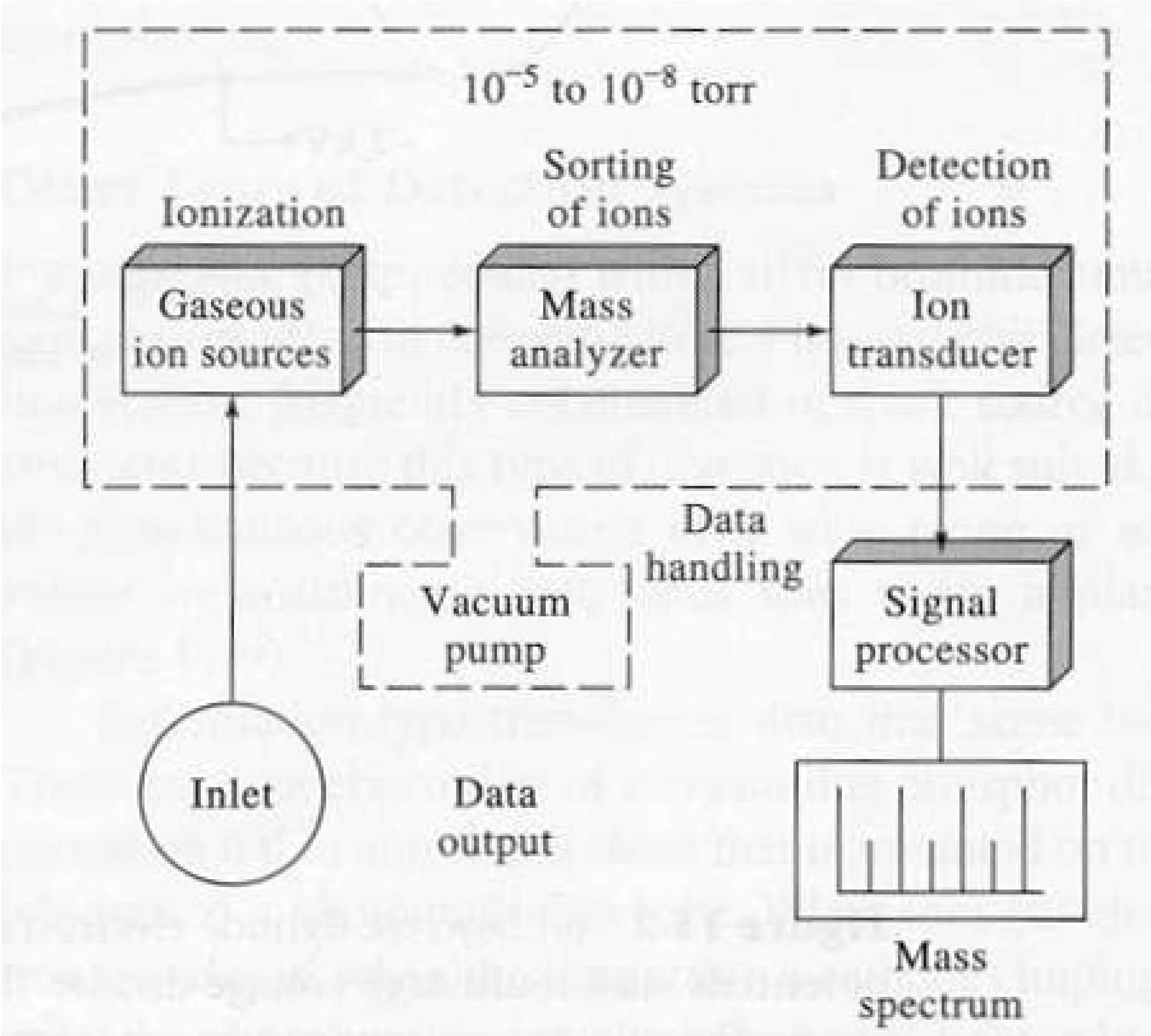
Chapter 11: Atomic Mass Spectrometry (Inorganic MS)

- Mass Spectrometers
- ICP-MS
- Spark Source MS
- Glow-Discharge MS
- Elemental Surface Analysis by MS
- Laser Ablation ICP-MS

Atomic Mass Spec processes

- Atomization (sample intro)
- Conversion to ions
- Separation based on m/z ratio
- Detection

In other forms of MS (GC-MS or MS of organic compounds), sample introduction does not involve making atoms, just getting molecules into the high vacuum system



Basic MS design components

Note high vacuum

Advantages of Atomic Mass Spec over Optical Atomic Spectrometry

1) Detection limits are better, sometimes several orders of magnitude better
2) Very simple spectra
3) Ability to measure isotope ratios

Disadvantages

1) Equipment cost
2) Instrument drift
3) Isotopic interferences

Atomic Mass Spec has been around for a long time but one of the most significant advances in this field occurred recently, the development of ICP-MS

TABLE 11-1 Types of Atomic Mass Spectrometry

Name	Acronym	Atomic Ion Sources	Typical Mass Analyzer
Inductively coupled plasma	ICPMS	High-temperature argon plasma	Quadrupole
Direct current plasma	DCPMS	High-temperature argon plasma	Quadrupole
Microwave-induced plasma	MIPMS	High-temperature argon plasma	Quadrupole
Spark source	SSMS	Radio-frequency electric spark	Double-focusing
Thermal ionization	TIMS	Electrically heated plasma	Double-focusing
Glow discharge	GDMS	Glow-discharge plasma	Double-focusing
Laser microprobe	LMMS	Focused laser beam	Time-of-flight
Secondary ion	SIMS	Accelerated ion bombardment	Double-focusing

