Chapter 10: Emission Spectroscopy Using Plasmas, Arcs or Sparks

- Inductively Coupled Plasma (ICP)
- Direct Current Plasma (DCP)
- Arcs and Sparks

Still talking about Optical Atomic Spectrometry

Focus primarily on plasmas as sources

Discuss instrument design

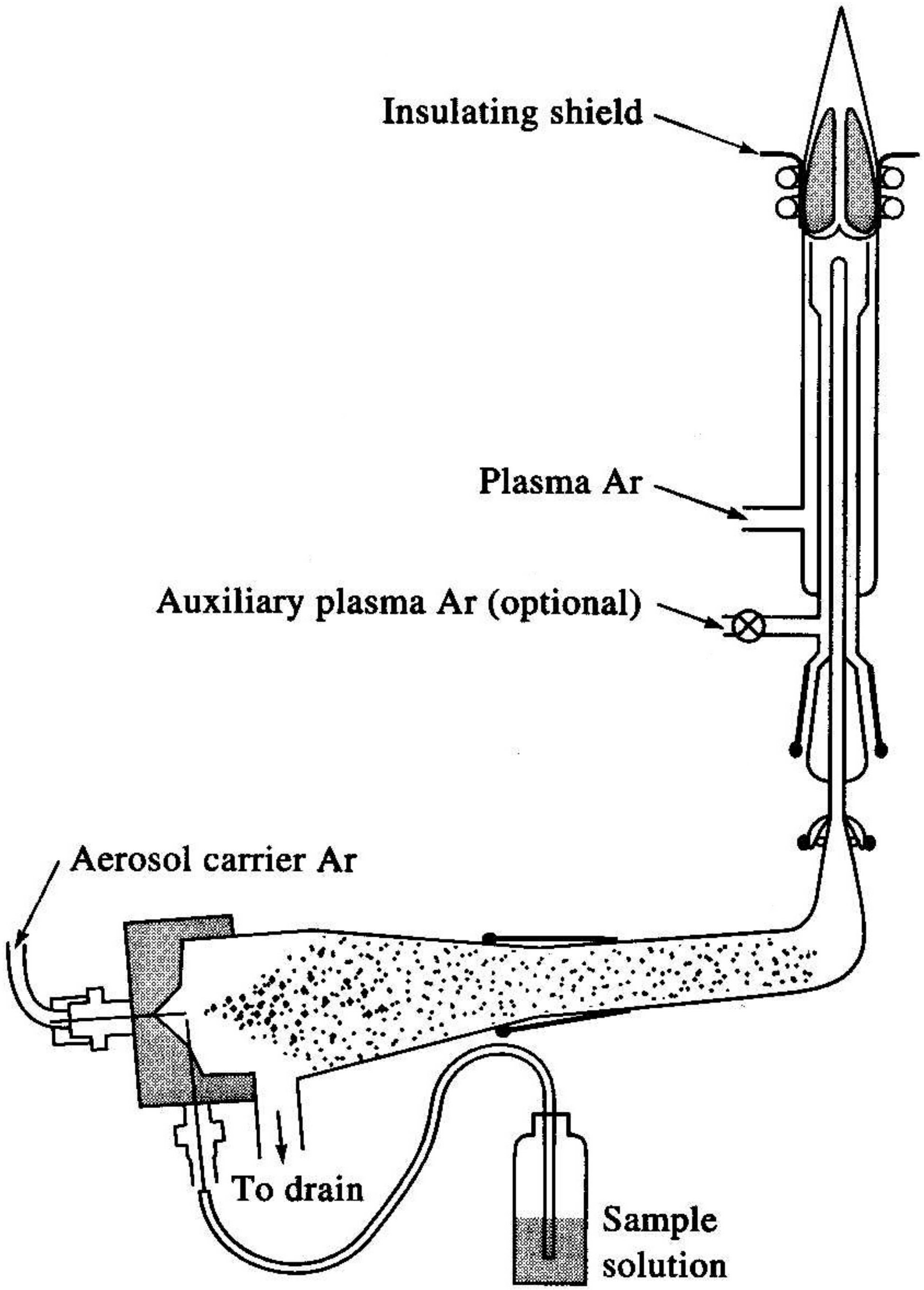
and other considerations

TABLE 10-1 Desirable Properties of an Emission Spectrometer

1. High resolution (0.01 nm or $\lambda/\Delta\lambda > 100{,}000$)
2. Rapid signal acquisition and recovery
3. Low stray light
4. Wide dynamic range ($>10^6$)
5. Accurate and precise wavelength identification and selection
6. Precise intensity readings (<1% RSD at 500 × the detection limit)
7. High stability with respect to environmental changes
8. Easy background corrections
9. Computerized operation: readout, storage data manipulation, etc.

Sources

- In AE the plasma, flame, arc or spark act as the device for atomization and the source to excite the atoms – no light source needed
- High temperatures generate a significant population of excited state atoms from the Boltzmann distribution
- High temp. sources also remove or burn off many potentially problematic molecular species that might result in interferences



ICP Torch with sample introduction system (nebulizer and spray chamber)

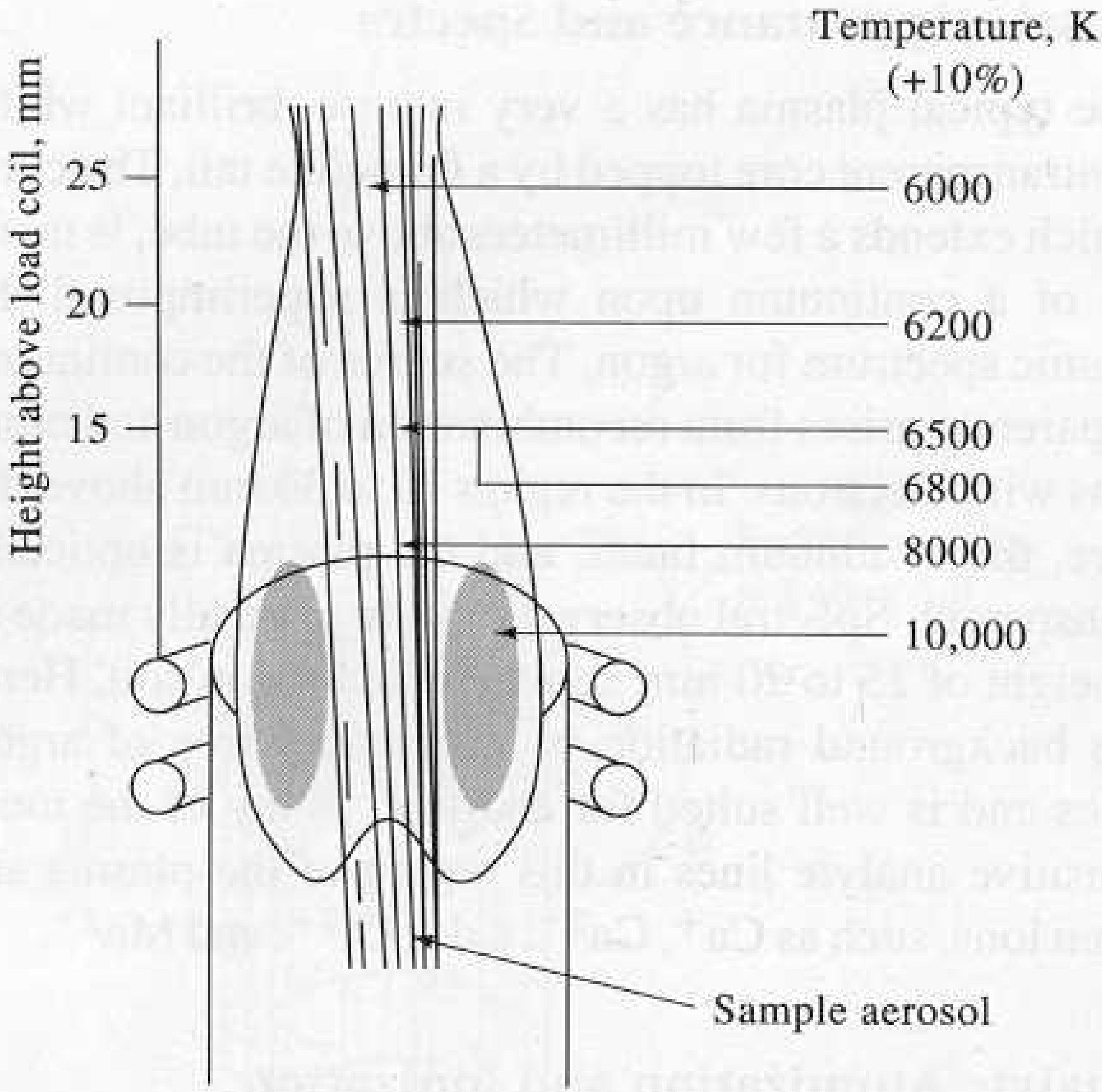


Figure 10-4 Temperatures in a typical inductively coupled plasma source. *(From V. A. Fassel,* Science, *1978,* 202, *186.*

ICP Temps.

