

ENVG 60500

FALL 2011

**ICP-MS (Inductively Coupled
Plasma Mass Spectrometry)**

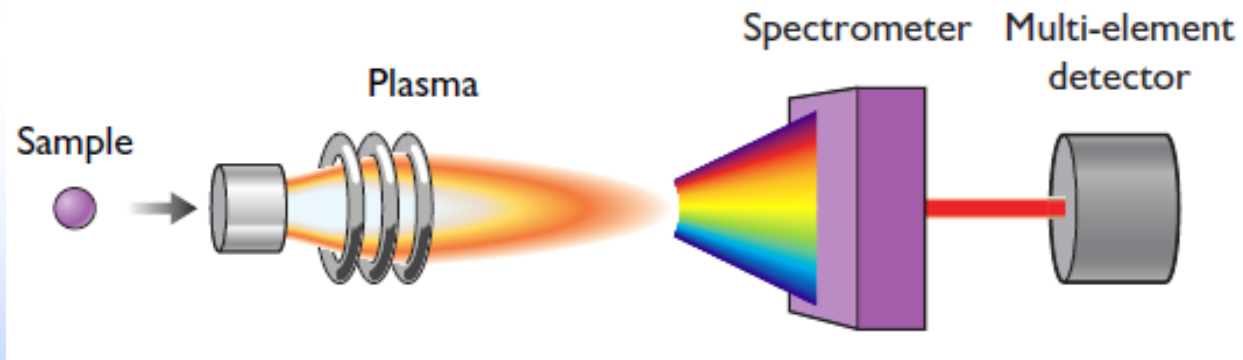
Analytical Techniques

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

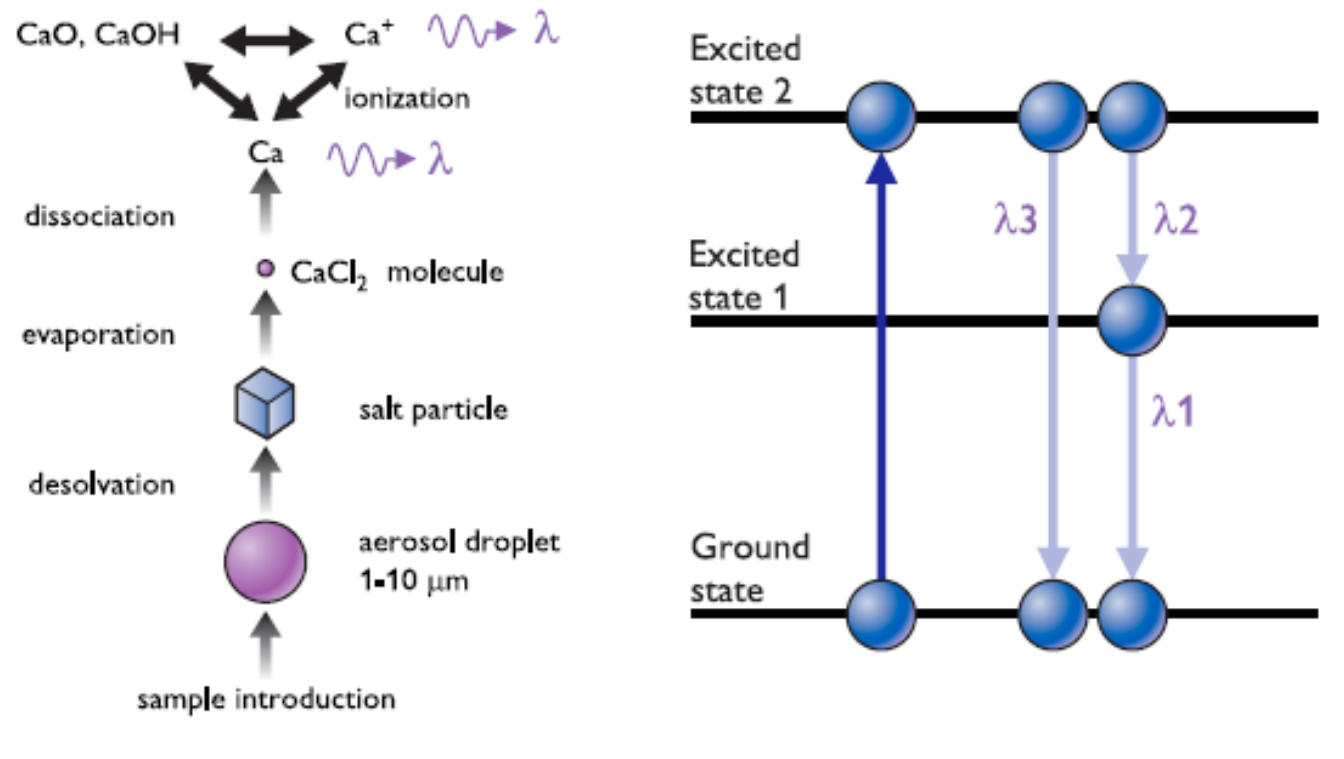
HISTORY

- 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 *ideal* 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 \ll 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