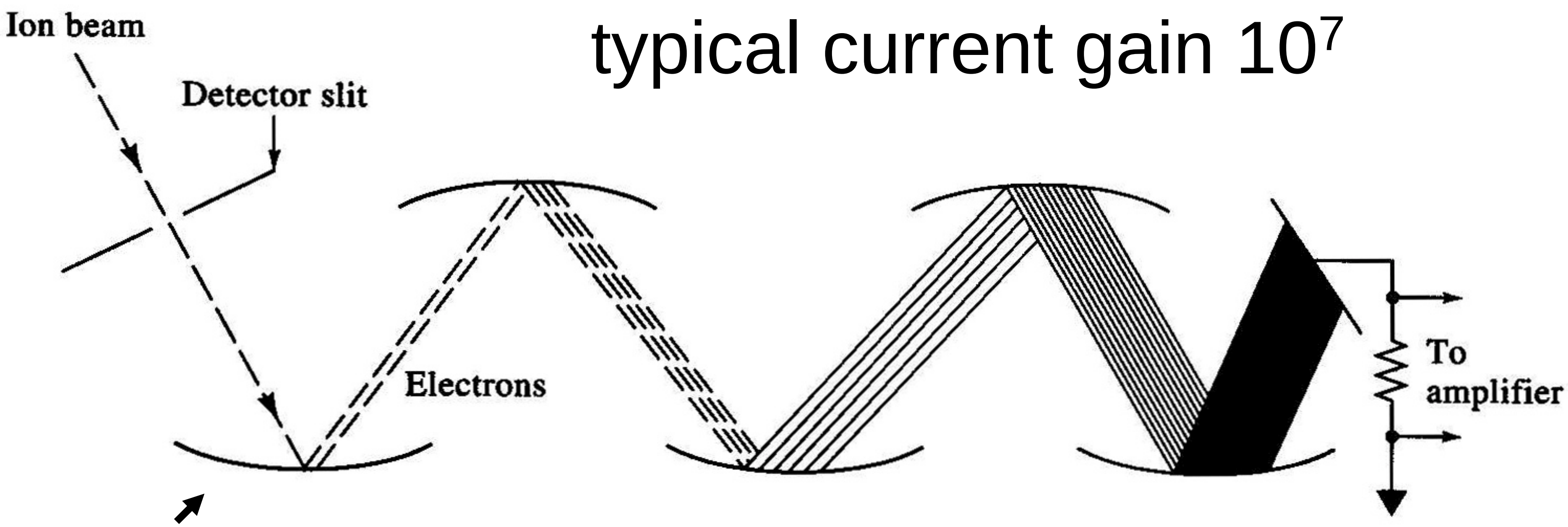
Detectors = Transducers for Mass Spec

1) Electron Multipliers – transducer of choice

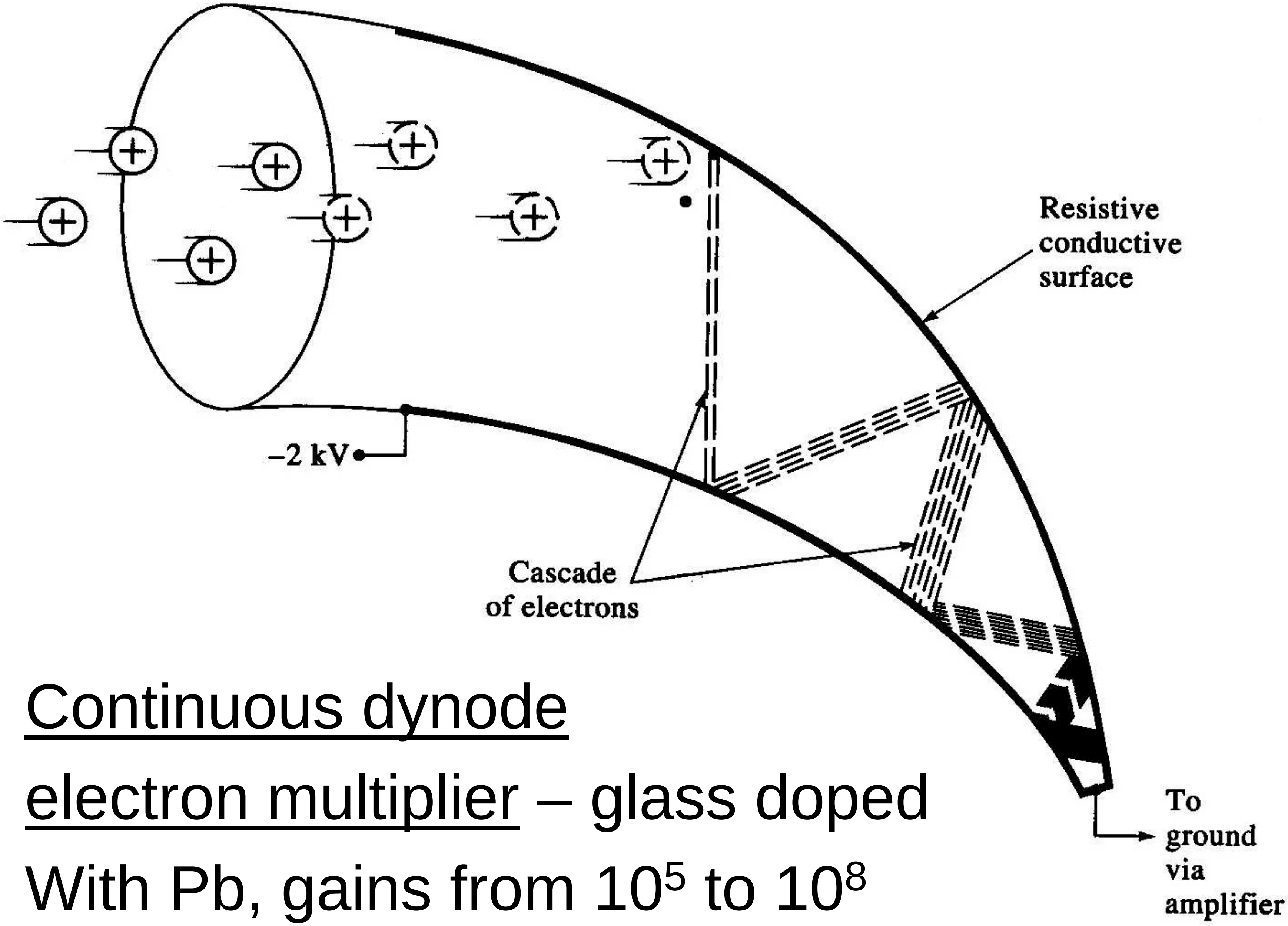
Discrete dynode electron multiplier works like a photomultiplier tube

ions → electrons → many electrons

typical current gain 10^7



Cu/Be surface



<u>Continuous dynode electron multiplier</u> – glass doped With Pb, gains from 10^5 to 10^8

2) Faraday Cup – historically important, not extremely sensitive, slow

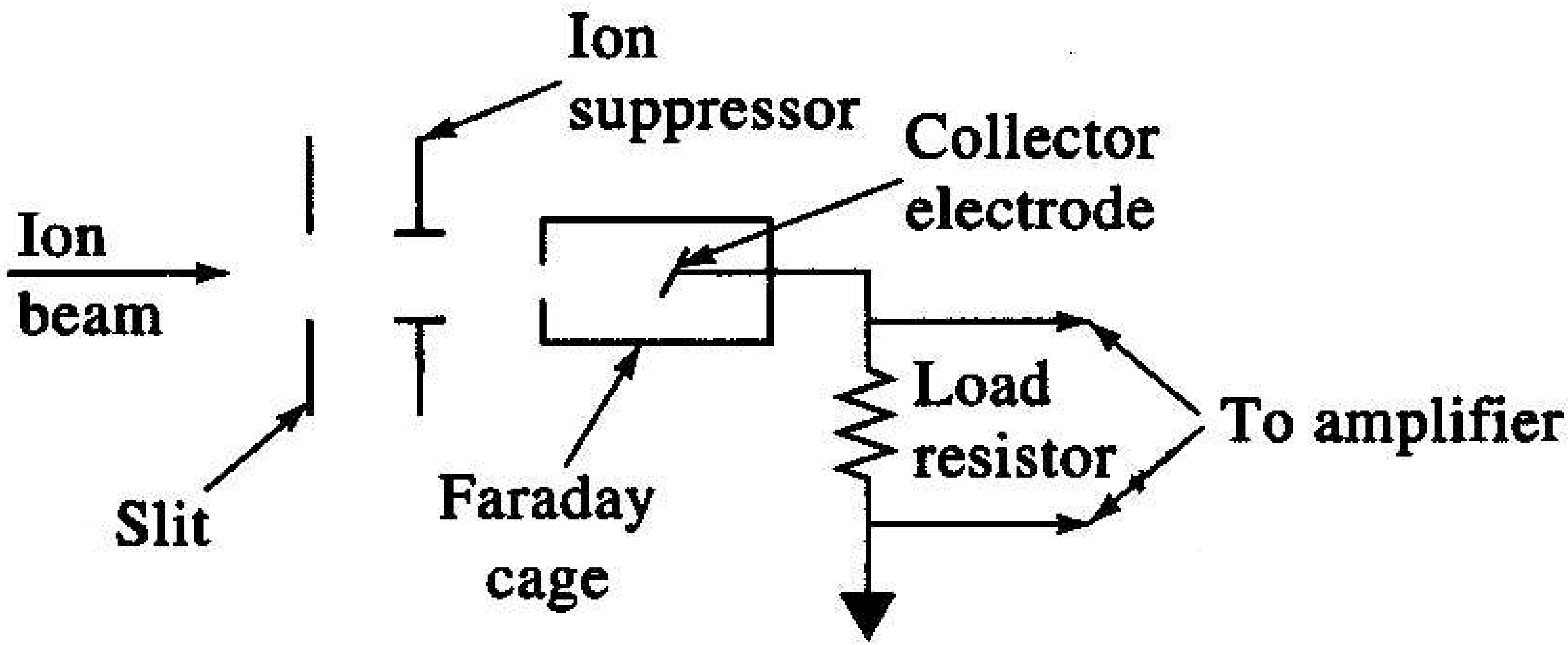


Figure 11-3 Faraday cup detector. The potential on the ion suppressor plates is adjusted to minimize differential response as a function of mass.