The viewing area for each element is typically reported as mm above the load coil

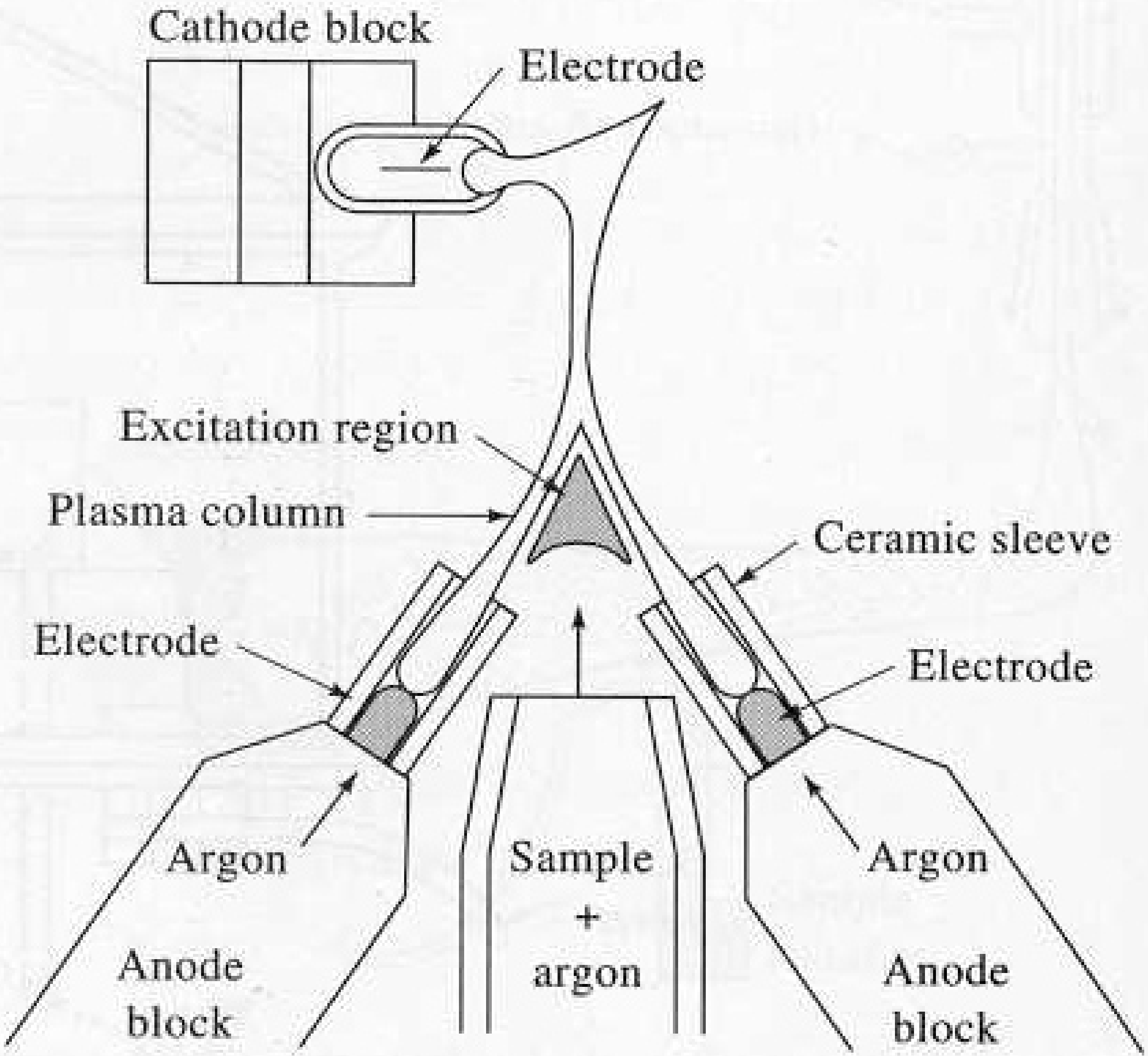


Figure 10-5 A three-electrode dc plasma jet. *(Courtesy of Spectra Metrics, Inc. Haverhill, MA.)*

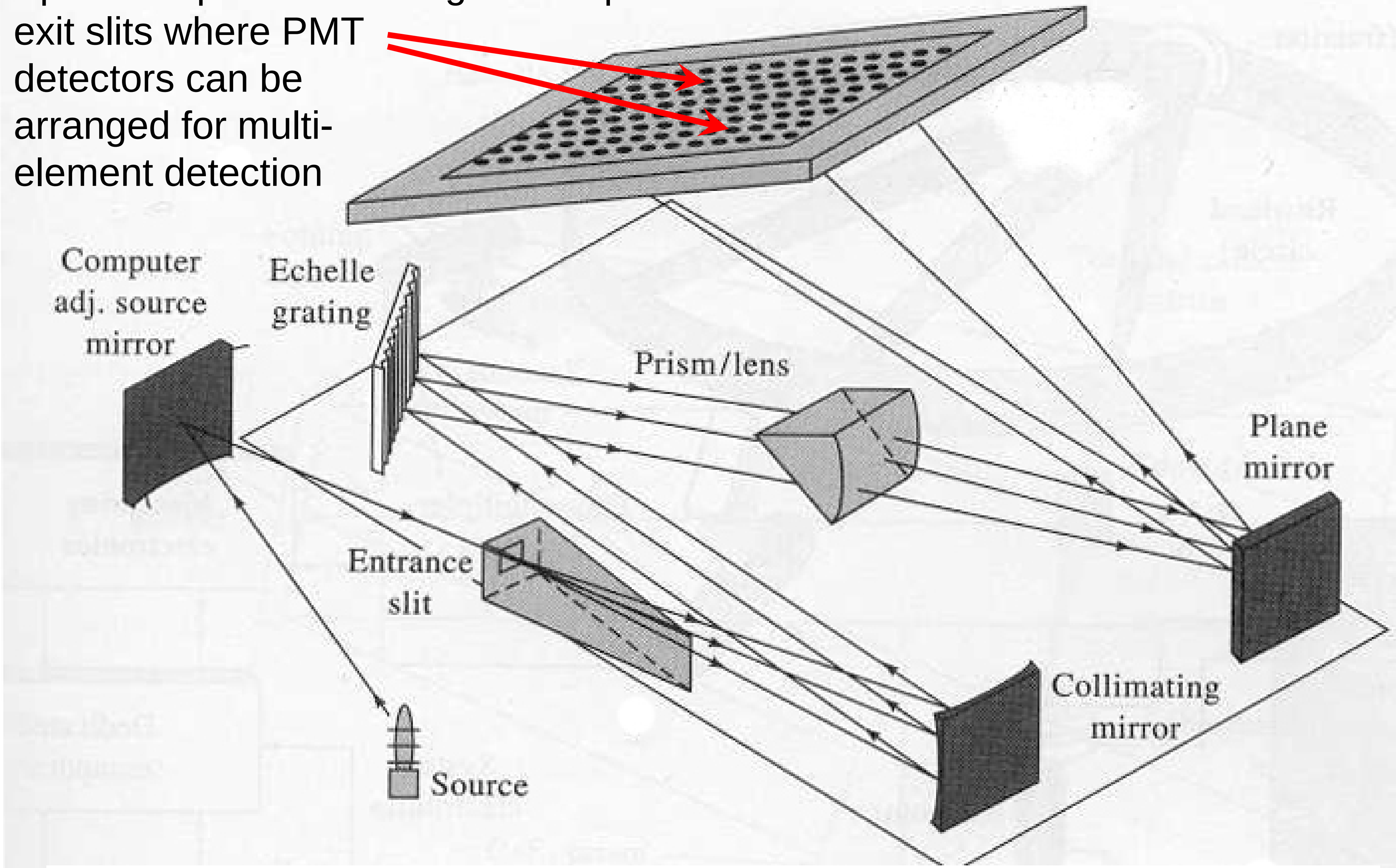
Direct Current Plasma (DCP) Torch

Lab will involve use of DCP for multielement analysis

Wavelength Selection Detection

- Same concepts as Molecular Spectroscopy
- Grating and prism based monochromators
- Need very high resolution because atomic lines are narrow & many – overlaps possible
- Can do simultaneous multi-element analysis
- Two types of general approaches:
  - Fixed optical arrangements = direct reading spec
  - Slew scanning or sequential analysis

