Chemistry 4631

Instrumental Analysis

Lecture 17

Inductively Coupled Plasma Spectrometry

There are three major techniques used for elemental analysis:

- **Optical spectrometry**
- **Mass spectrometry**
- **X-ray spectrometry**

Inductively Coupled Plasma Spectrometry

ICP

Advantages

- Lower susceptibility to chemical interferences (higher temperatures)
- Good emission spectra for most elements with same experimental setup (can record all at the same time)
- Can determine low concentrations of refractory compounds (i.e. oxides)
- Can determine non-metals (ie. Cl, Br, I, S)
- Larger linear range

Inductively Coupled Plasma Spectrometry

ICP

Disadvantages

- Spectra are highly complex (increases probability of interferences for quantitative work)
- Need more expensive optical equipment (more difficult to maintain)

Inductively Coupled Plasma Spectrometry

What is a Plasma?

- electrically conducting gaseous mixture
- contains high concentration of cations and electrons (net charge zero)
- very high temperatures (10,000 K)

Inductively Coupled Plasma Spectrometry

Types of Plasma

- Inductively coupled plasma (ICP)
- Direct current plasma (DCP)
- Microwave induced plasma (MIP)

Inductively Coupled Plasma Spectrometry

Inductively coupled plasma (ICP)

ICP source is called a torch.

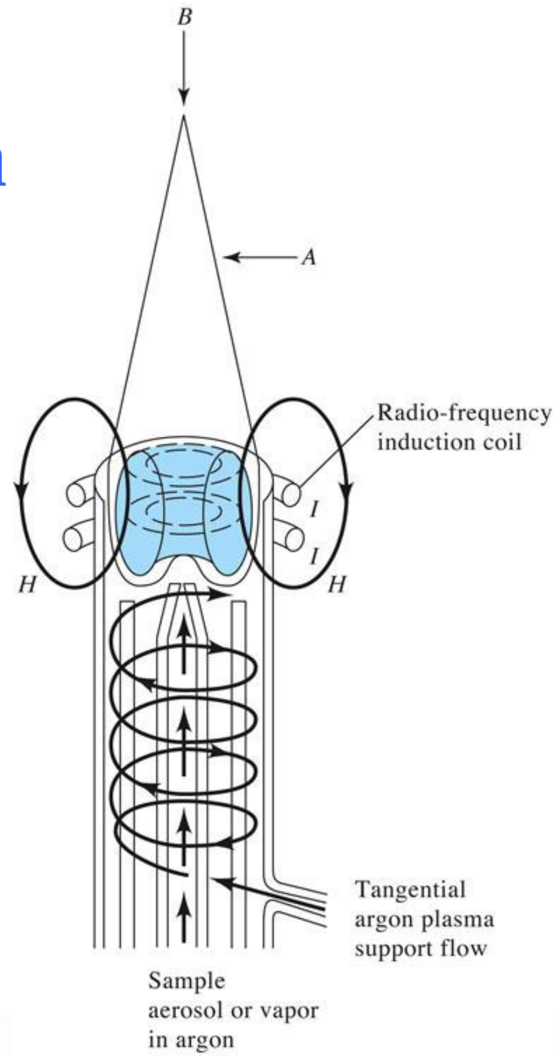
Consist of

- three concentric quartz tubes

- water cooled induction coil

Inductively Coupled Plasma Spectrometry

ICP torch



Ar gas flows thru the quartz tubes at a rate of 5 – 20 mL/min.

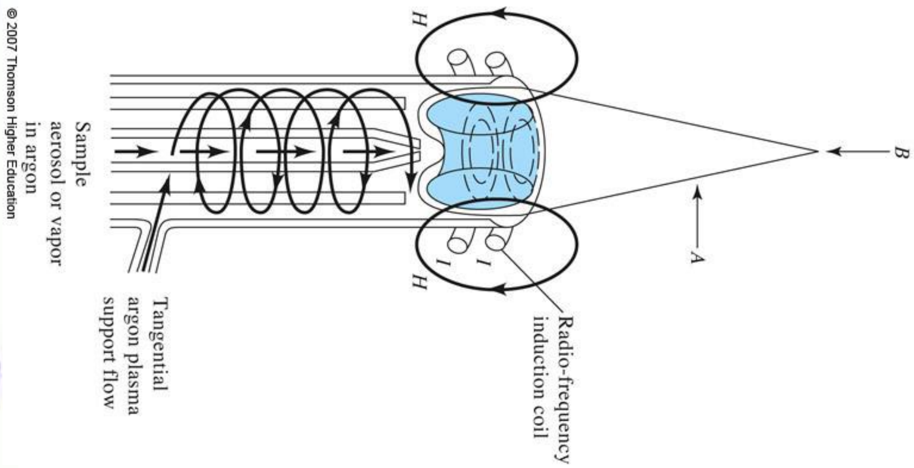
Ionization of Ar is initiated with a Tesla coil.

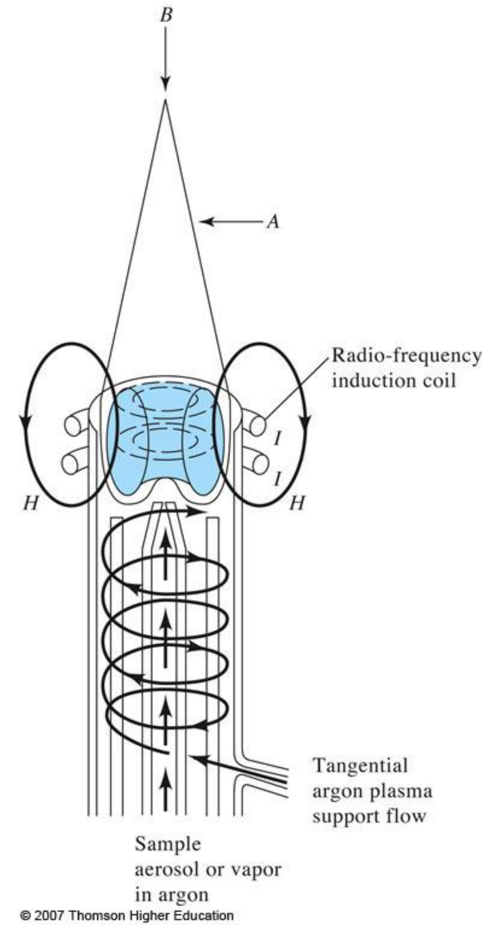
The ions interact with a fluctuating magnetic field produced by an induction coil.