Separation of ions = Mass Analyzers

1) Quadrupole Mass Analyzers

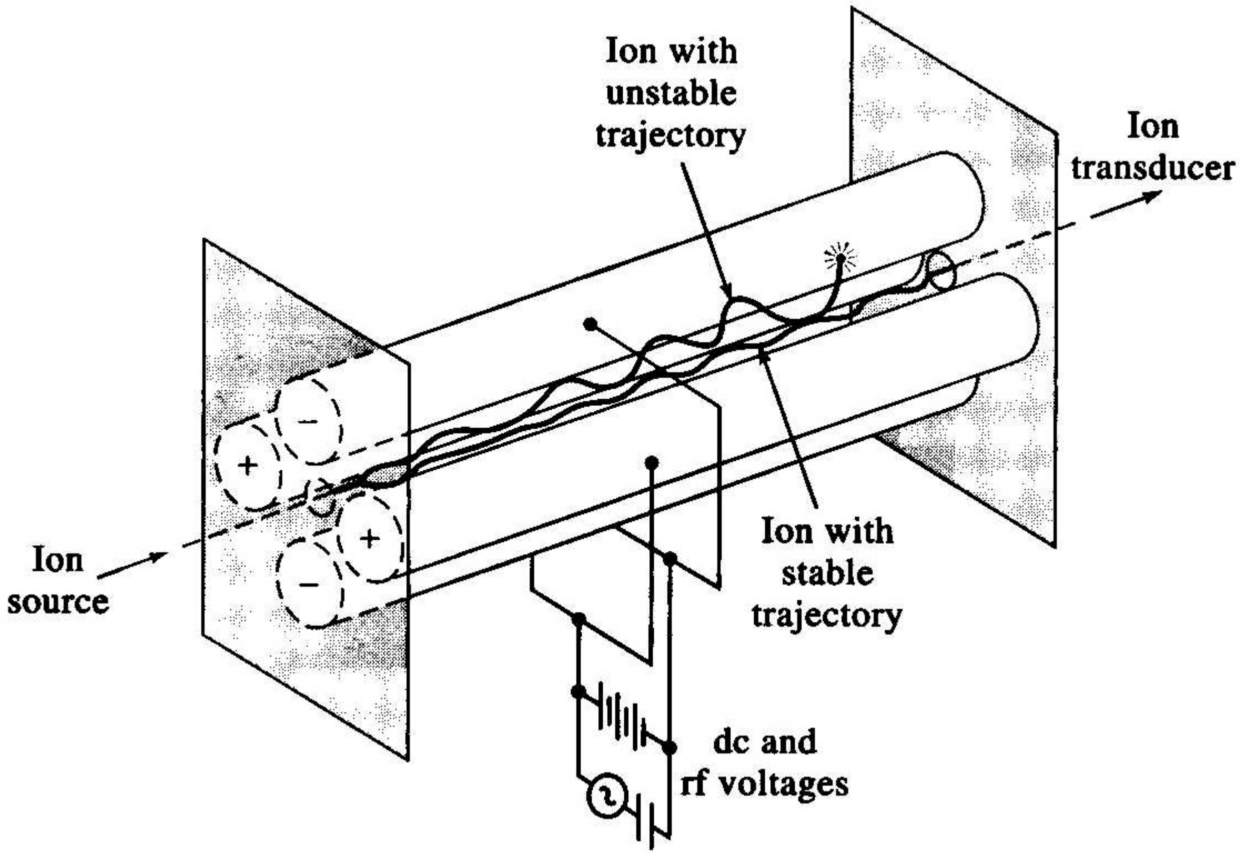


Figure 11-4 A quadrupole mass spectrometer.

Important device that acts as a mass filter passing only ions of certain m/z

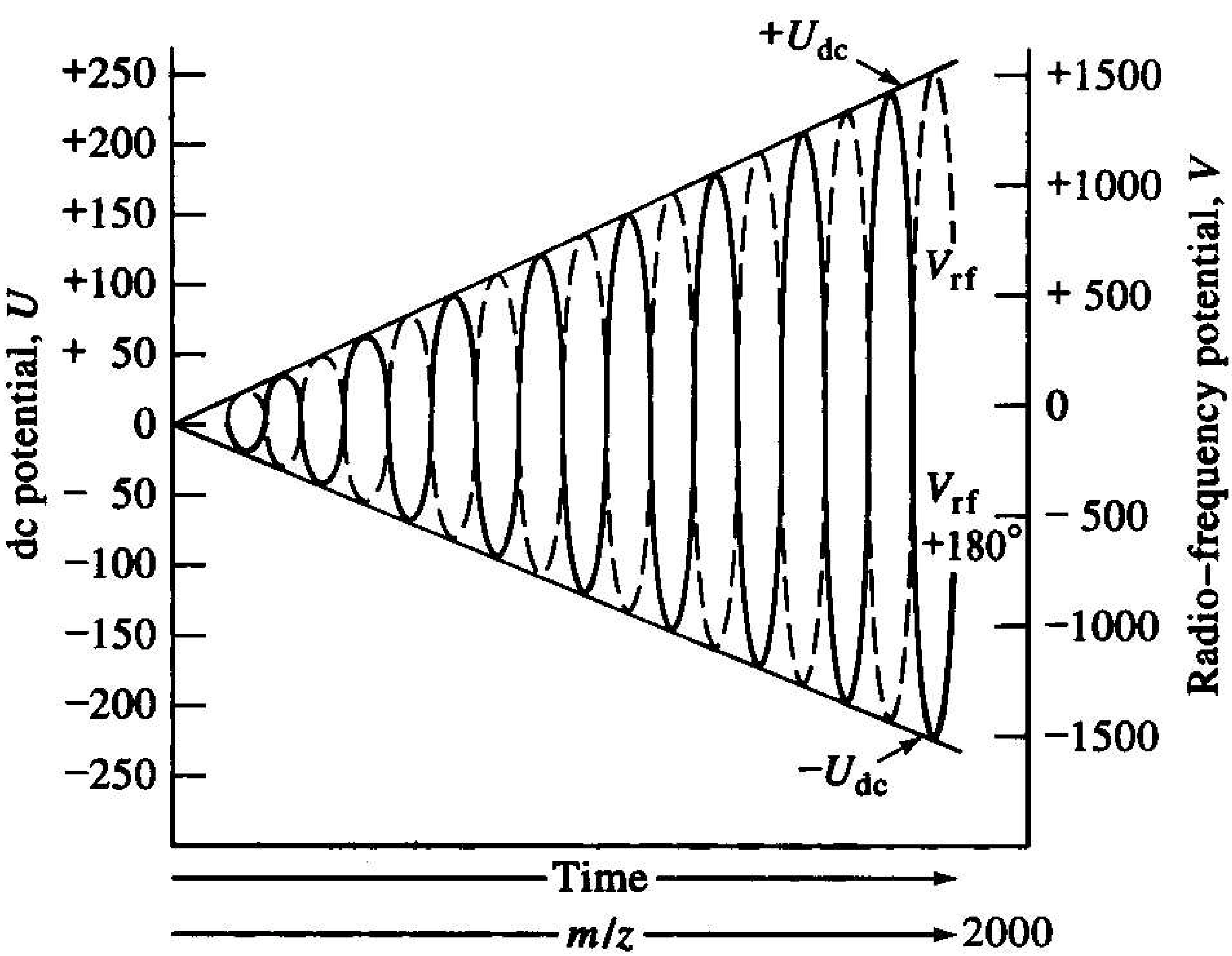


Figure 11-7 Voltage relationships during a mass scan with a quadrupole analyzer.