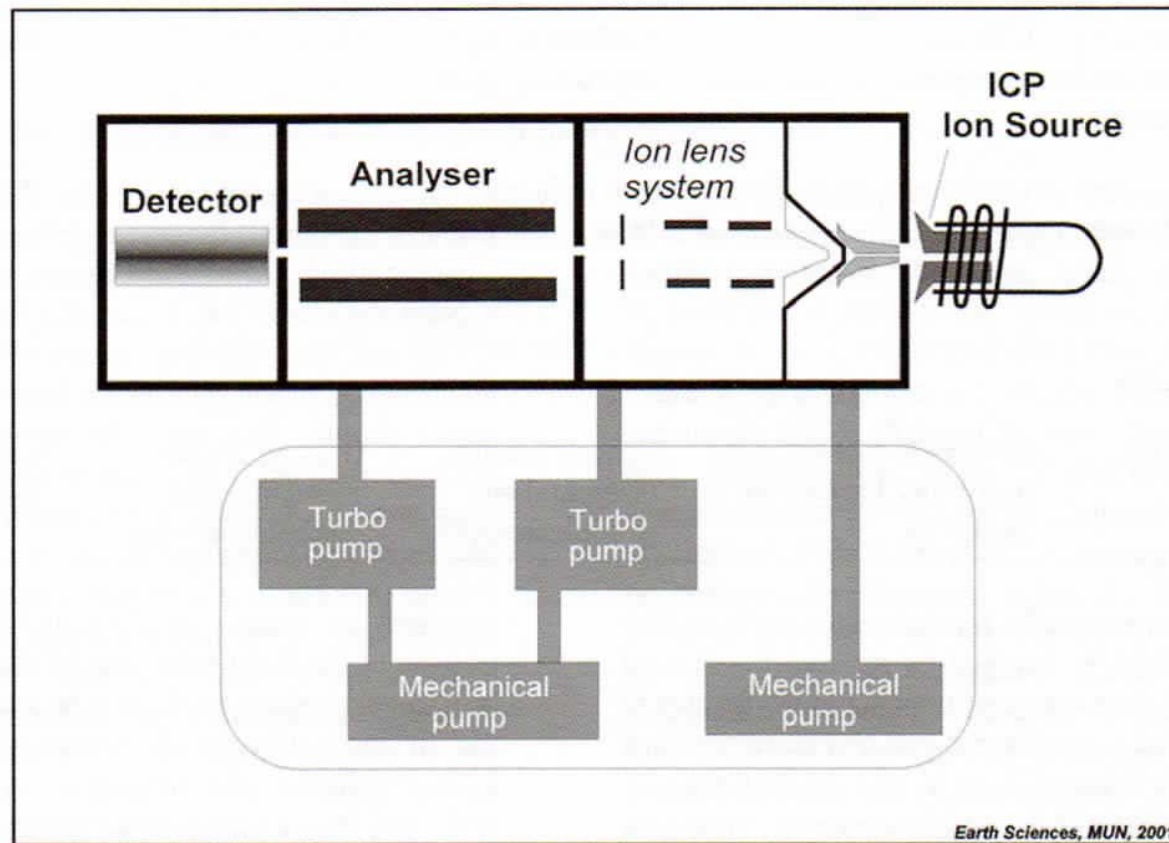
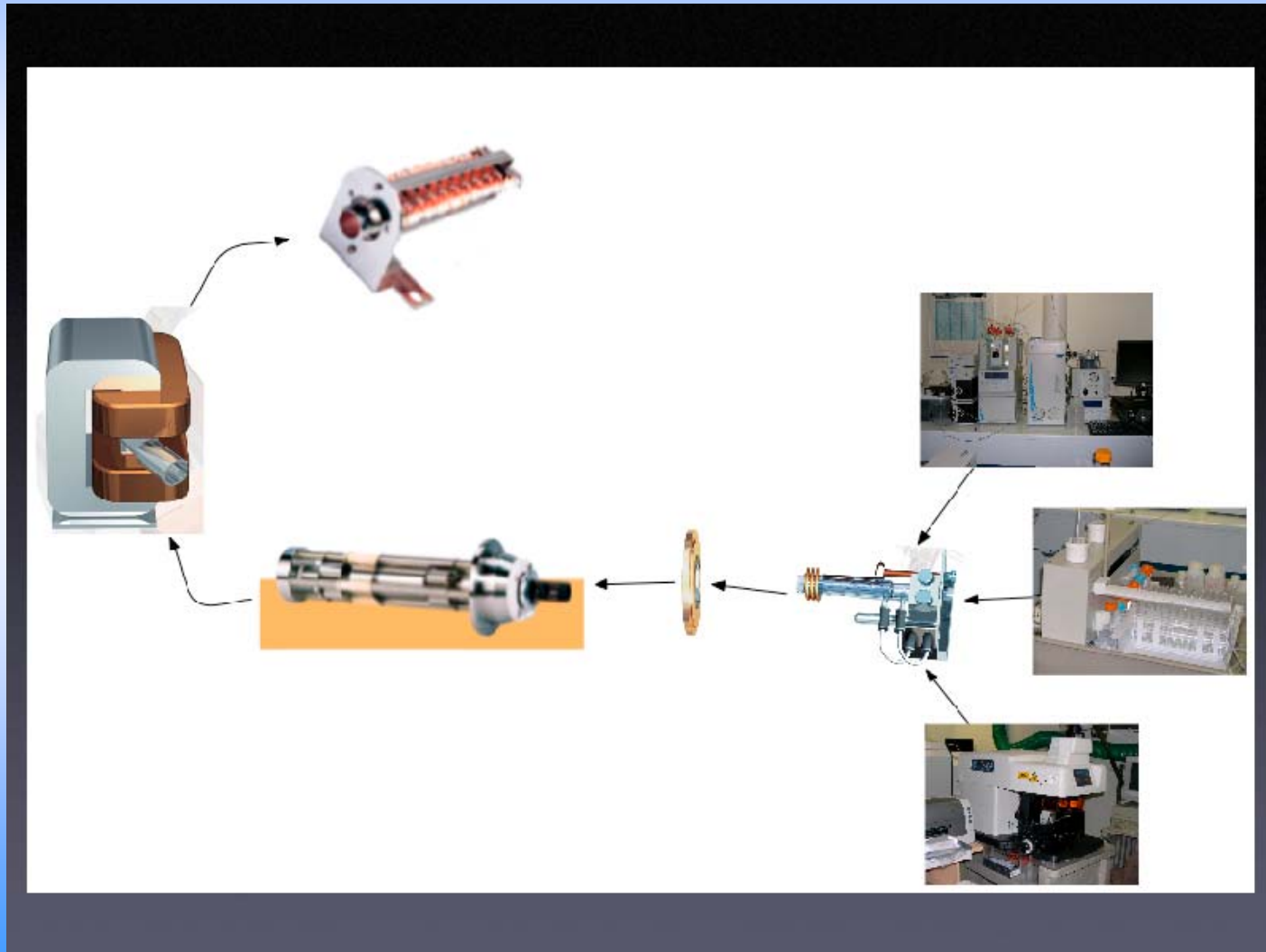


FIG 1-1. Schematic diagram of an inductively coupled plasma mass spectrometer showing the 4 main parts, as discussed in this chapter: the vacuum system; the ion source or ICP; the analyzer; and the detector.