Aperature plate consisting of multiple exit slits where PMT detectors can be arranged for multi-element detection



High resolution Echelle Polychromator as used in the DC Plasma AE Spectrometer & other instruments

Another diagram of an Echelle optical system employing a Charge Injection Transducer (i.e. a 2D array based detector)

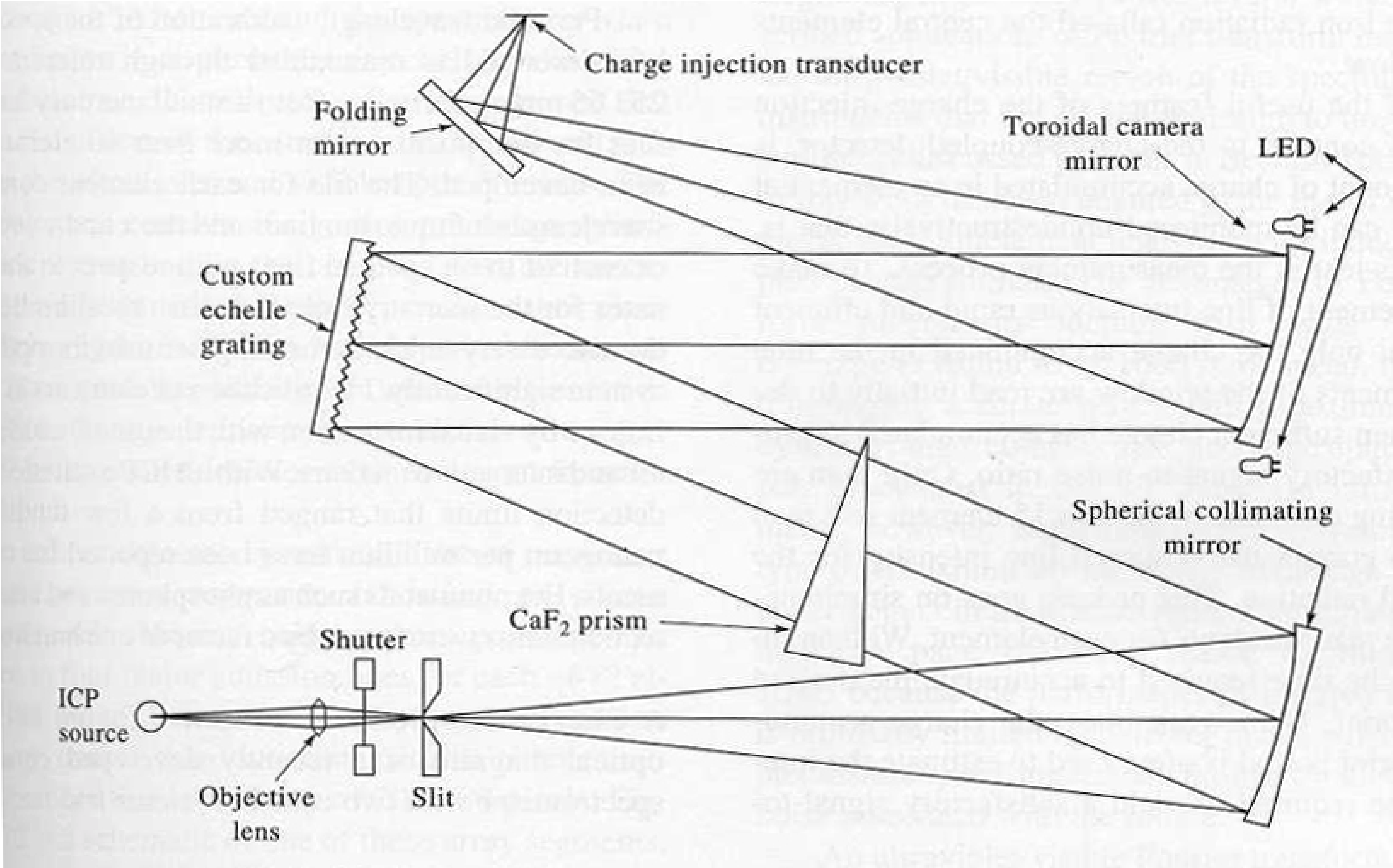


Figure 10-9 Optical diagram of an echelle spectrometer with a charge-injection detector.
(From R. B. Bilhorn and M. B. Denton, Appl. Spectrosc., 1990, 44, 1615. With permission.)

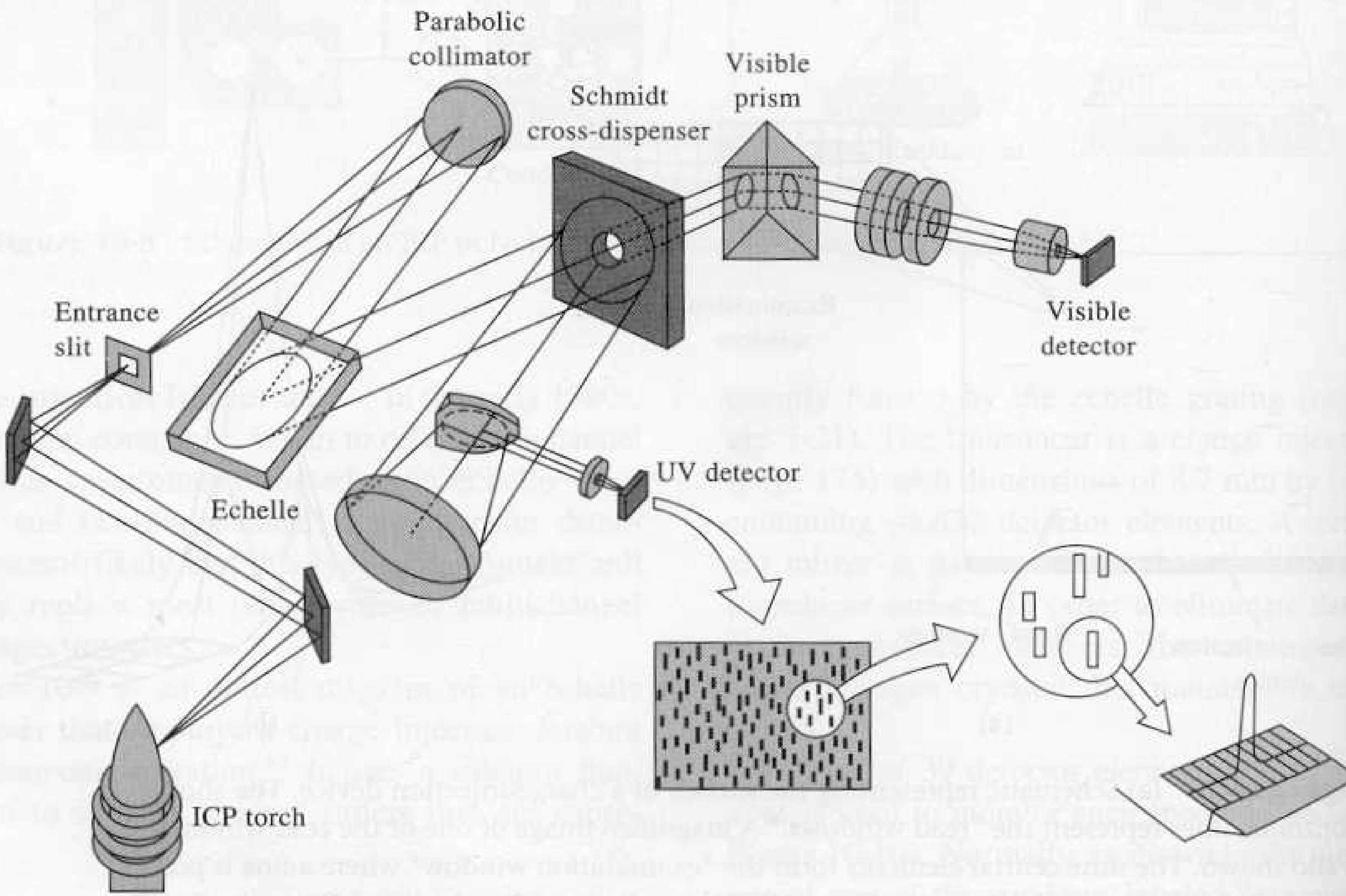


Figure 10-11 An echelle spectrometer with segmented array of charge-coupled devices. *(From T. W. Barnard et al.,* Anal. Chem., *1993, 65, 1232. With permission.)*