Separation of ions = Mass Analyzers

1) Quadrupole Mass Analyzers

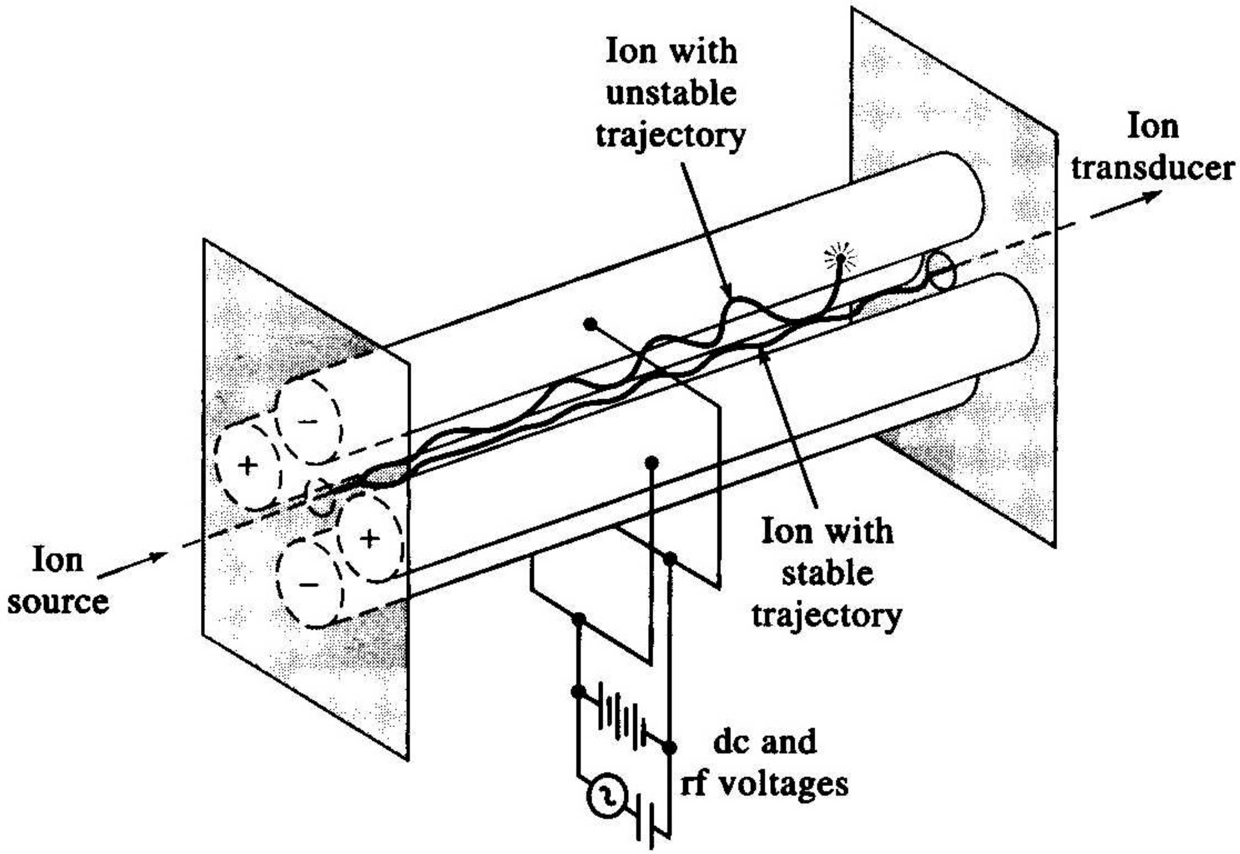
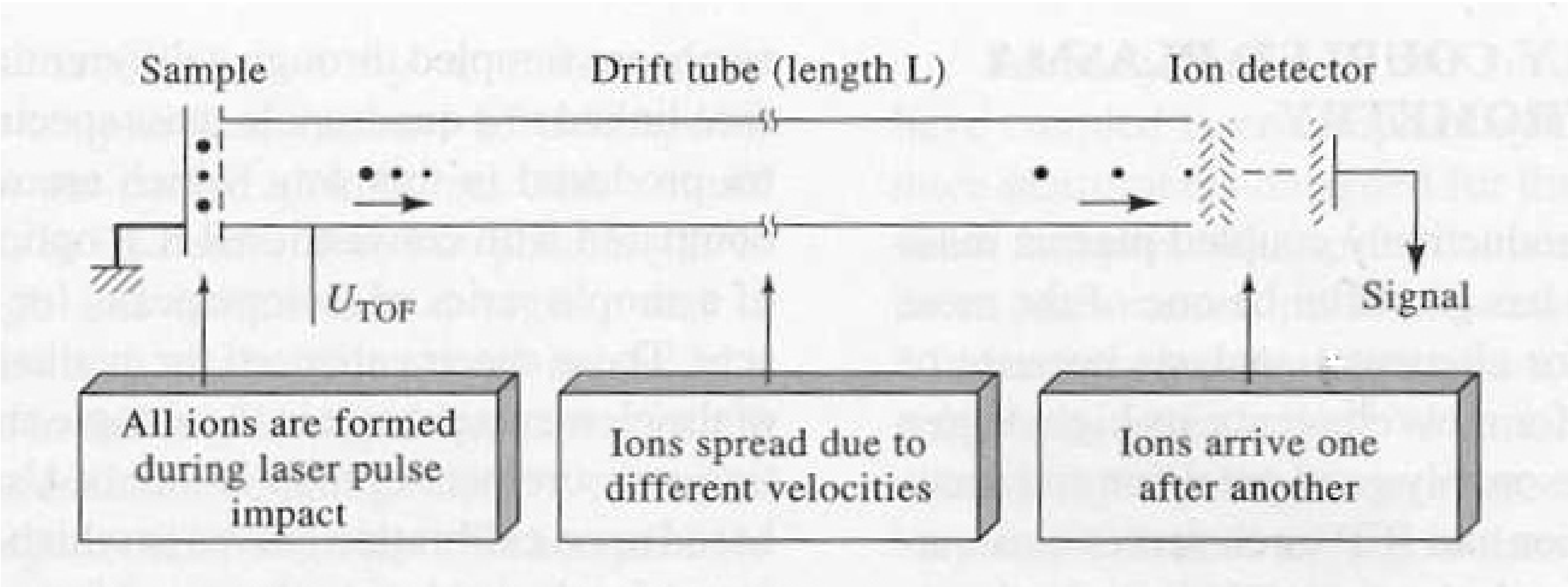


Figure 11-4 A quadrupole mass spectrometer.

