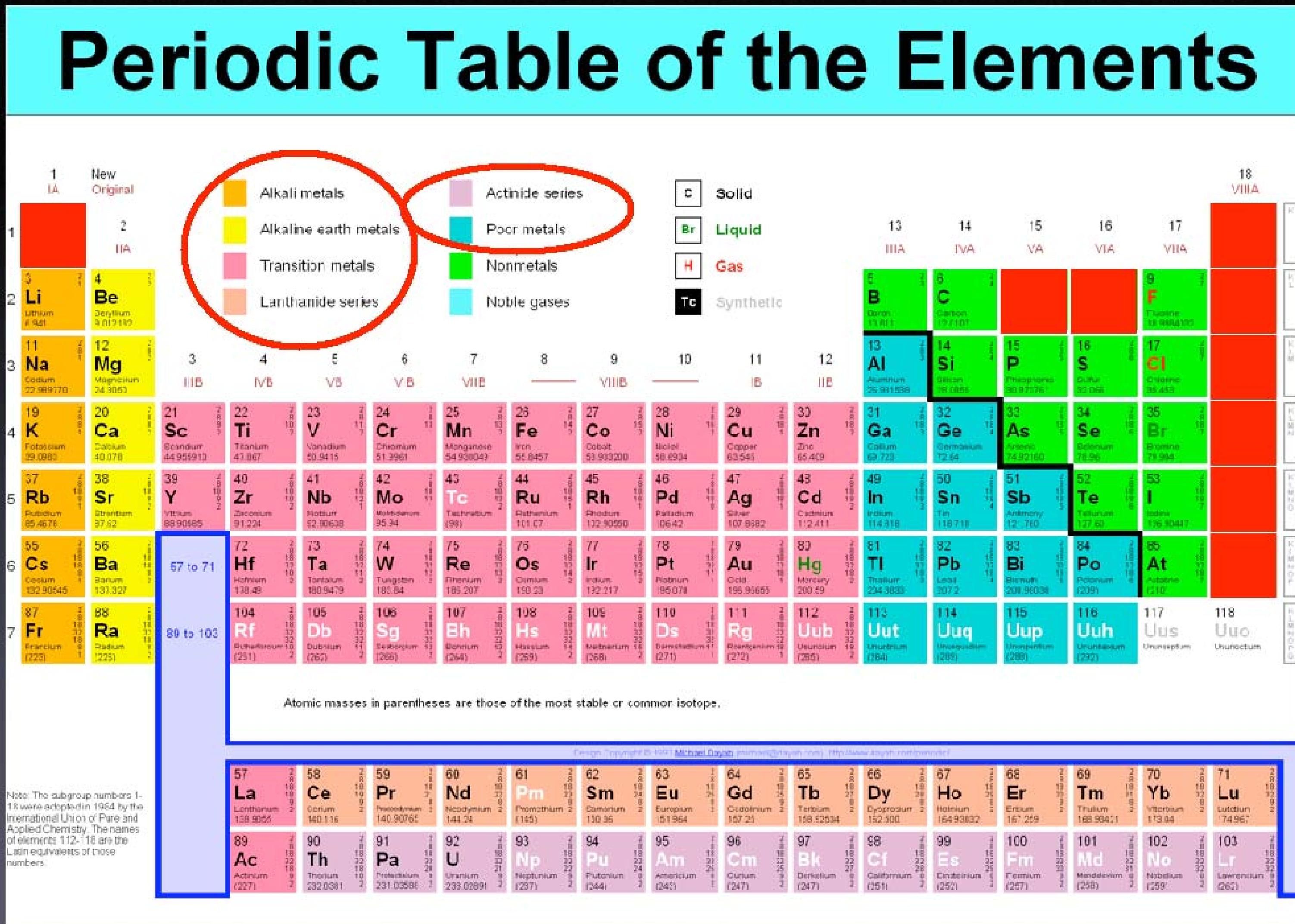
H 0.1																	He
Li 100	Be 75											B 58	C 5	N 0.1	O 0.1	F 9×10^{-4}	Ne 6×10^{-6}
Na 100	Mg 98											Al 98	Si 85	P 33	S 14	Cl 0.9	Ar 0.04
K 100	Ca 99(1)	Sc 100	Ti 99	V 99	Cr 98	Mn 95	Fe 96	Co 93	Ni 91	Cu 90	Zn 75	Ga 98	Ge 90	As 52	Se 33	Br 5	Kr 0.6
Rb 100	Sr 96(4)	Y 98	Zr 99	Nb 98	Mo 98	Tc	Ru 96	Rh 94	Pd 93	Ag 93	Cd 65	In 99	Sn 96	Sb 78	Te 66	I 29	Xe 8.5
Cs 100	Ba 91(9)	La 90(10)	Hf 96	Ta 95	W 94	Re 93	Os 78	Ir	Pt 62	Au 51	Hg 38	Tl 100	Pb 97(.01)	Bi 92	Po	At	Rn
Fr	Ra	Ac	Unq	Unp	Unh	Uns	Uno										