Induction coil powered by rf generator at 0.5 to 2 kW and 27.12 or 40.68 MHz.

Inductively Coupled Plasma Spectrometry

The torch can be arranged





Axially **or** **Radially**

Inductively Coupled Plasma Spectrometry

Axial Arrangement

Advantages

- Increased radiation intensity
- Longer path length
- Higher precision
- Lower detection limits
- Better for ICPMS

Disadvantages

- Plasma tail in the light path
- Thermal and contaminant degradation of spectrometer optics

Inductively Coupled Plasma Spectrometry

Plasma Properties

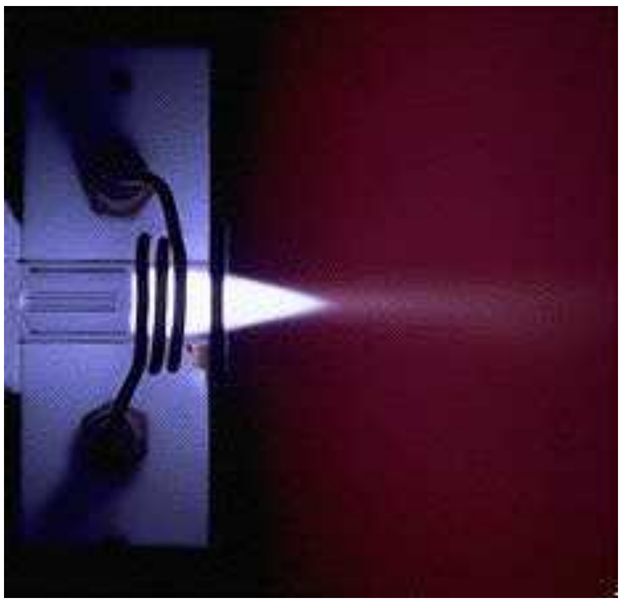
- **Very intense**
- **Brilliant white**
- **Nontransparent core (few mm above the tube)**
- **Flamelike tail (on top of core) (6000-6500 K)**

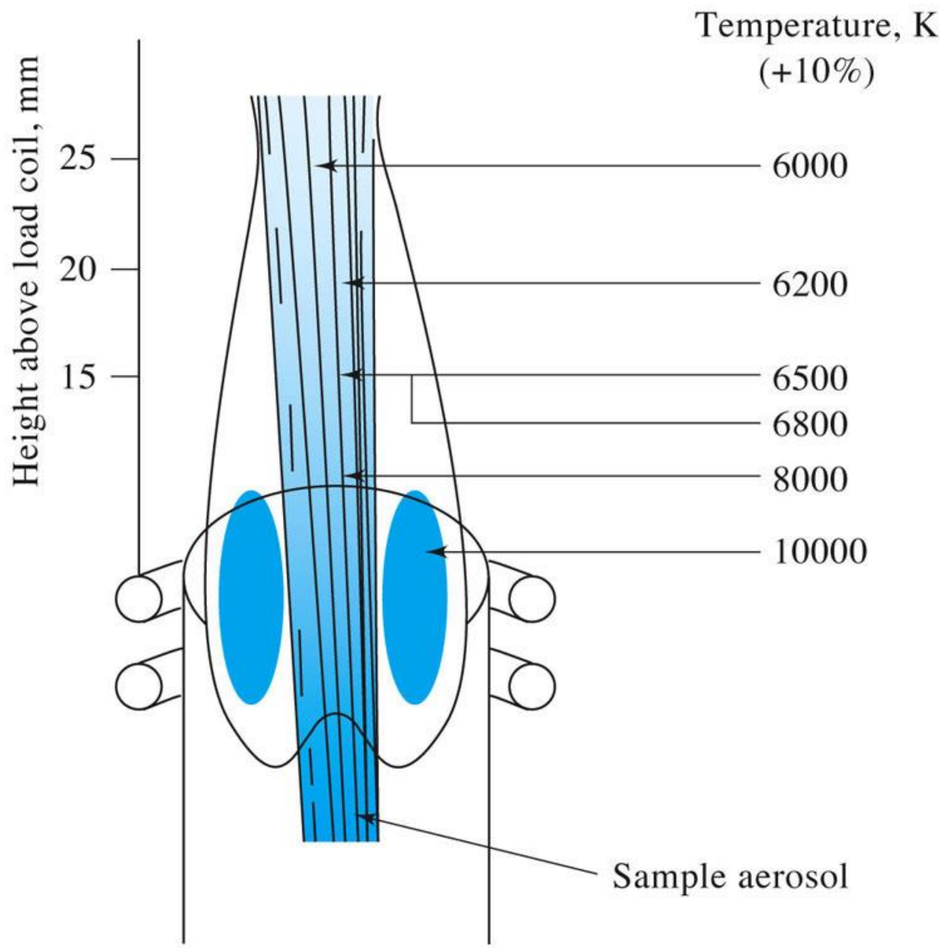
Core produces the atomic spectrum of Ar superimposed on a continuum.

Above the core (15-30 mm), continuum fades and plasma is optically transparent.