ICP-MS MAIN COMPONENTS



ICP-MS

MAIN COMPONENTS

- VACUUM SYSTEM

- 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
1 Bar	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

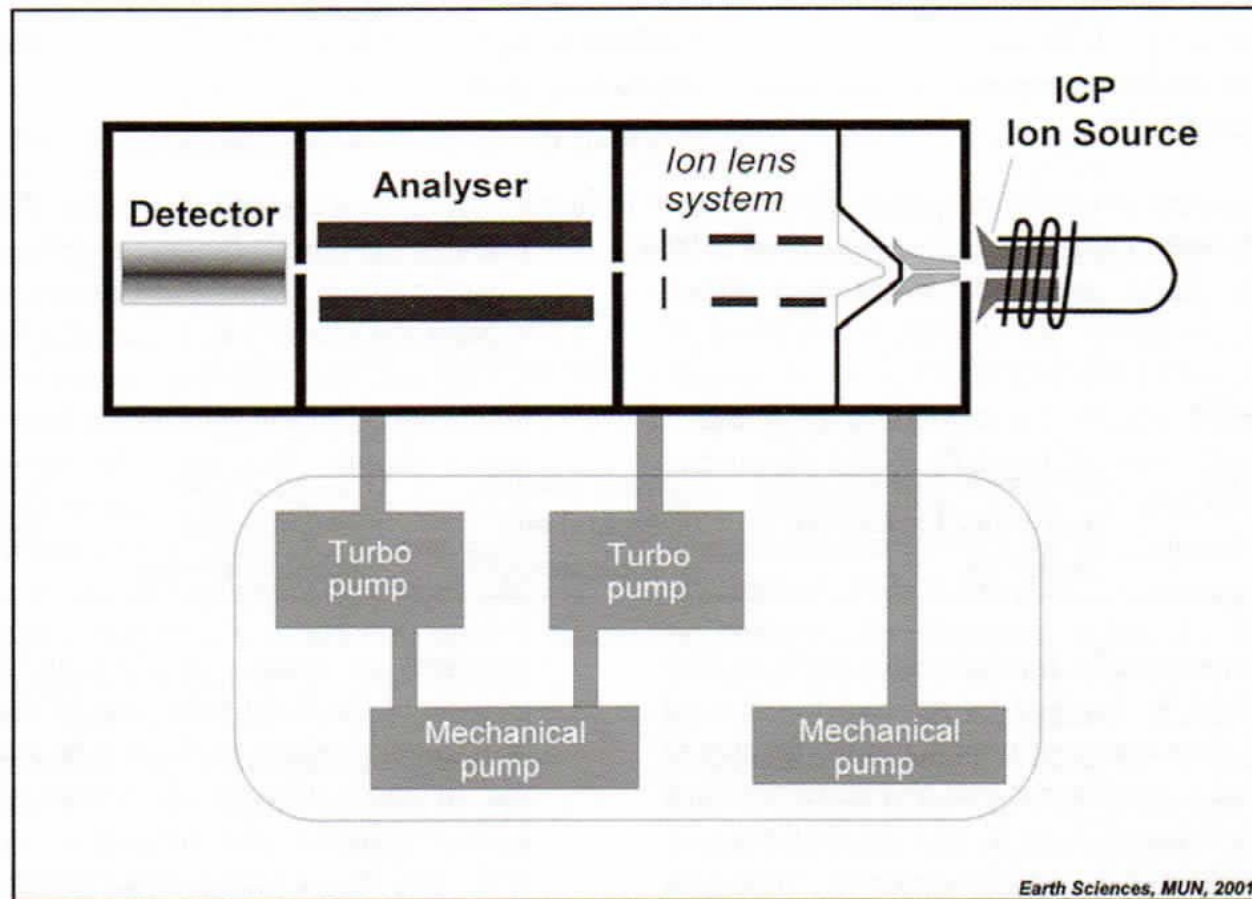


FIG 1-1. Schematic diagram of an inductively coupled plasma mass spectrometer showing the 4 main parts, as discussed in this chapter: the vacuum system; the ion source or ICP; the analyzer; and the detector.

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.