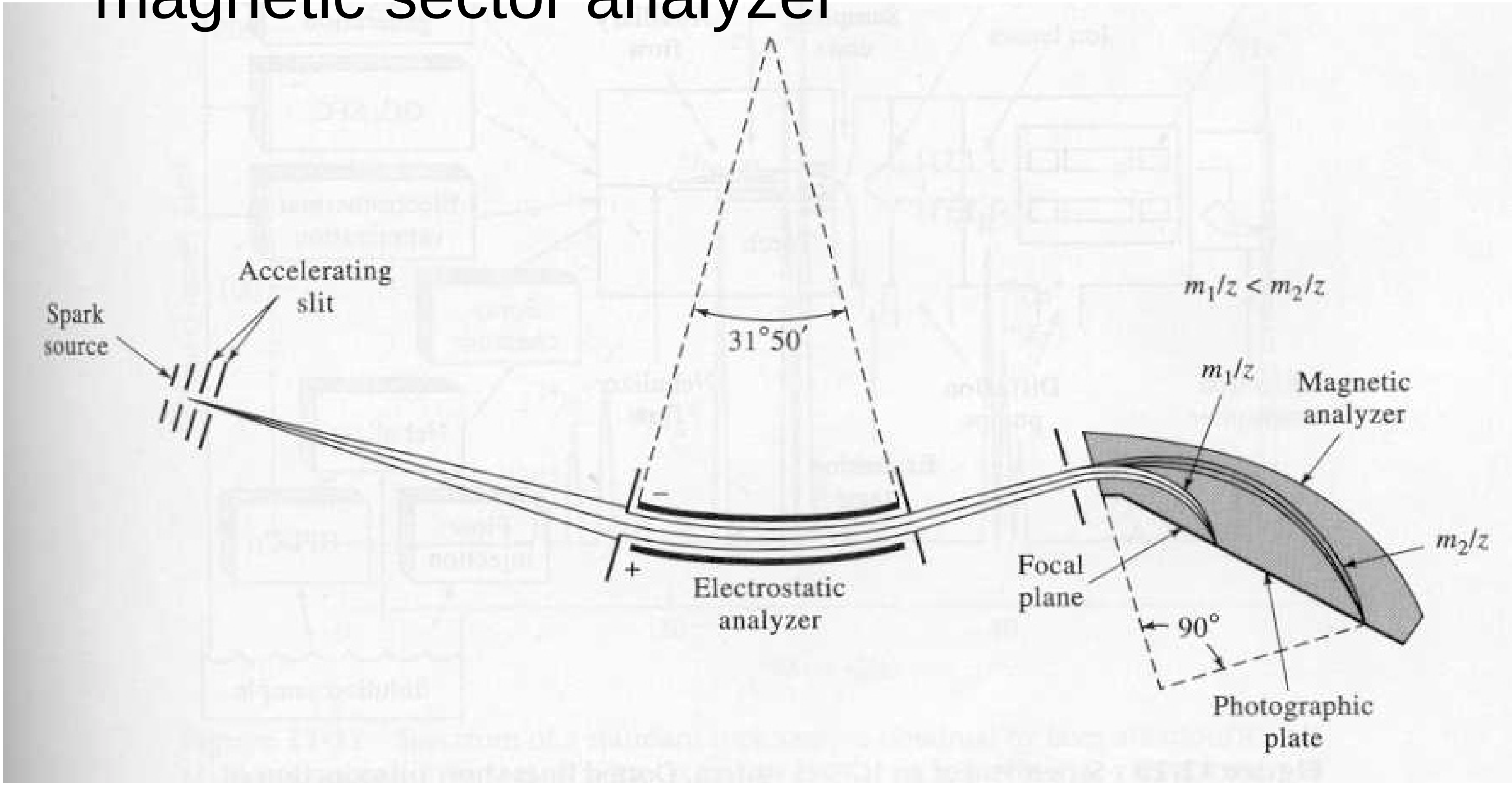
Important device that acts as a mass filter passing only ions of certain m/z

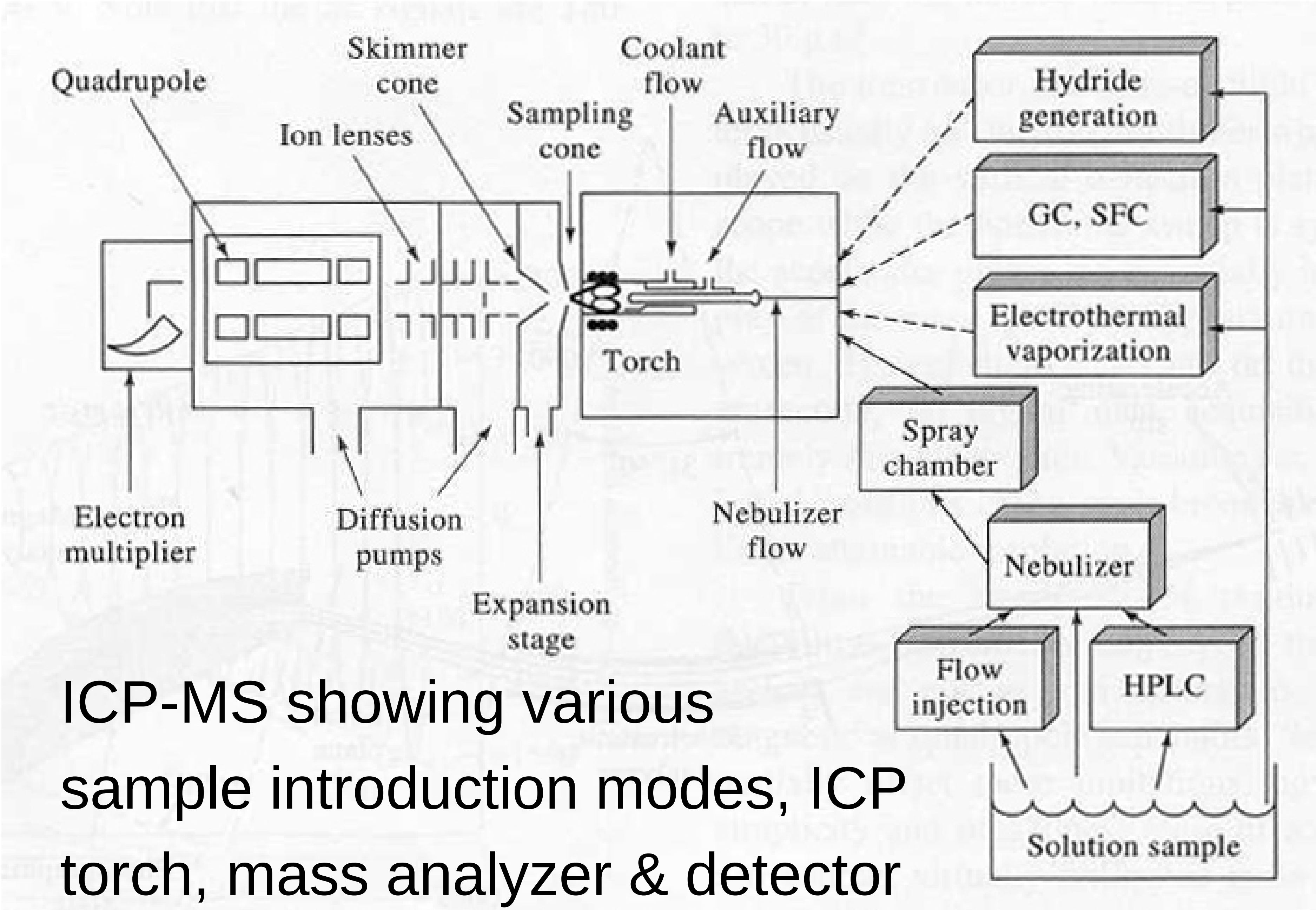
2) Time of Flight Mass Analyzers



Ions are accelerated into a field-free drift tube approximately 1 m long & separated based on kinetic energy (1 – 30 µs)

3) Double-Focusing Mass Analyzer employs electrostatic analyzer & magnetic sector analyzer