Inductively Coupled Plasma Spectrometry

Plasma Properties





Inductively Coupled Plasma Spectrometry

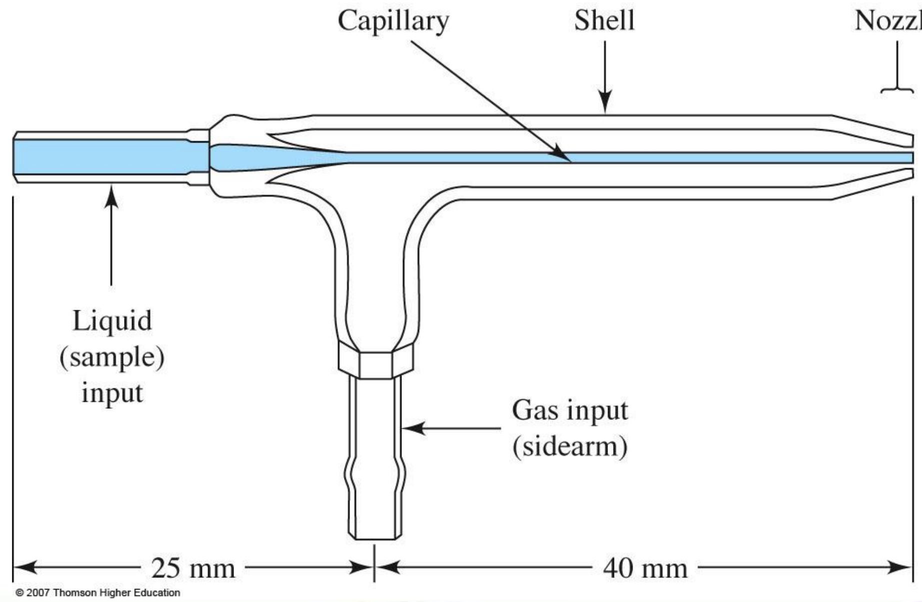
Sample Introduction

Samples can be aerosols, vapor, or solid.

Inductively Coupled Plasma Spectrometry

Sample Introduction

- For liquids can aspirate the sample into the plasma – similar to AA.
- Use nebulization to break the liquid into fine droplets.

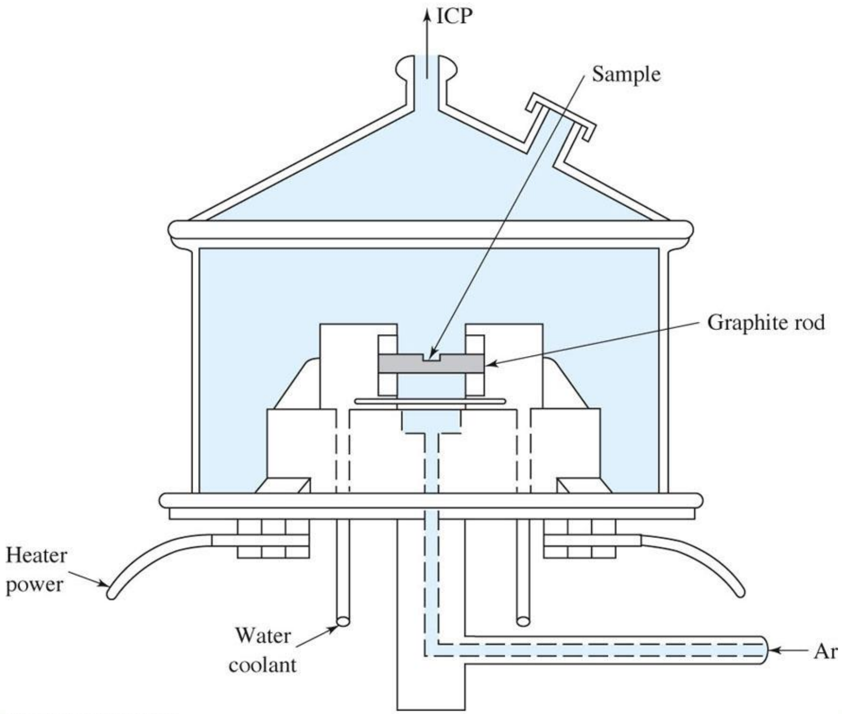


Inductively Coupled Plasma Spectrometry

Sample Introduction

For liquids and solids can use electrothermal vaporization similar to AA.

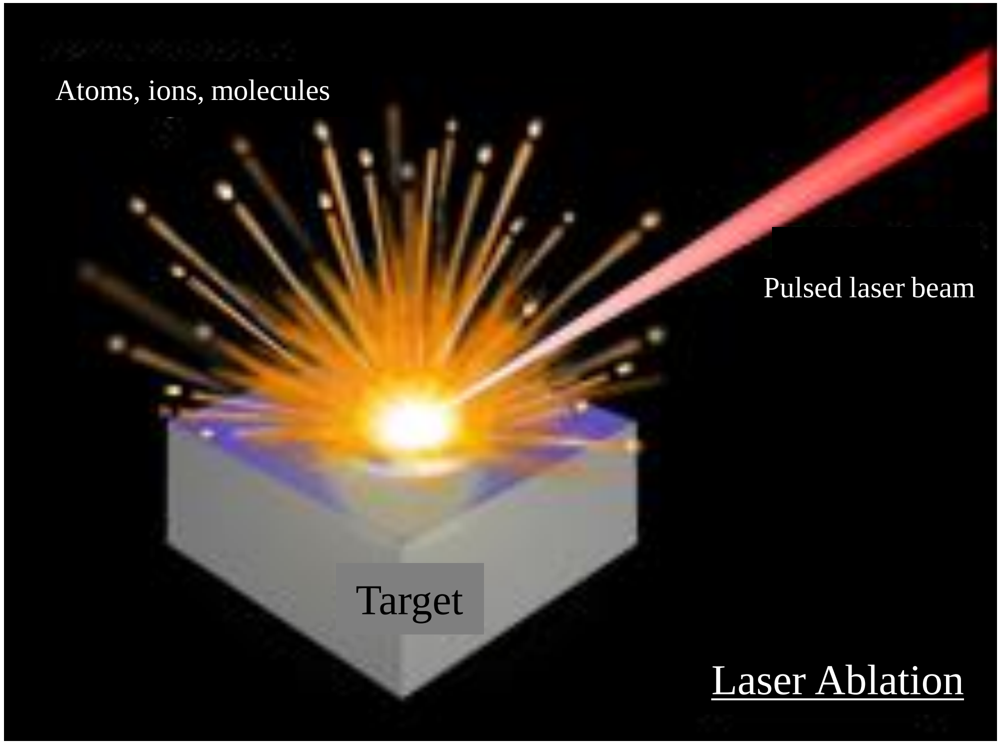
For sample introduction only not for sample atomization.



Inductively Coupled Plasma Spectrometry

Sample Introduction

For solid samples can use laser ablation.



Inductively Coupled Plasma Spectrometry

Atomization of Sample

- **Samples reside in the plasma for ~2 ms before being measured.**
- **Temperatures range from 5500 to 8000 K.**

Inductively Coupled Plasma Spectrometry

Advantages

- More complete atomization in plasma.
- Fewer chemical interferences.
- Less oxide formation.
- Plasma temperature is more uniform.
- Larger linear range for calibration curves.
- Plasma produces significant ionization – a plus for ICPMS.