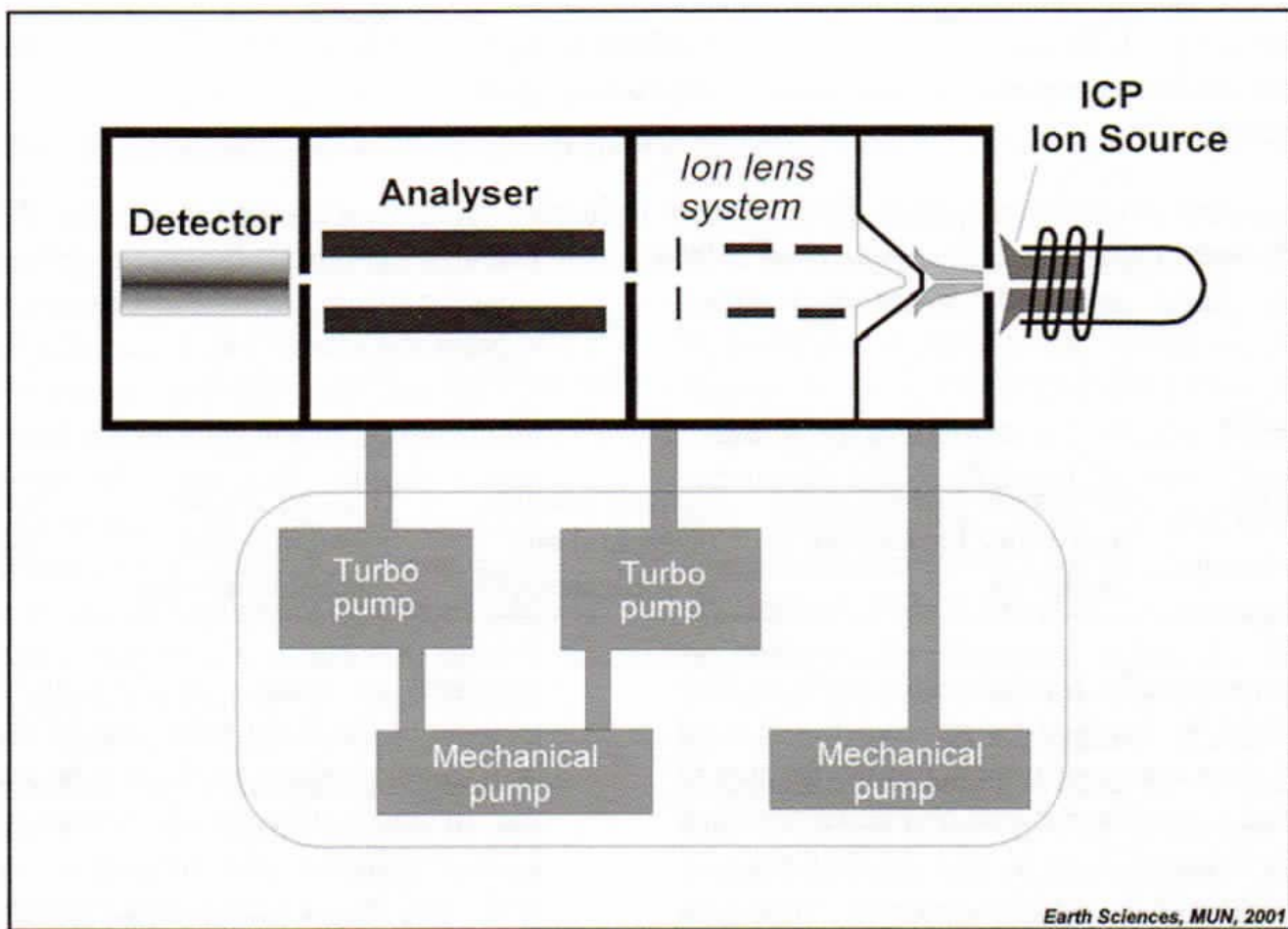


FIG 1-1. Schematic diagram of an inductively coupled plasma mass spectrometer showing the 4 main parts, as discussed in this chapter: the vacuum system; the ion source or ICP; the analyzer; and the detector.