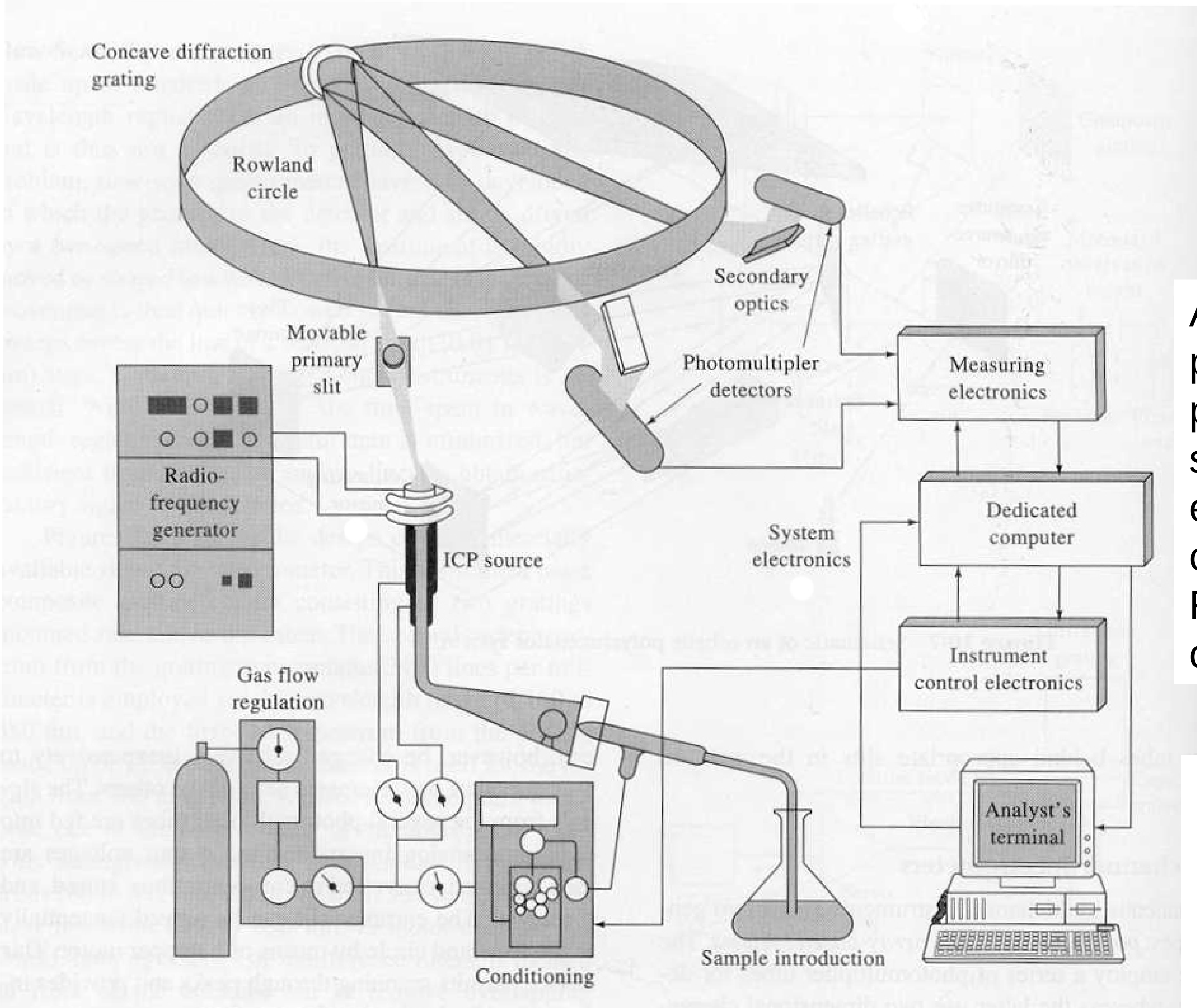


Figure 10-8 Schematic of an ICP polychromator. *(Courtesy of Thermo Jarrell Ash Corp.)*

Another plasma polychromator system employing the classic Rowland circle design

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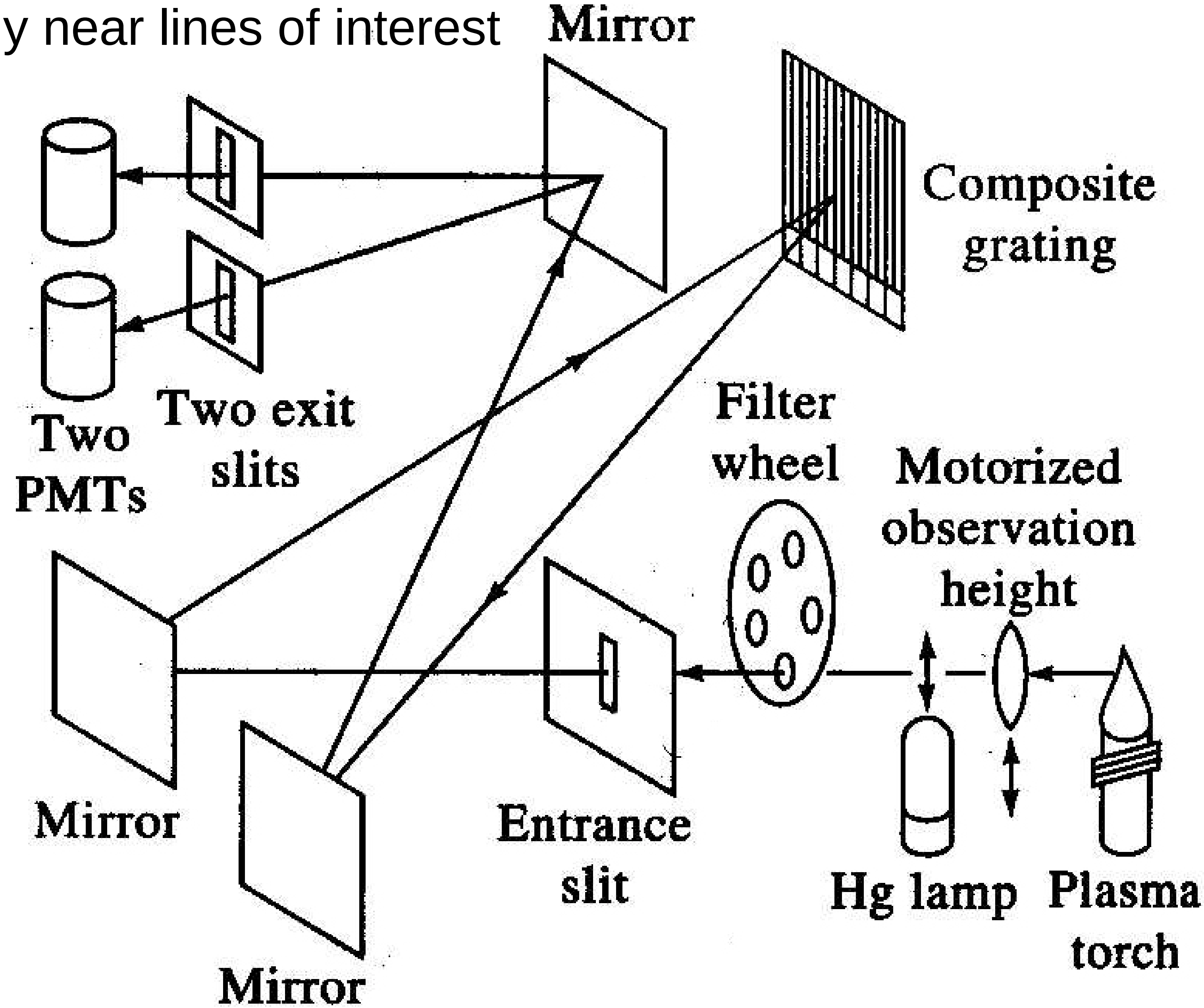
entrance slit, grating & exit slits are located in a circular arrangement