Inductively Coupled Plasma Spectrometry

Spectrometers

Several companies offer ICP instruments.

Wavelength range ~ 170-800 nm.

Types

- Sequential
- Simultaneous multichannel
- Fourier transform

Inductively Coupled Plasma Spectrometry

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% relative standard deviation 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.

Inductively Coupled Plasma Spectrometry

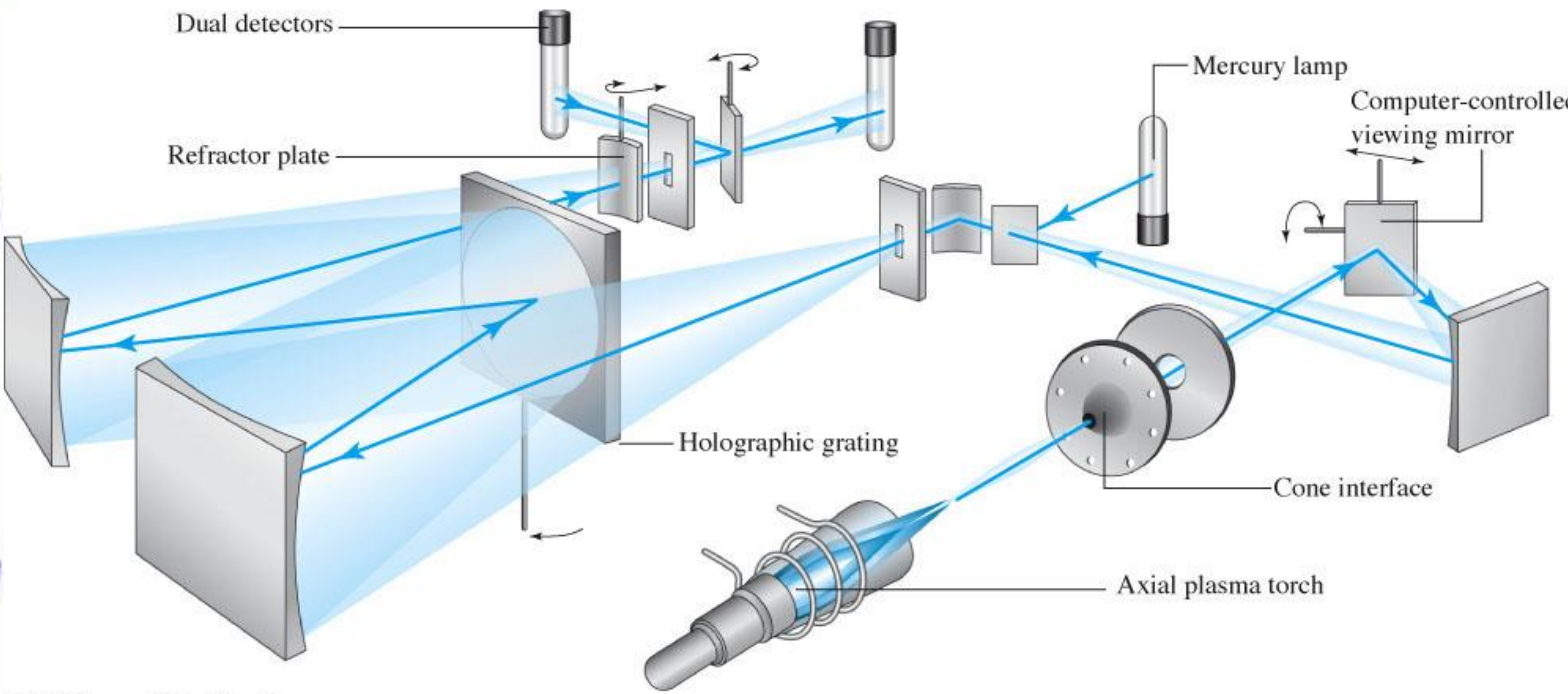
Sequential Instruments

Grating monochromator

- holographic type (2400 – 3600 grooves/mm)
- can rotate the grating or fix the grating and move the slit and PMT
- can use 2 PMT's to scan UV and vis separately and Hg lamp to calibrate wavelength.

Inductively Coupled Plasma Spectrometry

Sequential Instrument



Inductively Coupled Plasma Spectrometry

Sequential Instruments

Slew-scan spectrometers

Instrument scans quickly to region of interest and then slows down to 0.01 – 0.001 nm steps.

Advantage – can measure ~ 15 elements in 5 minutes.

Disadvantage – consume more sample than other instrument designs.