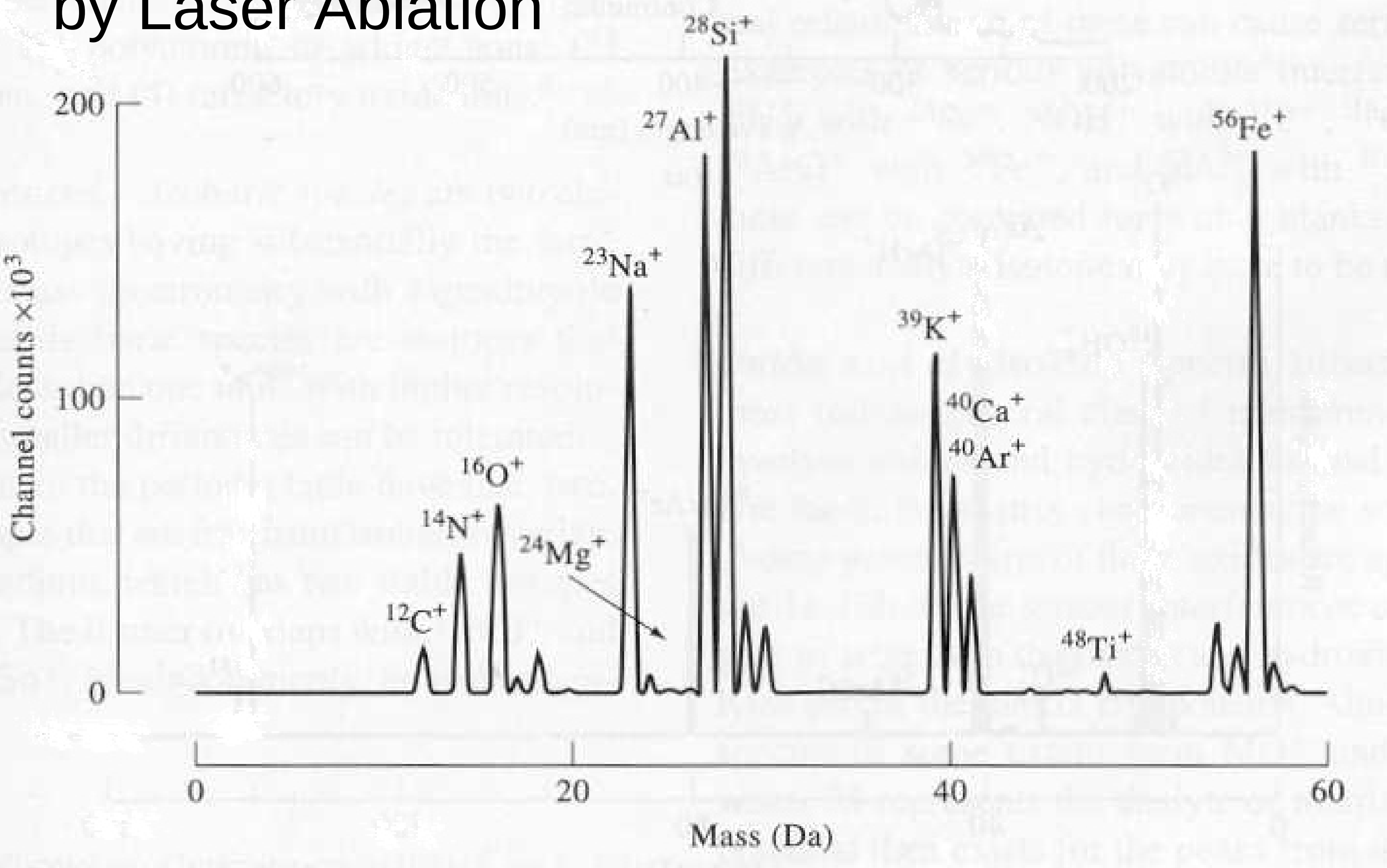


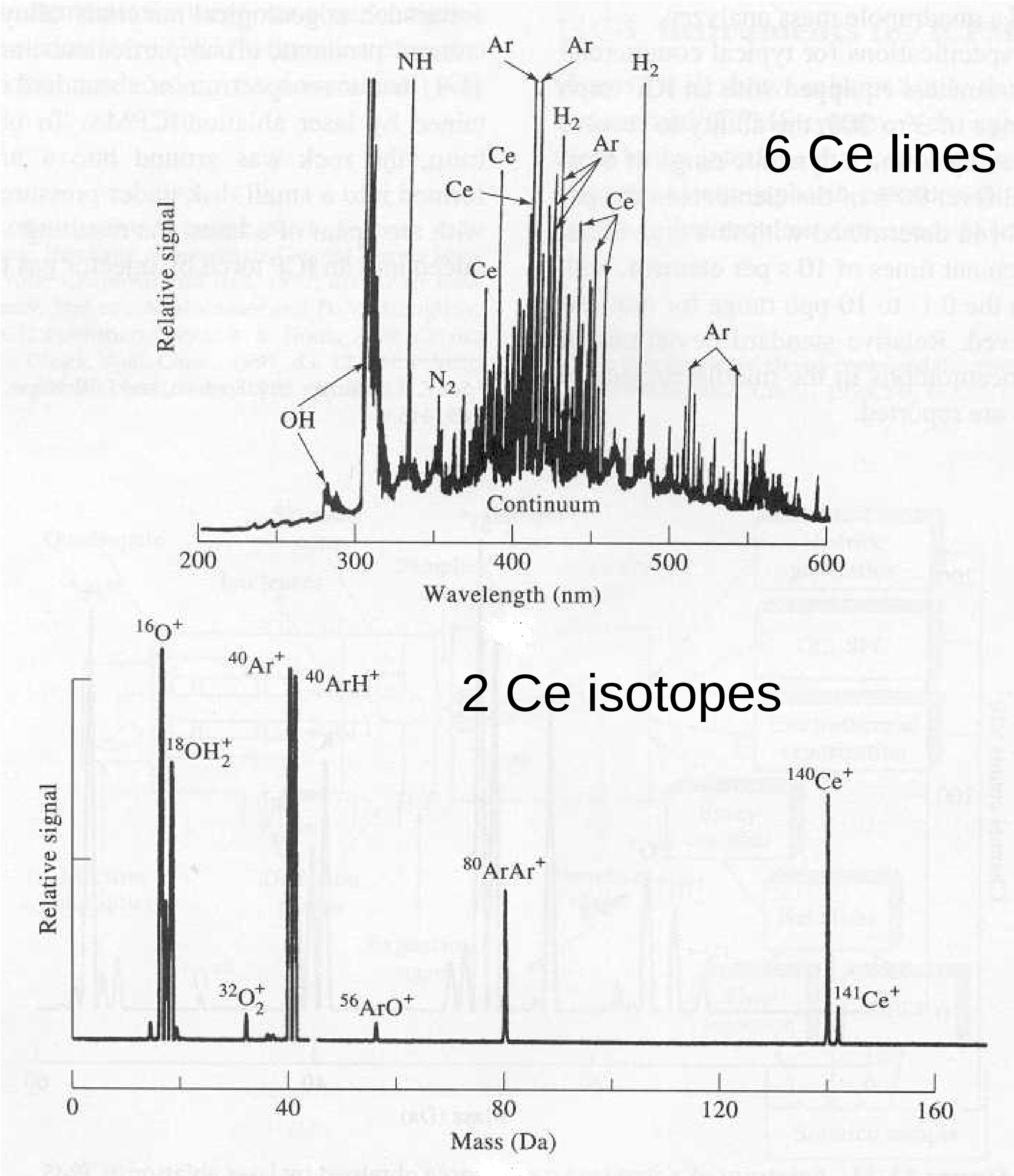
ICP-MS showing various sample introduction modes, ICP torch, mass analyzer & detector

ICP-MS

- Developed early 1980’s
- Low detection limits (0.1 to 10 ppb)
- High selectivity
- Good precision (2 - 4%) & accuracy
- m/z range 3 - 300 = 90% of periodic table
- Resolution 1 m/z
- Dynamic range 10^6
- Approximately 10 sec measurement time
- Various sample introduction methods