Slew-Scan spectrometer scans rapidly between lines & slowly near lines of interest



Analytical considerations

- More than one emission line can be used for analytical purposes
  - To avoid interferences
  - To reduce sensitivity
- Calibration curves highly linear – large dynamic range
- Internal standards sometimes used to remove matrix interferences
- Spectrochemical buffers added to samples & standards to control ionization

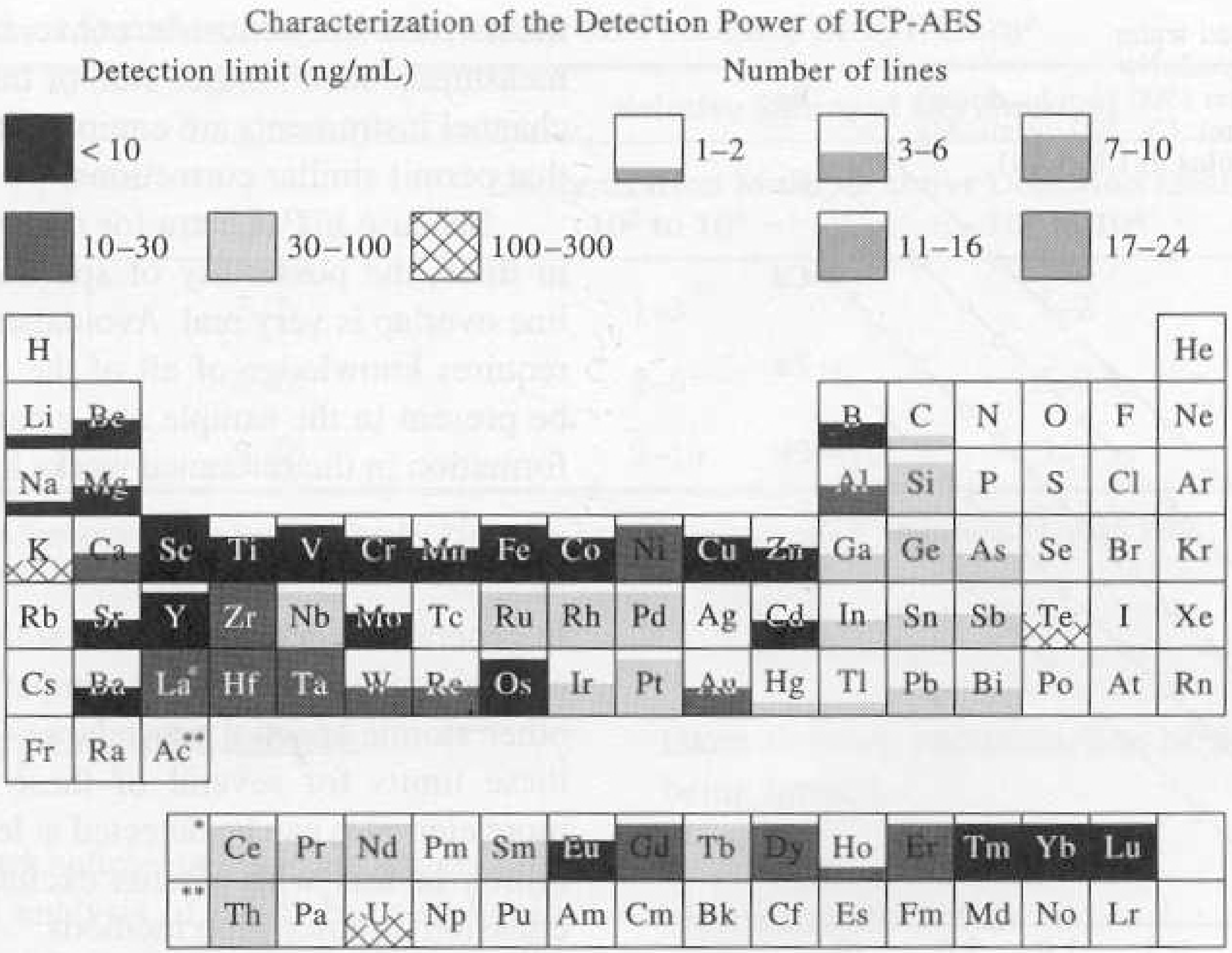


Figure 10-13 Periodic table characterizing the detection power and number of useful emission lines of ICP by employing a pneumatic nebulizer. The degree of shading indicates the range of detection limits for the useful lines. The area of shading indicates the number of useful lines.

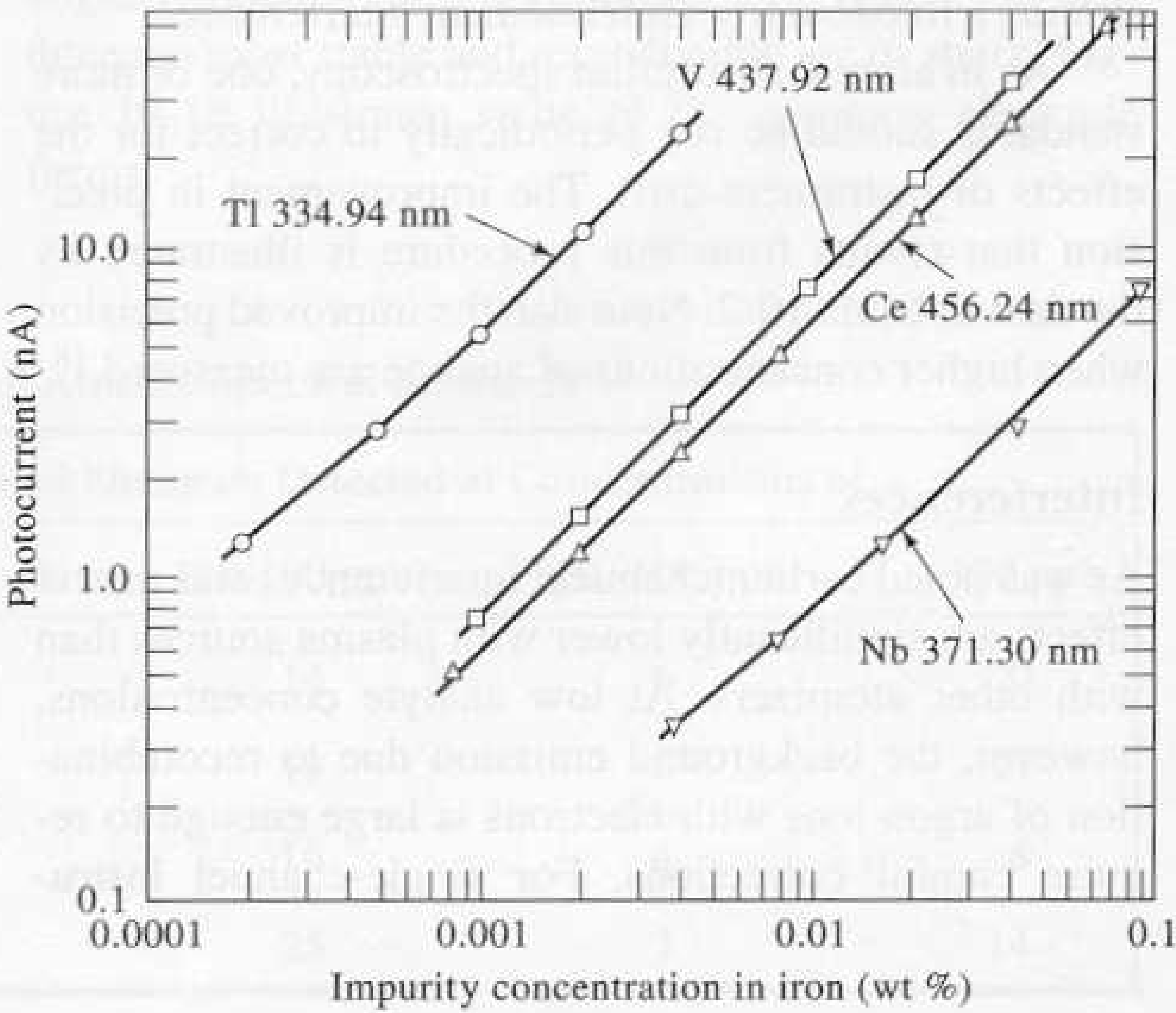


Figure 10-14 Typical calibration curves. *(From V. A. Fassel and R. N. Kniseley,* Anal. Chem., *1974, 46, 1117A. With permission.)*