Inductively Coupled Plasma Spectrometry

Sequential Instruments

Scanning Echelle Spectrometers

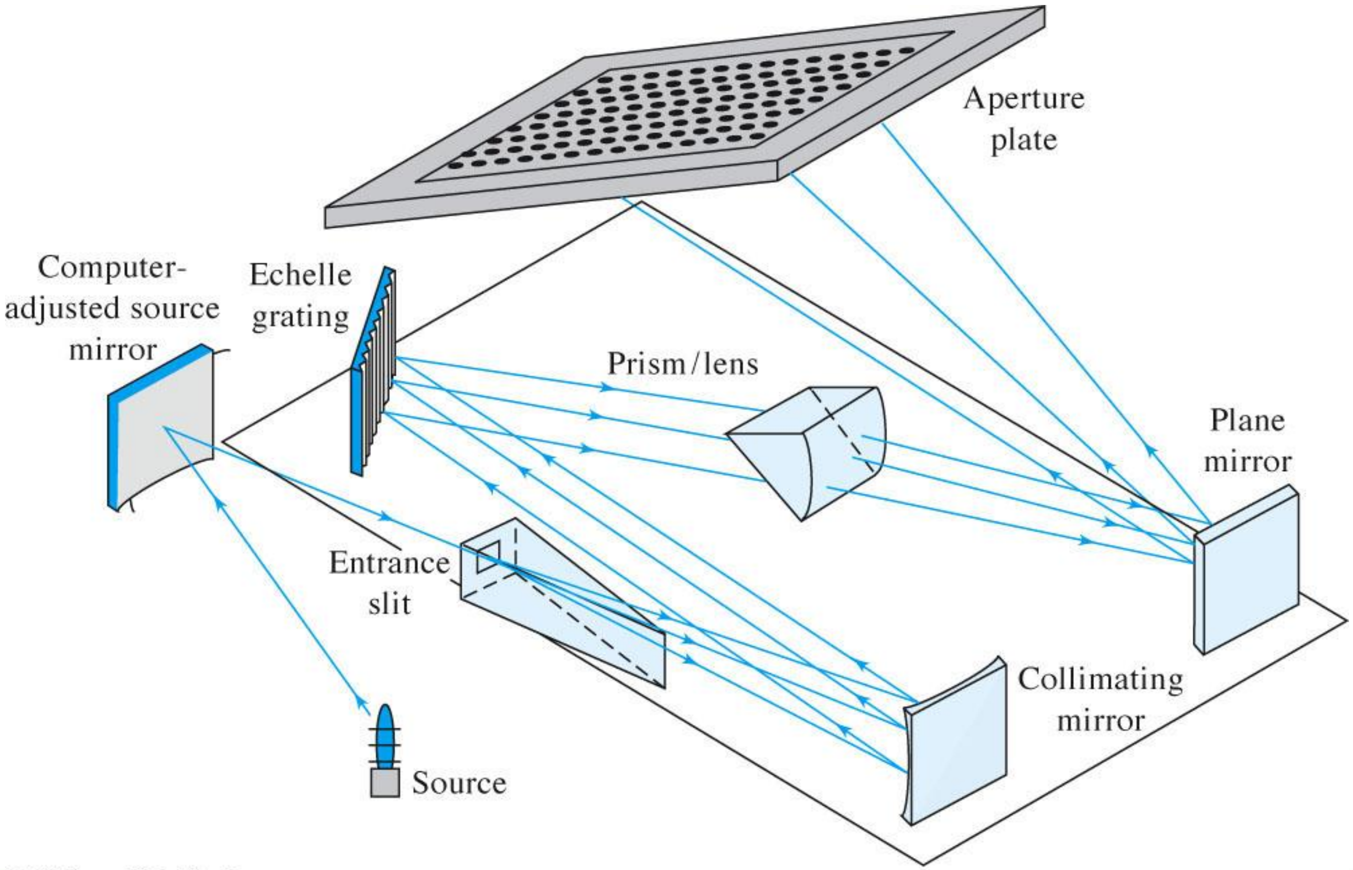
Move the PMT in x and y direction to scan an aperture plate with 300 slits.

Movement to each slit takes 1 sec.

Inductively Coupled Plasma Spectrometry

Sequential Instruments

Scanning Echelle Spectrometers



Inductively Coupled Plasma Spectrometry

Multichannel Spectrometers

Types

- Polychromators (use a series of PMTs)
- Spectrographs (use CIDs or CCDs)

Inductively Coupled Plasma Spectrometry

Multichannel Spectrometers

Polychromators

Use a Paschen-Runge design

- The entrance slit, exit slit, and grating surface are located on the circumference of a Rowland circle.
- Radiation from each fixed slit hits the PMTs.
- The slits can be moved by a stepper motor to scan through peaks.