ICP Mass Spectrum of rock sample produced by Laser Ablation





Comparison of ICP optical emission spectrum & ICP-MS spectrum for 100 ppm cerium (Ce)

Spectroscopic Interferences

1) Isobaric interferences – element isotopes with same m/z (e.g. $^{113}In^+$ & $^{115}In^+$ overlap with $^{113}Cd^+$ & $^{115}Sn^+$)
2) Polyatomic ion interferences – formed from interactions of species in plasma
3) Oxide & Hydroxide species interference – MO^+ or MOH^+ formed in plasma
4) Matrix effects – similar to optical atomic spectrometry

TABLE 11-2 Calcium Oxide and Hydroxide Species and Other Potential Interferences in the Mass Region for Ni Determination

m/z	Element	Interferences
56	Fe(91.66)	^{40}ArO, ^{40}CaO
57	Fe(2.19)	$^{40}ArOH$, $^{40}CaOH$
58	Ni(67.77), Fe(0.33)	^{42}CaO, NaCl
59	Co(100)	^{43}CaO, $^{42}CaOH$
60	Ni(26.16)	$^{43}CaOH$, ^{44}CaO
61	Ni(1.25)	$^{44}CaOH$
62	Ni(3.66)	^{46}CaO, Na_2O, NaK
63	Cu(69.1)	$^{46}CaOH$, $^{40}ArNa$
64	Ni(1.16), Zn(48.89)	$^{32}SO_2$, $^{32}S_2$, ^{48}CaO
65	Cu(30.9)	$^{33}S^{32}S$, $^{33}SO_2$, $^{48}CaOH$

Multielement Analysis

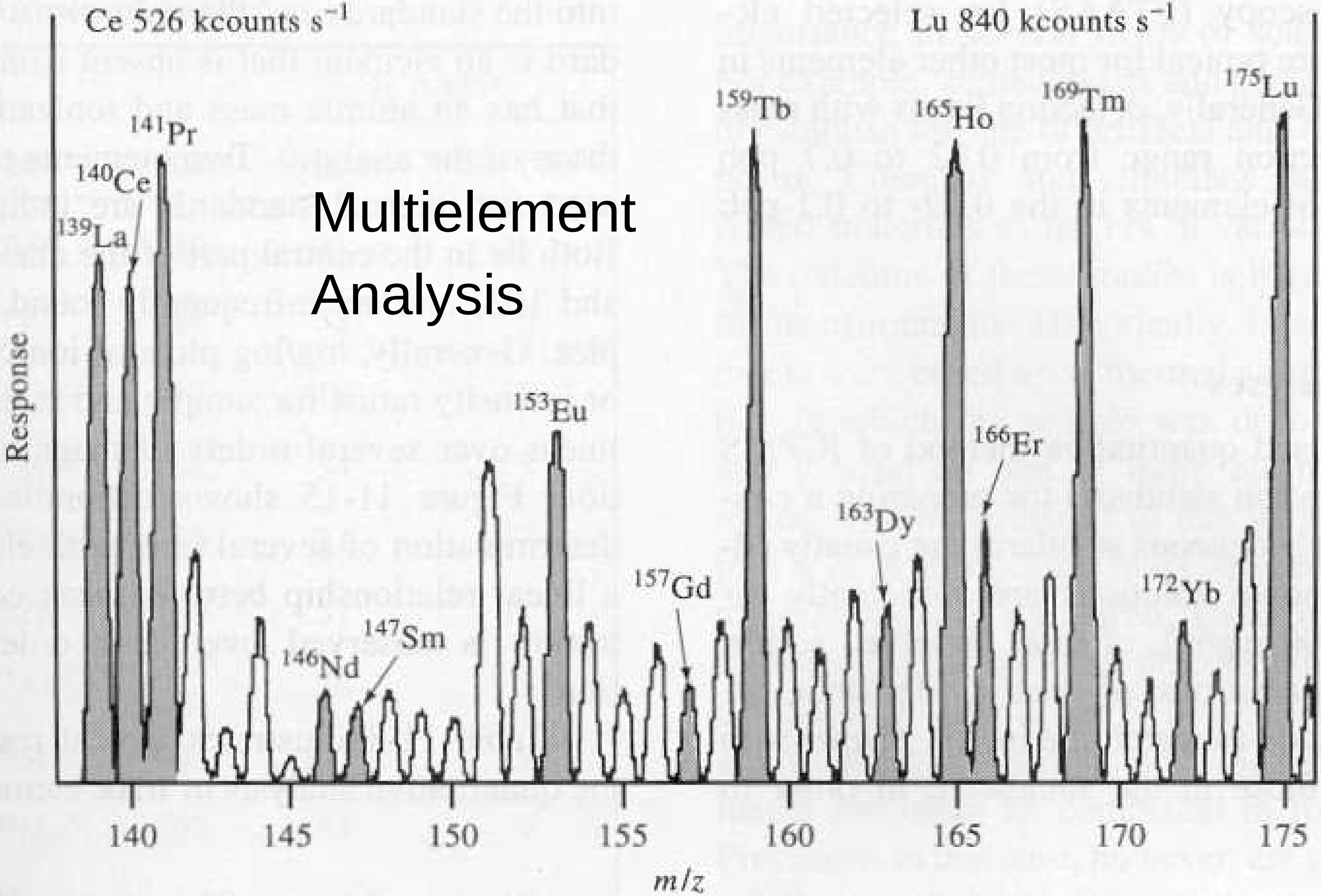


Figure 11-13 ICPMS spectrum for the rare earth elements. Solutions contain 1 μg/mL of each element. *(From K. E. Jarvis,* J. Anal. Atom. Spectrom., *1989*, 4, *563.*