ICP Calibration curves for several metals, log-log plots

note linearity over at least 2 orders of magnitude

Tl & Nb lines are curved possibly due to improper back-ground correction

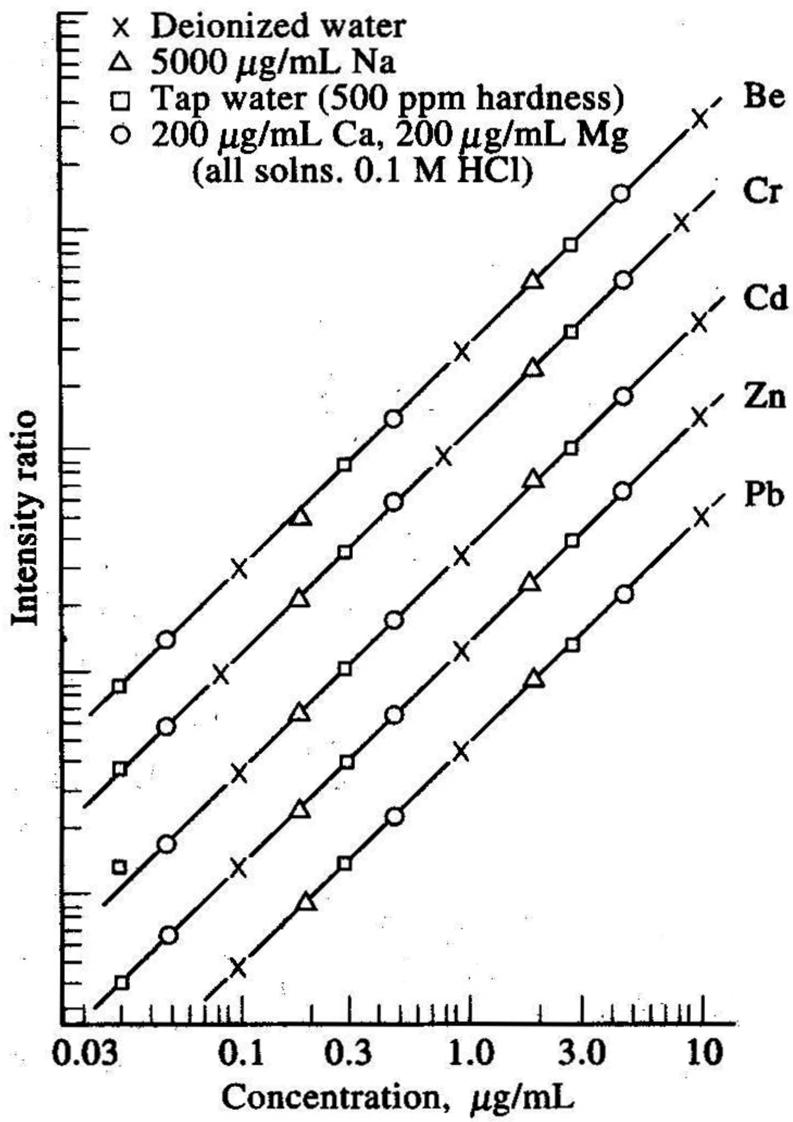


Figure 10-15 Calibration curves with an inductively coupled plasma source. Here, an yttrium line at 242.2 nm served as an internal standard. Notice the lack of interelement interference. *From V. A. Fassel, Science,* ***1978****, 202, 187.*

Four types of samples are compared here to show the lack of any effect for matrix species like Na, Ca & Mg vs. distilled water

Electrodes for arc & spark emission spectrometry
samples are coated on surface or placed wells

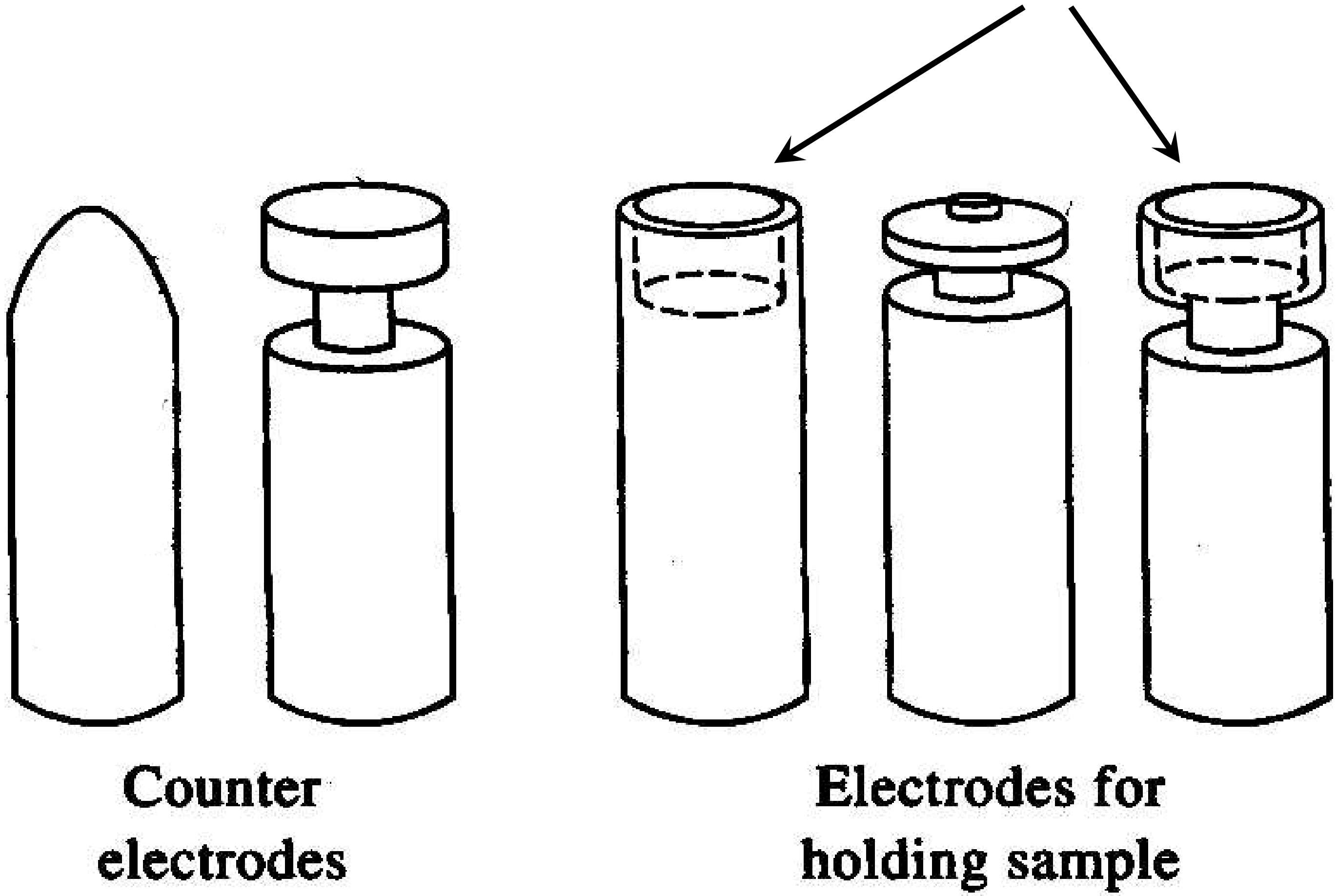
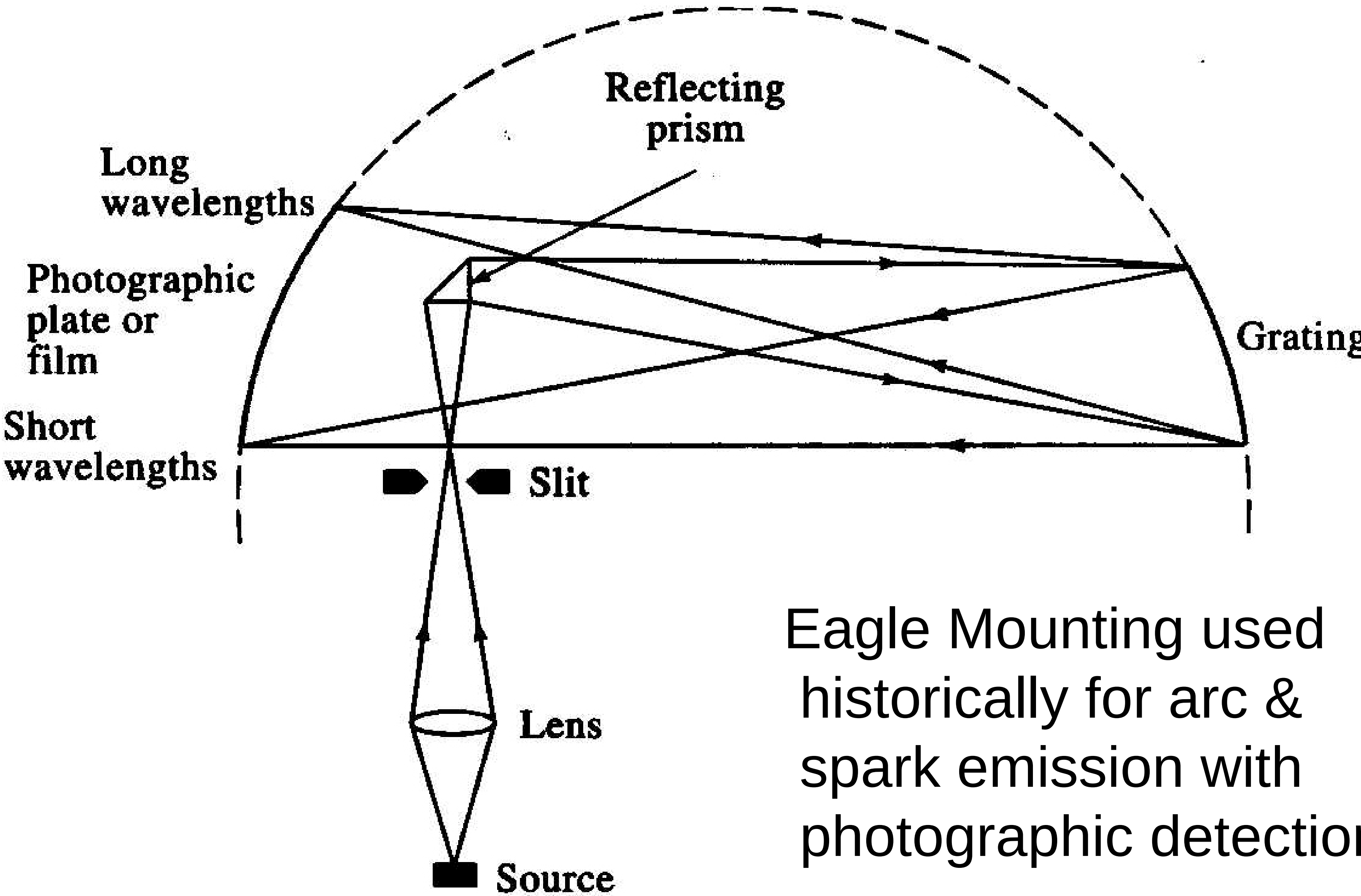