Inductively Coupled Plasma Spectrometry

Multichannel Spectrometers

Polychromators

Advantages

-high precision

Disadvantages

-cost

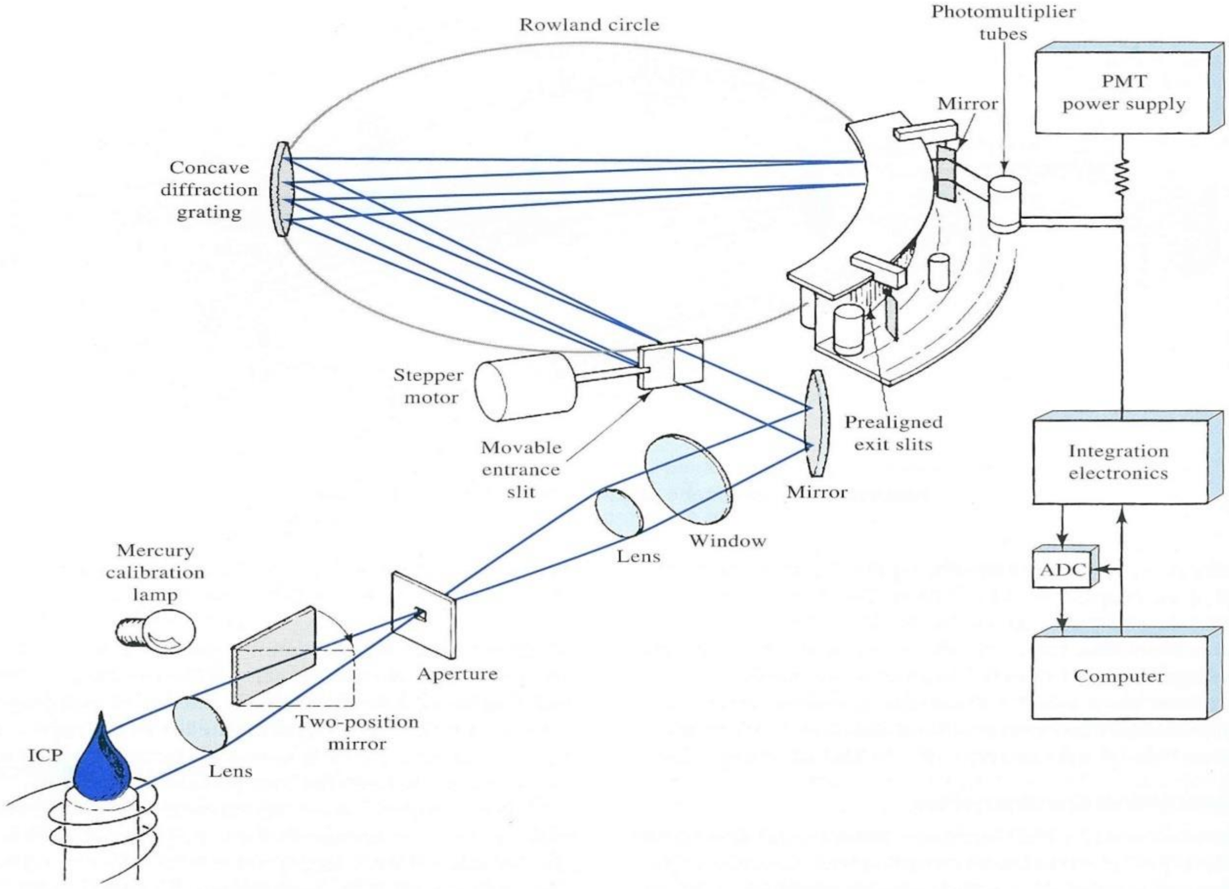


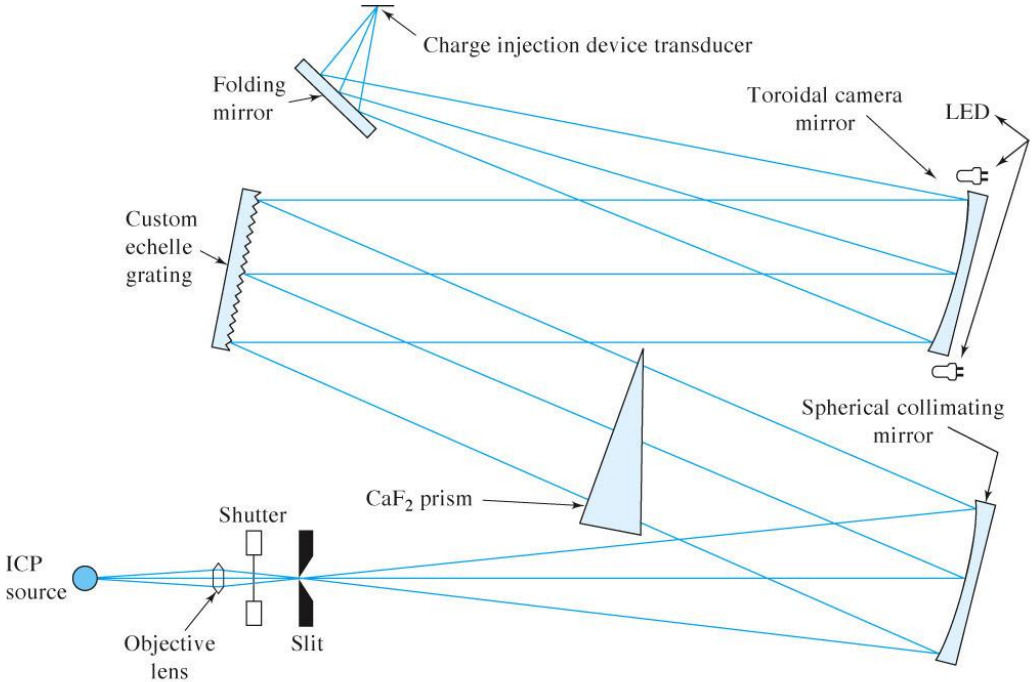
FIGURE 10-8 Direct-reading ICP emission spectrometer. The polychromator is of the Paschen-Runge design. It features a concave grating and produces a spectrum around a Rowland circle. Separate exit slits isolate each spectral line, and a separate photomultiplier tube converts the optical information from each channel into an electrical signal. Notice the radial viewing geometry. PMT = photomultiplier tube. (From J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, p. 241, Upper Saddle River, NJ: Prentice-Hall, 1988, with permission.)

Inductively Coupled Plasma Spectrometry

Multichannel Spectrometers

Spectrographs

Charge-Injection Devices – based on echelle spectrometers and 2D array devices



Inductively Coupled Plasma Spectrometry

Multichannel Spectrometers

Spectrographs

Charge-Coupled Devices – 2 CCD's – one for vis and one for UV.

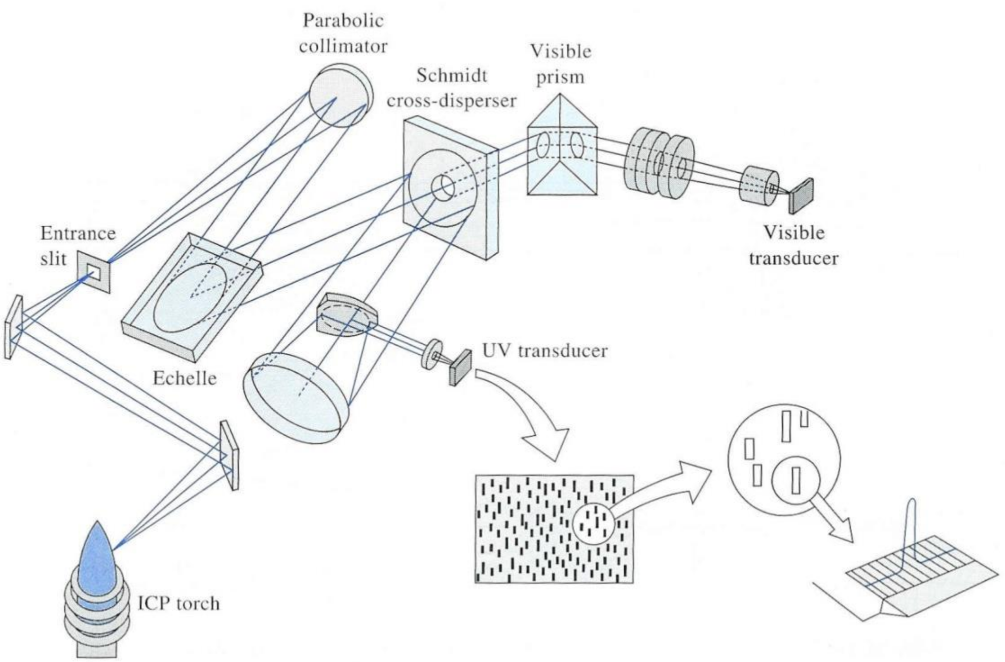


FIGURE 10-11 An echelle spectrometer with segmented array of CCDs. (From T. W. Barnard et al., *Anal. Chem.*, **1993**, *65*, 1231. Figure 1, p. 1232. Copyright 1993 American Chemical Society.)