Ce 96(2)	Pr 90(10)	Nd 99*	Pm	Sm 97(3)	Eu 100*	Gd 93(7)	Tb 99*	Dy 100*	Ho	Er 99*	Tm 91(9)	Yb 92(8)	Lu
Th 100*	Pa	U 100*	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 2.3 Calculated values for degree of ionisation (%) of M^+ and M^{2+} at $T_i = 7500$ K, $n_e = 1 \times 10^{15}$ cm^3. Elements marked by an asterisk yield significant amounts of M^{2+} but partition functions are not available (after Houk, 1986).

Table 2.1 Distribution of ionisation energies among the elements for singly and doubly charged ions at 1 eV intervals (from Gray, 1989a)

Ionisation energy (eV)	Elements	*2⁺ ions*
< 7	Li, Na, Al, K, Ca, Sc, Ti, V, Cr, Ga, Rb, Sr, Y, Zr, Nb, In, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Ra, Ac, Th, U	
7–8	Mg, Mn, Fe, Co, Ni, Cu, Ge, Mo, Tc, Ru, Rh, Ag, Sn, Sb, Ta, W, Re, Pb, Bi	
8–9	B, Si, Pd, Cd, Os, Ir, Pt, Po	
9–10	Be, Zn, As, Se, Te, Au	Ba, Ce, Pr, Nd, Ra
10–11	P, S, I, Hg, Rn	Ca, Sr, La, Sm, Eu, Tb, Dy, Ho, Er
11–12	C, Br	Sc, Y, Gd, Tm, Yb, Th, U, Ac
12–13	Xe	Ti, Zr, Lu
13–14	H, O, Cl, Kr	V, Nb, Hf
14–15	N	Mg, Mn, Ge, Pb
15–16	Ar	All other elements
> 16	He, F, Ne	