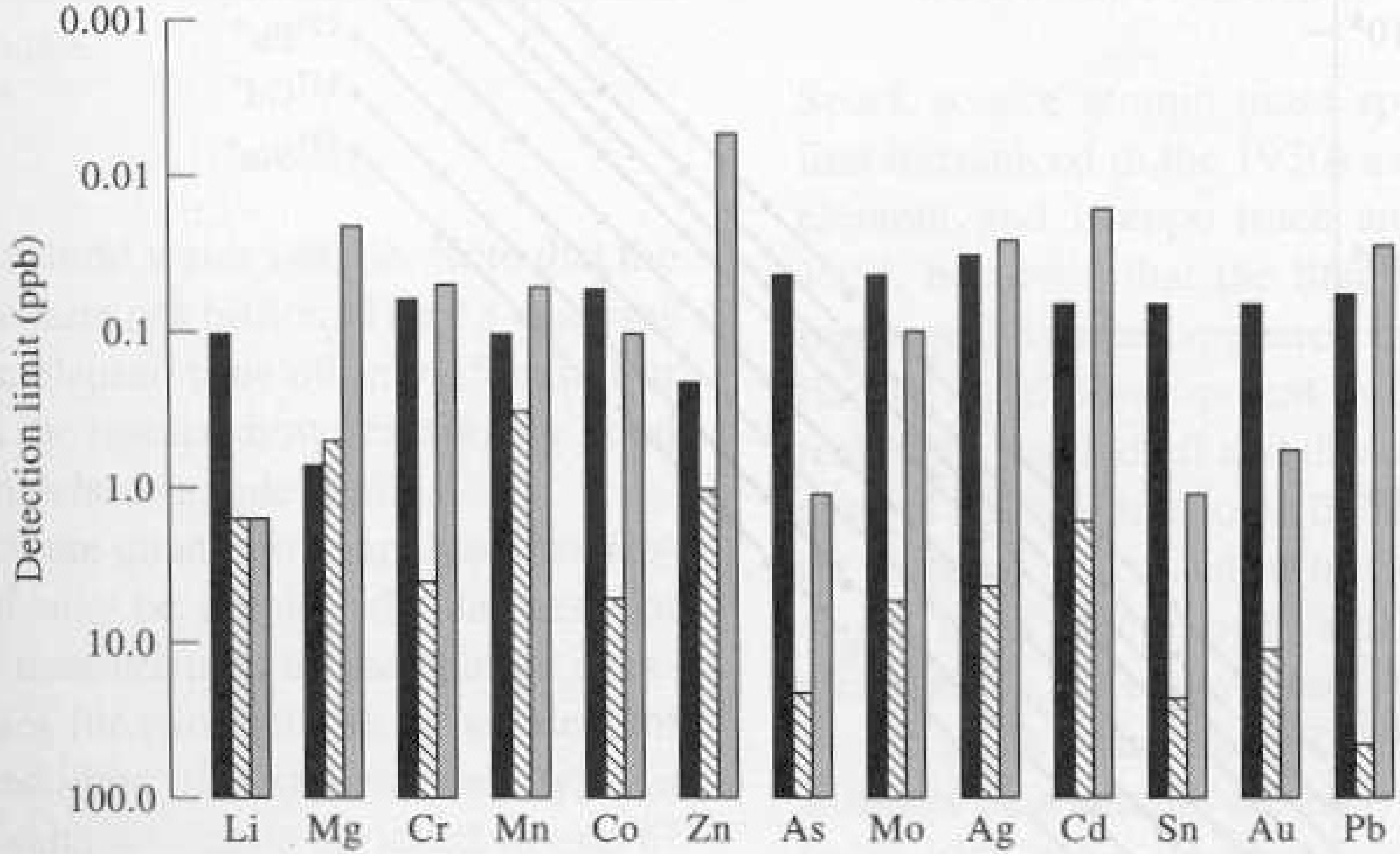


Figure 11-14 Detection limits for selected elements by ICPMS (black bars) compared with those for ICP OES (cross-hatched bars) and ETAAS (gray bars) (inductively coupled plasma optical emission spectrometry and electrothermal atomic absorption spectrometry, respectively), plotted on a logarithmic scale in concentrations of ppb (or μg/L). Because ETAAS detection limits are inherently in mass units (pg), they have been converted to concentration by assuming a 20 μL sample. *(From M. Selby and G. M. Hieftje,* Amer. Lab., *1987 (8), 20. With permission.)*

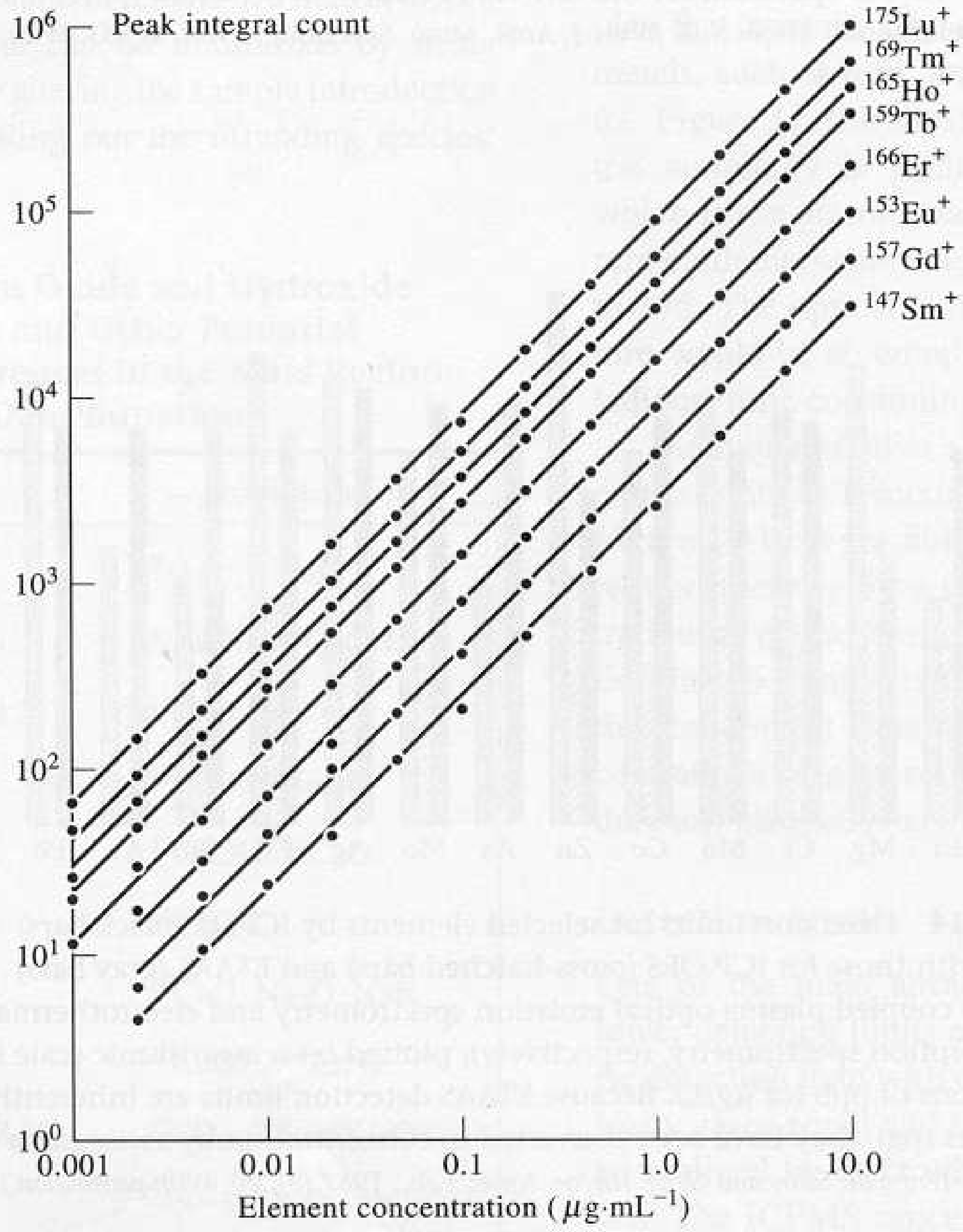


Figure 11-15 ICPMS calibration curves for several rare earth elements.

Good linearity

TABLE 11-3 Quantitative Determination of Trace Elements in a Standard Sample of Water

Element	Ion	NBS[a]	ICP-MS[a] Mean	ICP-MS[a] RSD (%)[b]
Beryllium	$^{9}Be^{+}$	19	21	20
Vanadium	$^{51}V^{+}$	54	52	6
Chromium	$^{52}Cr^{+}$	17	18	12
Manganese	$^{55}Mn^{+}$	32	34	5
Cobalt	$^{59}Co^{+}$	19	21	7
Zinc	$^{66}Zn^{+}$	69	57	11
Arsenic	$^{75}As^{+}$	77	76	5
Strontium	$^{88}Sr^{+}$	243	297	7
Molybdenum	$^{98}Mo^{+}$	97	134	9
Silver	$^{107}Ag^{+}$	2.8	3.5	16
Cadmium	$^{114}Cd^{+}$	10	13	22
Barium	$^{138}Ba^{+}$	47	74	17
Lead	$^{208}Pb^{+}$	27	31	8

[a] Concentration in parts per billion.
[b] Based on 10 determinations.

Isotope Ratio Measurements – ICP-MS makes measurement of isotope ratios for a sample become relatively easy in many cases. This is a powerful technique that can identify elements from different sources, allow use of tracers, etc.

Chapter 26: An Introduction to Chromatographic Separations

- Column Chromatography
- Migration Rates
  - Distribution Contstants
  - Retention Times
  - Selectivity Factor
- Zone Broadening & Column Efficiency
- Optimizing Performance
- Resolution