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 9x10 ⁻⁴	Ne 6x10 ⁻⁴
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
< 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
10-11	P, S, I, Hg, Rn
11-12	C, Br
12-13	Xe
13-14	H, O, Cl, Kr
14-15	N
15-16	Ar
> 16	He, F, Ne

2 ⁺ ions
Ba, Ce, Pr, Nd, Ra
Ca, Sr, La, Sm, Eu, Tb, Dy, Ho, Er
Sc, Y, Gd, Tm, Yb, Th, U, Ac
Ti, Zr, Lu
V, Nb, Hf
Mg, Mn, Ge, Pb
All other elements

Periodic Table of the Elements

1 IA New Original	2 IIA											13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
3 Li Lithium (7.016)	4 Be Beryllium (9.01218)											5 B Boron (10.811)	6 C Carbon (12.011)	7 N Nitrogen (14.0064)	8 O Oxygen (15.9994)	9 F Fluorine (18.9984)	10 Ne Neon (20.1797)
11 Na Sodium (22.98977)	12 Mg Magnesium (24.305)	3 IIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 Al Aluminum (26.981538)	14 Si Silicon (28.0855)	15 P Phosphorus (30.97376)	16 S Sulfur (32.06)	17 Cl Chlorine (35.453)	18 Ar Argon (39.948)
19 K Potassium (39.0983)	20 Ca Calcium (40.078)	21 Sc Scandium (44.95591)	22 Ti Titanium (47.867)	23 V Vanadium (50.9415)	24 Cr Chromium (51.9961)	25 Mn Manganese (54.93804)	26 Fe Iron (55.845)	27 Co Cobalt (58.9332)	28 Ni Nickel (58.6934)	29 Cu Copper (63.546)	30 Zn Zinc (65.409)	31 Ga Gallium (69.723)	32 Ge Germanium (72.64)	33 As Arsenic (74.9216)	34 Se Selenium (78.96)	35 Br Bromine (79.904)	36 Kr Krypton (83.798)
37 Rb Rubidium (85.4678)	38 Sr Strontium (87.62)	39 Y Yttrium (88.90585)	40 Zr Zirconium (91.224)	41 Nb Niobium (92.90638)	42 Mo Molybdenum (95.94)	43 Tc Technetium (98)	44 Ru Ruthenium (101.07)	45 Rh Rhodium (102.9055)	46 Pd Palladium (106.42)	47 Ag Silver (107.8682)	48 Cd Cadmium (112.411)	49 In Indium (114.818)	50 Sn Tin (118.710)	51 Sb Antimony (121.757)	52 Te Tellurium (127.6)	53 I Iodine (126.90447)	54 Xe Xenon (131.29)
55 Cs Cesium (132.90545)	56 Ba Barium (137.327)	67 to 71	72 Hf Hafnium (178.49)	73 Ta Tantalum (180.9479)	74 W Tungsten (183.84)	75 Re Rhenium (186.207)	76 Os Osmium (190.23)	77 Ir Iridium (192.222)	78 Pt Platinum (195.078)	79 Au Gold (196.96657)	80 Hg Mercury (200.59)	81 Tl Thallium (204.3833)	82 Pb Lead (207.2)	83 Bi Bismuth (208.98038)	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 to 103	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (269)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium (294)	118 Uuo Ununoctium (294)

- Alkali metals
- Alkaline earth metals
- Transition metals
- Lanthanide series
- Actinide series
- Poor metals
- Nonmetals
- Noble gases

- C** Solid
- Br** Liquid
- H** Gas
- Tc** Synthetic

Atomic masses in parentheses are those of the most stable or common isotope.