Inductively Coupled Plasma Spectrometry

Schmidt cross-dispenser

1) Split the light into separate UV and vis channels

2) Serve as a grating that separates light by order

3) Optically correct for spherical aberrations

Inductively Coupled Plasma Spectrometry

Fourier Transform Spectrometers

Advantages

- Wide wavelength coverage (170 – 1000 nm)
- Speed
- High resolution
- Accurate measurements
- Large dynamic range
- Compact size
- Large optical output

Disadvantages

- Very high cost (mostly research instrument)

Inductively Coupled Plasma Spectrometry

ICP Measurements

All metallic elements can be determined.

B, P, N, S, and C using a vacuum spectrometer at wavelengths below 180 nm.

Alkali metals are difficult since the prominent lines for Li, K, Rb, Cs are located in the near IR range.

Inductively Coupled Plasma Spectrometry

ICP Measurements

[a] The detection limits are based on a 98% confidence level (3 standard deviations).
[b] Identifying a single part per trillion of an element in a solution is analogous to locating a single white raisin in a house (2,700 sq. ft) full of regular raisins.

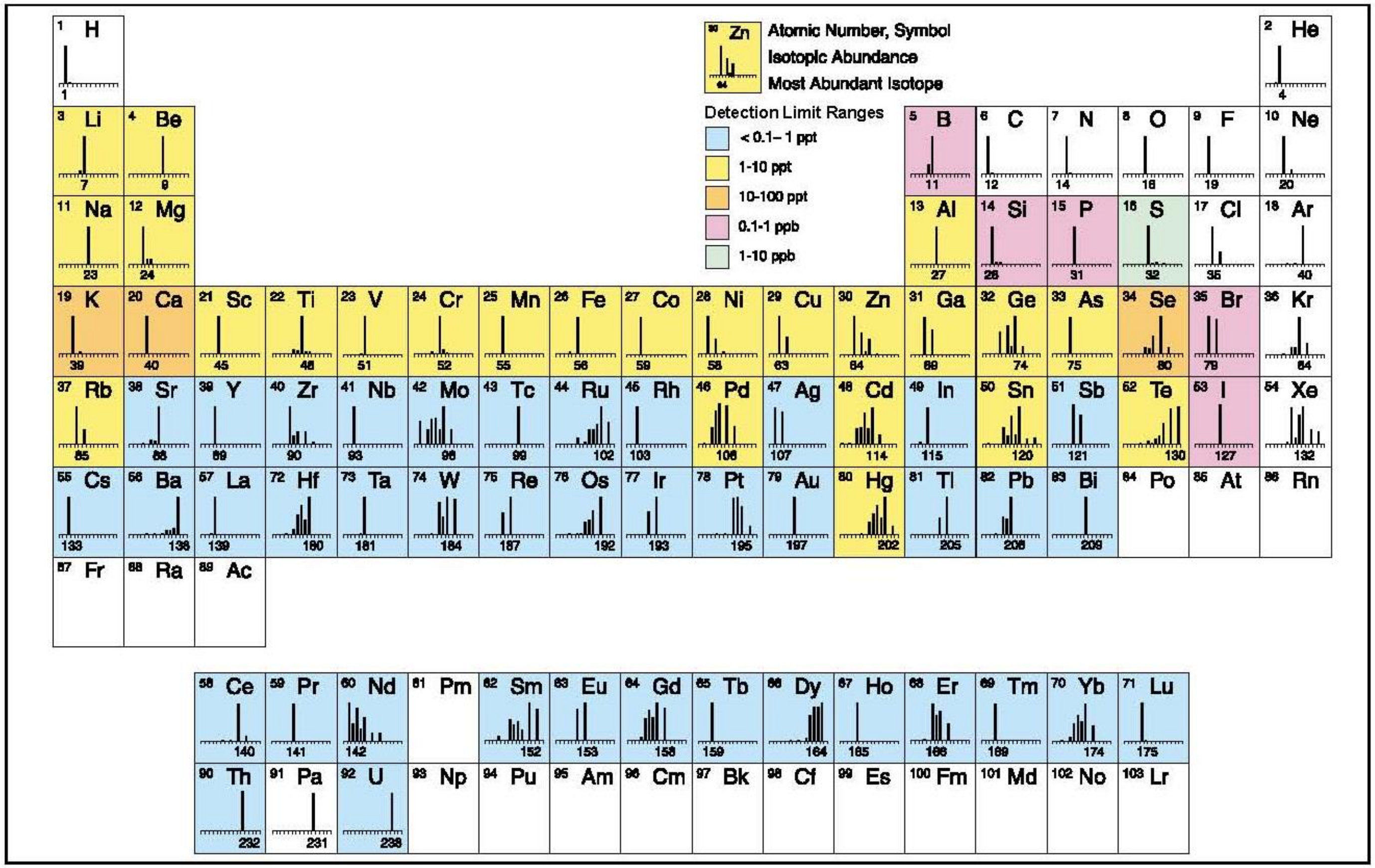


Figure 1. Elements determined by ICP-MS and approximate detection capability.