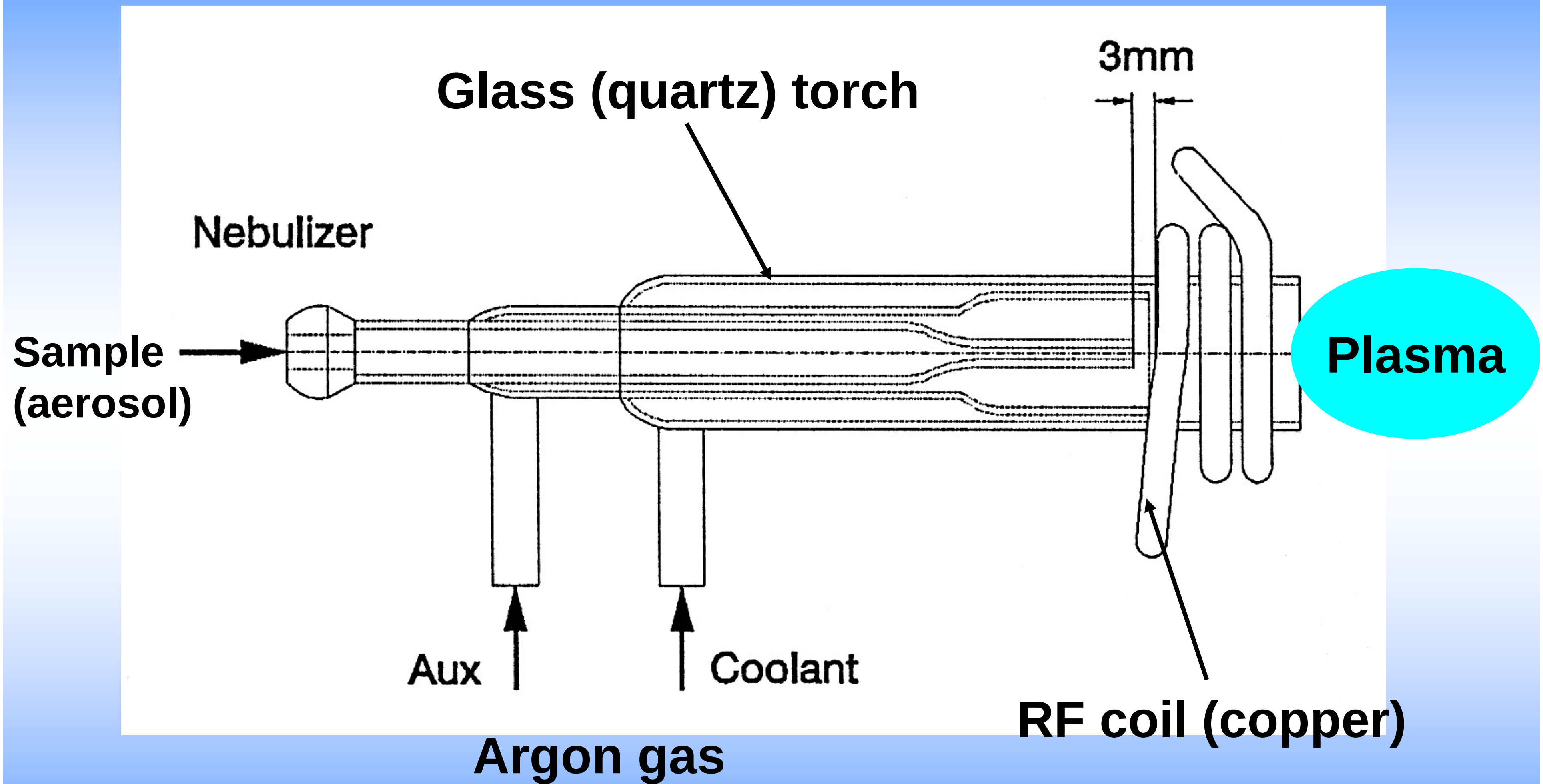


http://www.dayah.com/periodic/

THE PLASMA

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

- What is a Plasma?
  - The magnetic field created by a RF (radio frequency) coil produces a current within a stream of **Argon (Ar)** gas, which is 'seeded' with energetic electrons
  - A 'spark' is passed through the Argon in the presence of the RF field of the coil to initiate the plasma
  - A steady-state plasma is produced when the rate at which electrons are released by ionizing collisions equals the rate at which they are lost by recombination.
  - A bluish-white light is characteristic of Ar ICP plasmas


3mm
Glass (quartz) torch
Nebulizer
Sample
(aerosol)
Plasma
Aux
Coolant
RF coil (copper)
Argon gas

Plasma

- **Why Argon (Ar)**?
  - It is an ‘inert’ or ‘noble’ gas, thus not explosive when subjected to an RF magnetic field or spark
  - It is relatively cheap to manufacture since the Ar is extracted directly from the atmosphere
  - The stream of Ar gas is usually between 8 to 20 Litres per minute