Image courtesy of 2007 Michael Dayag, www.dayag.com, <http://www.dayag.com>

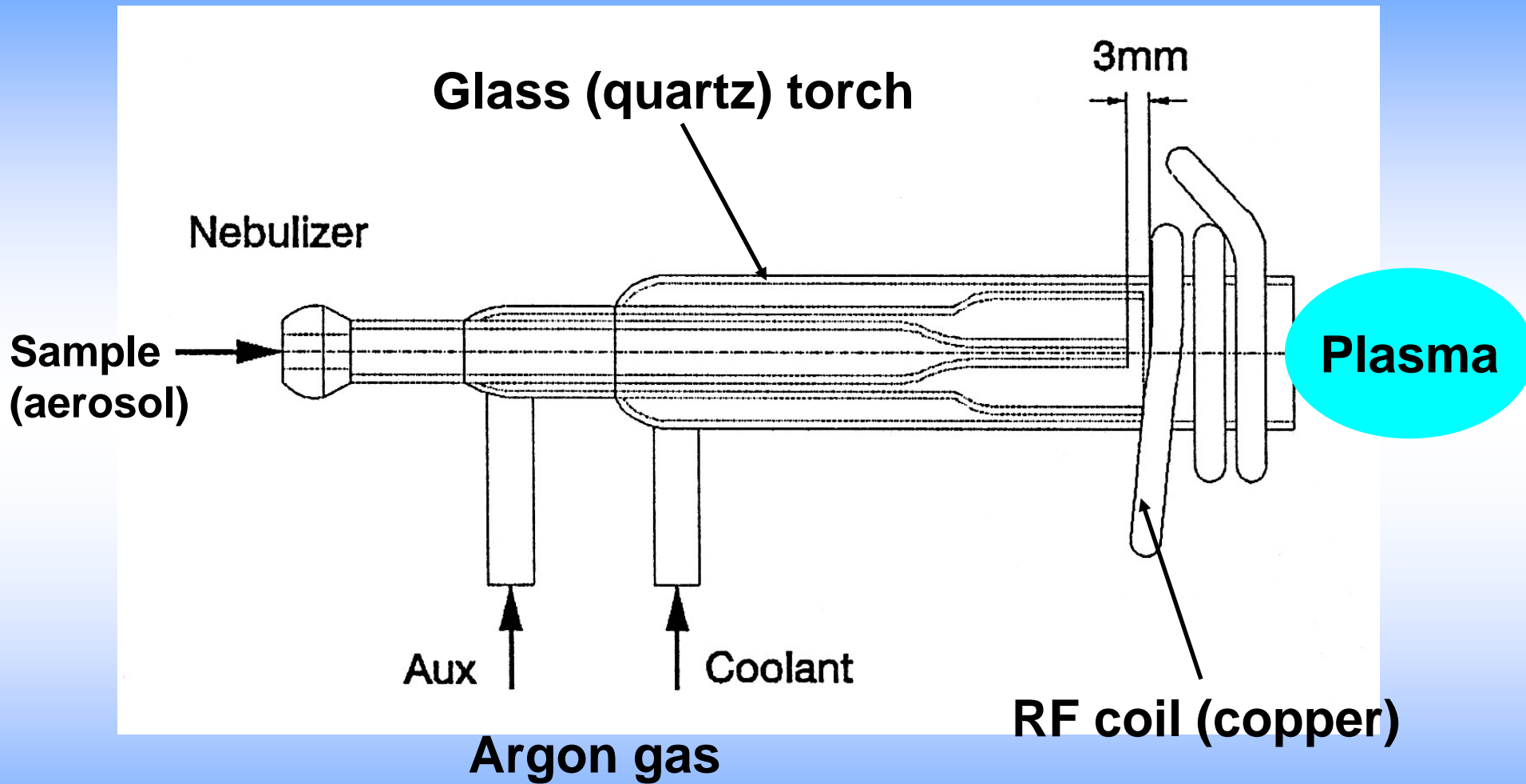
Note: The subgroup numbers 1-18 were adopted in 1964 by the International Union of Pure and Applied Chemistry. The names of elements 112-116 are the Latin equivalents of those numbers.

57 La Lanthanum (138.9055)	58 Ce Cerium (140.116)	59 Pr Praseodymium (140.90766)	60 Nd Neodymium (144.24)	61 Pm Promethium (145)	62 Sm Samarium (150.36)	63 Eu Europium (151.964)	64 Gd Gadolinium (157.25)	65 Tb Terbium (158.92534)	66 Dy Dysprosium (162.500)	67 Ho Holmium (164.93032)	68 Er Erbium (167.259)	69 Tm Thulium (168.93421)	70 Yb Ytterbium (173.04)	71 Lu Lutetium (174.967)
89 Ac Actinium (227)	90 Th Thorium (232.0381)	91 Pa Protactinium (231.03688)	92 U Uranium (238.02891)	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

THE PLASMA

Inductively **C**oupled **P**lasma **M**ass **S**pectrometry (**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



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