Inductively Coupled Plasma Spectrometry

ICP Measurements

Detection Limits

TABLE 10-3 Comparison of Detection Limits for Several Atomic Spectral Methods

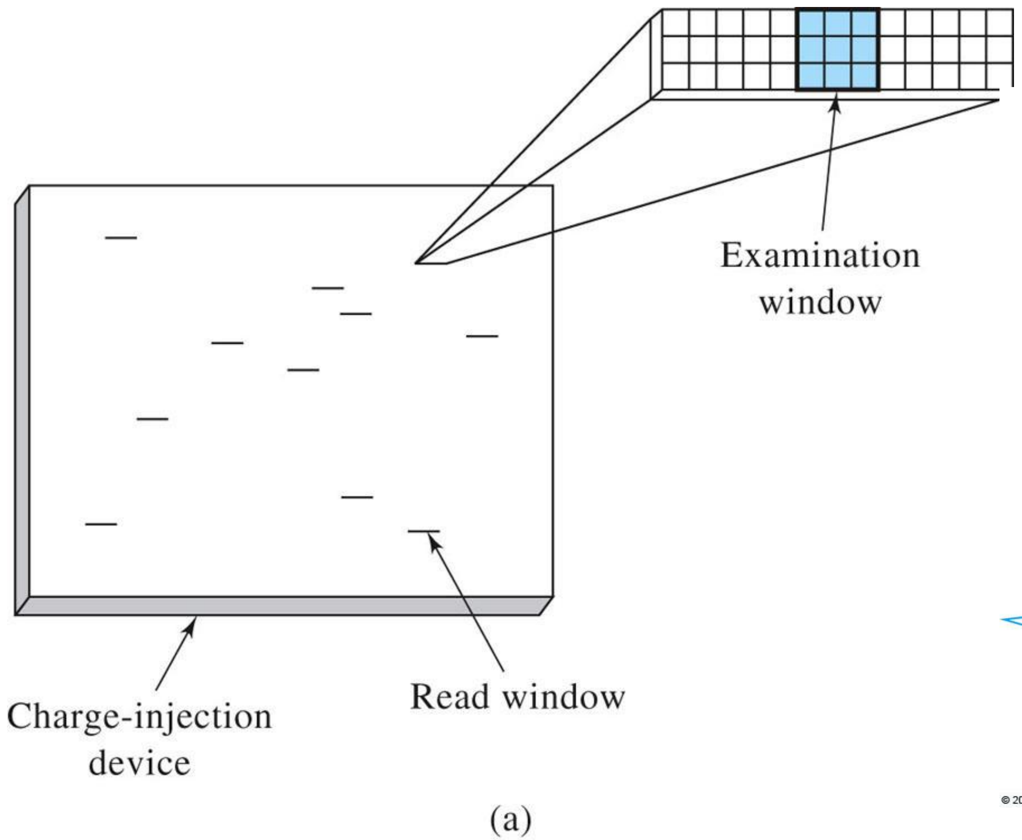
	Number of Elements Detected at Concentrations of				
Method	**<1 ppb**	**1–10 ppb**	**11–100 ppb**	**101–500 ppb**	**>500 ppb**
ICP emission	9	32	14	6	0
Flame atomic emission	4	12	19	6	19
Flame atomic fluorescence	4	14	16	4	6
Flame atomic absorption	1	14	25	3	14

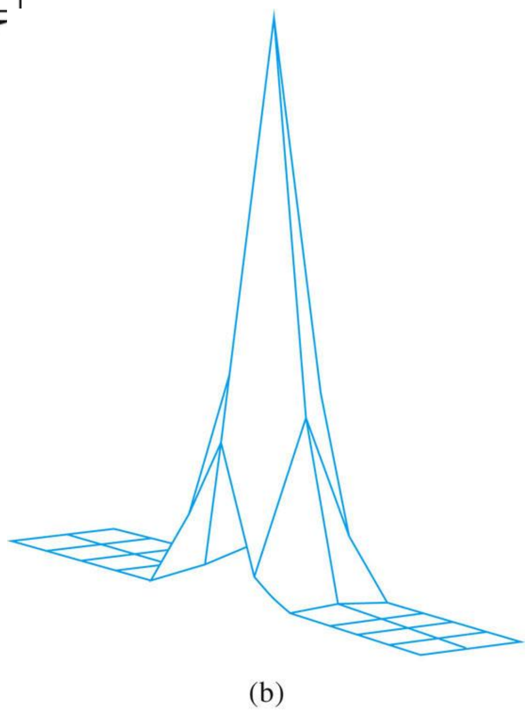
Assignment

- Read Chapter 8
- Read Chapter 9
- HW8 Chapter 8: 1, 4-9
- HW9 Chapter 9: 1-5, 7-9, 19
- HW8 – Due 3/04/24
- HW9 – Due 3/06/24

- Read Chapter 10
- HW10 Chapter 10: 1, 2, 6-11
- HW10 Due 3/08/24

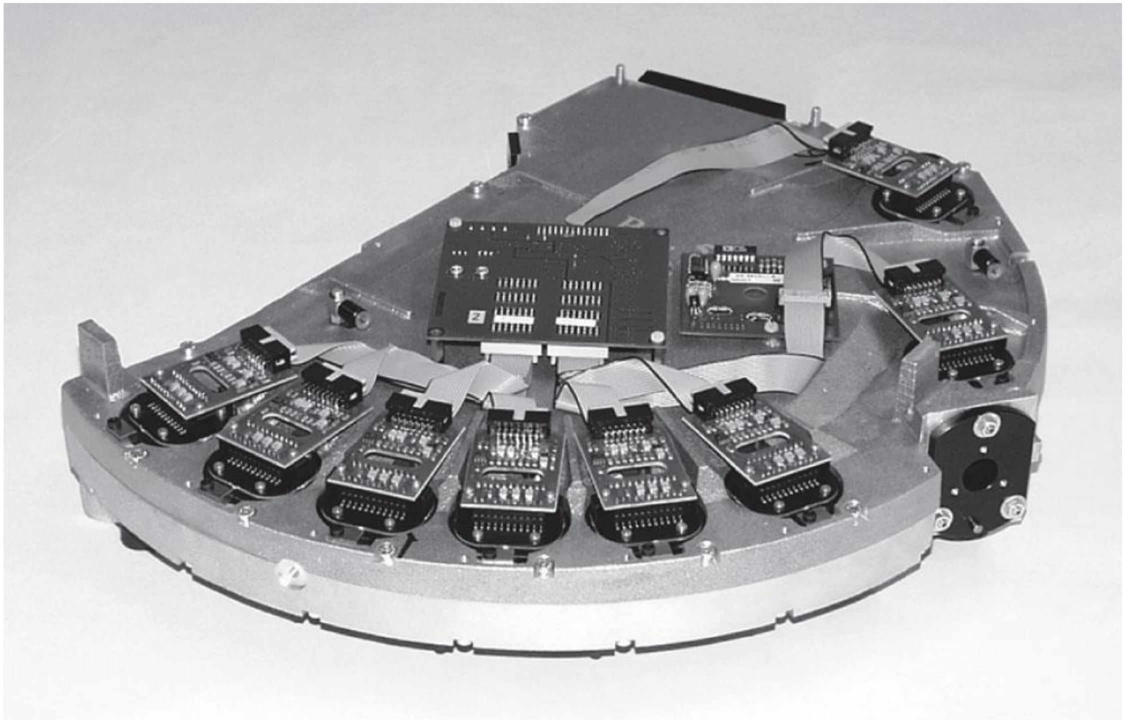
Inductively Coupled Plasma Spectrometry





Inductively Coupled Plasma Spectrometry

Atomization



(a)