Figure 10-16 Some typical graphite electrode shapes. Narrow necks are to reduce thermal conductivity.



Eagle Mounting used historically for arc & spark emission with photographic detection

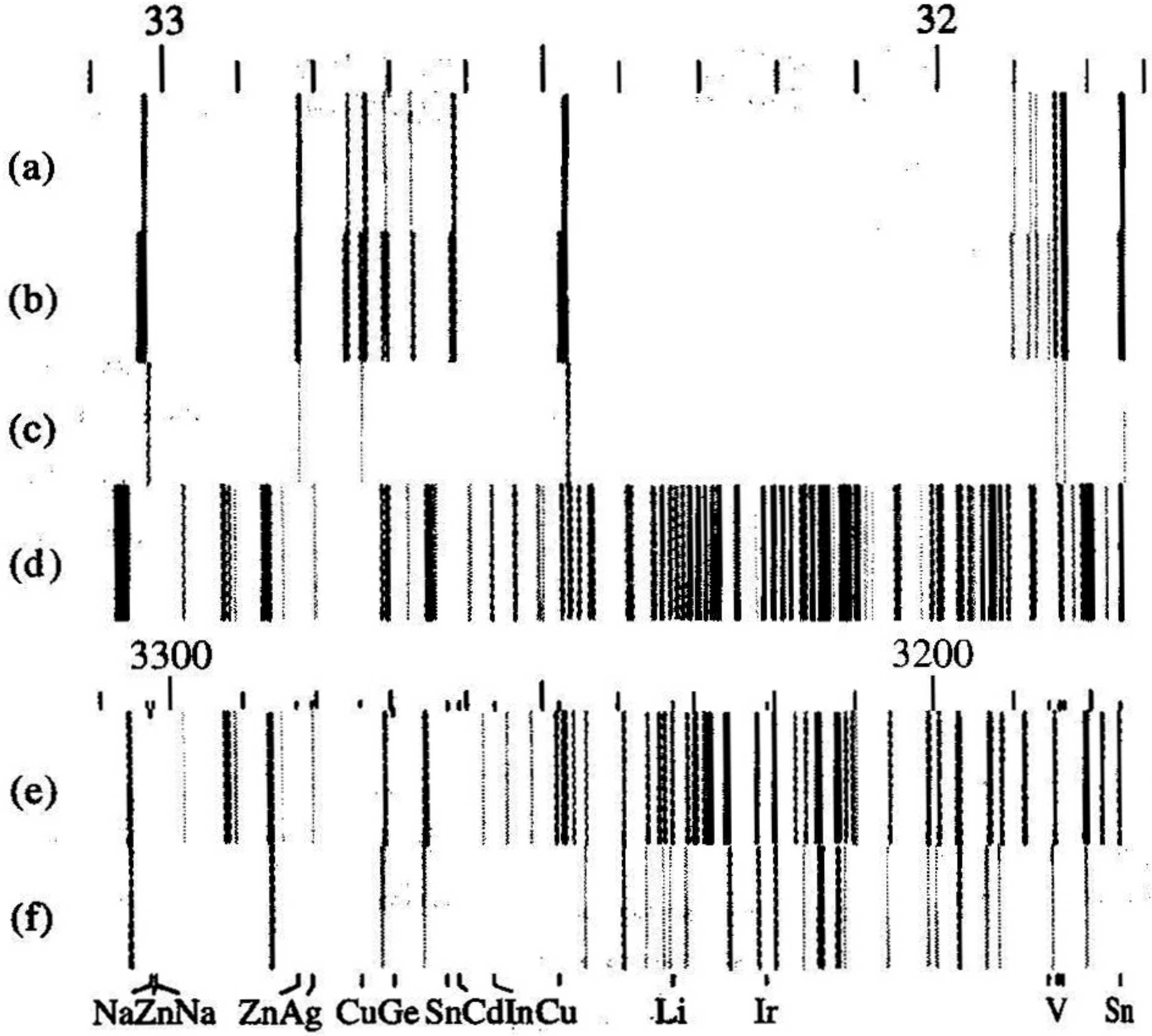


Figure 10-18 Projected spectra by a comparator-densitometer: (a), (b), and (c) spectra of sample at three different exposures; (d) iron spectrum on the sample plate; (e) and (f) iron spectra on the master plate.

Photographic detection gives line spectra

Lines can be compared with a densitometer for intensity & semi-quantitative analysis

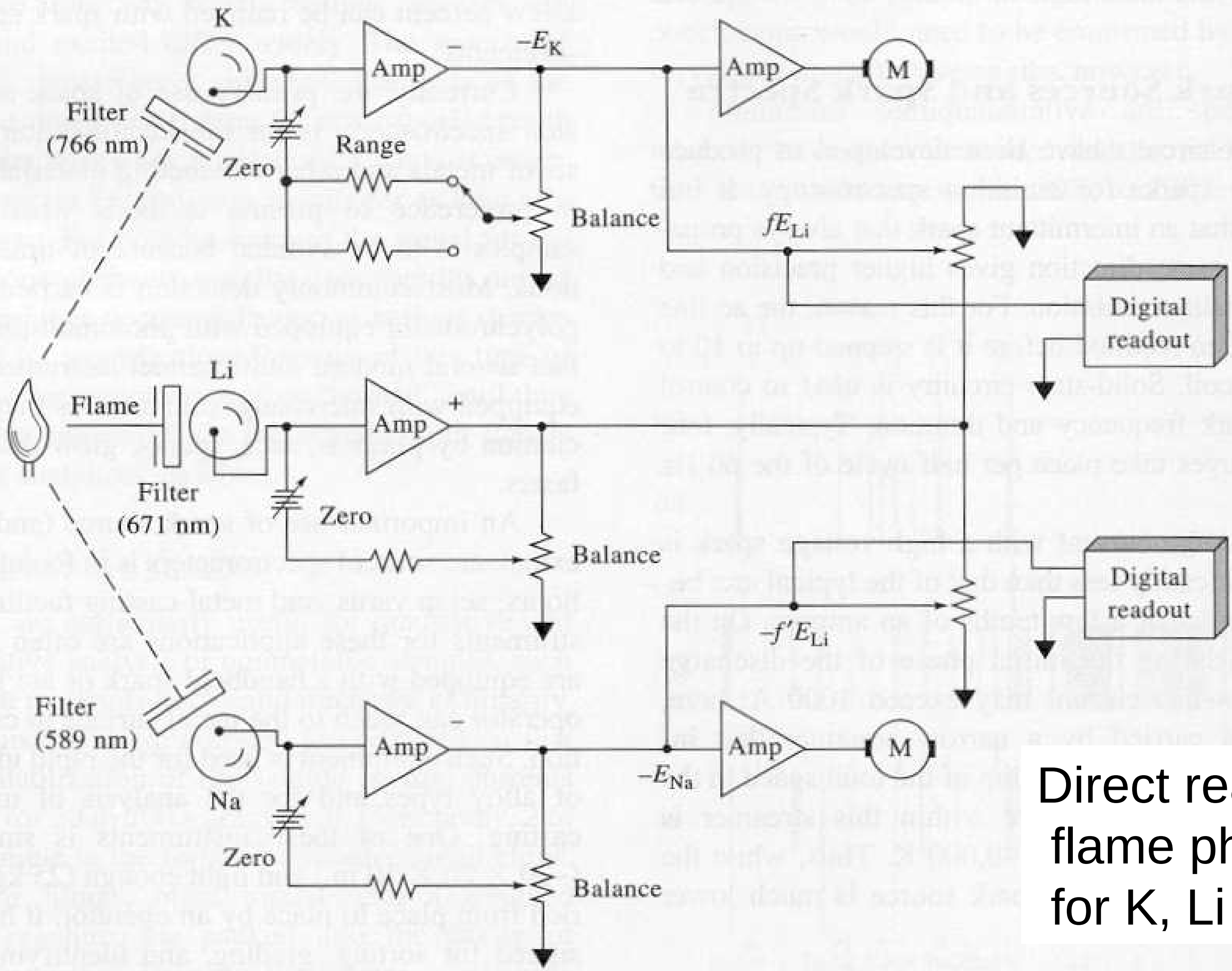


Figure 10-19 A three-channel photometer for monitoring emission by K, Li, and Na. *(From J. D. Ingle Jr. and S. R. Crouch,* Spectrochemical Analysis, *p. 254. Englewood Cliffs, NJ: Prentice-Hall, 1988. With permission.)*

Direct reading
flame photometer
for K, Li & Na

TABLE 10-2 Effect of Standardization Frequency on Precision of ICP Data*

Frequency of Recalibration, hr	Relative Standard Deviation, % — Concentration Multiple above Detection Limit: 10^1 to 10^2	10^2 to 10^3	10^3 to 10^4	10^4 to 10^5
0.5	3–7	1–3	1–2	1.5–2
2	5–10	2–6	1.5–2.5	2–3
8	8–15	3–10	3–7	4–8

*Data from: R. M. Barnes, in *Applications of Inductively Coupled Plasmas to Emission Spectroscopy*, R. M. Barnes, Ed., p. 16. Philadelphia: The Franklin Institute Press, 1978. With permission.

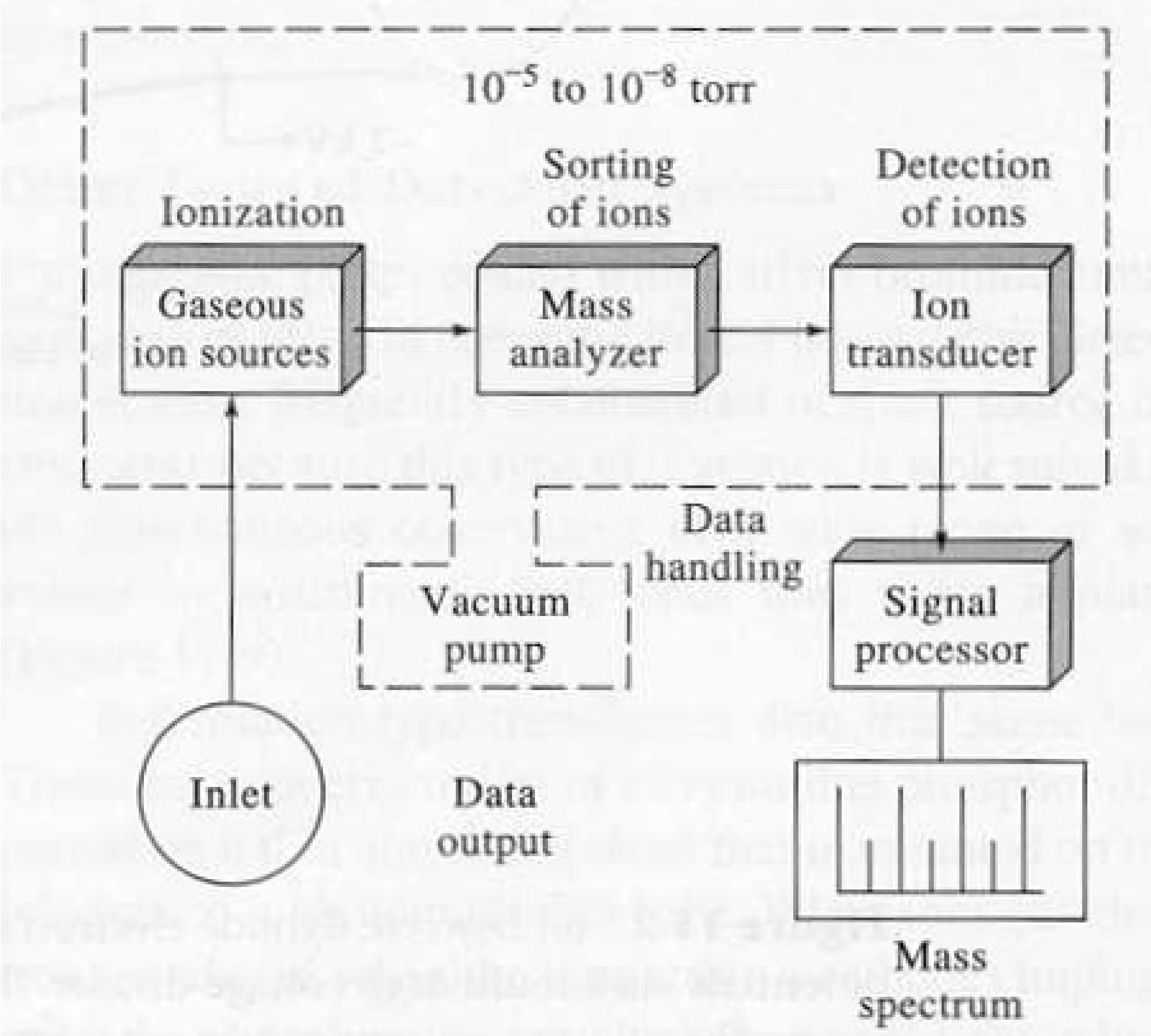
Chapter 11: Atomic Mass Spectrometry (Inorganic MS)

- 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