**Quantitative chemical analysis of water and rock samples**

**Inductively Coupled Plasma Atomic Emission Spectroscopy**

**(ICP-AES)**

*Reading Assignments: Manning and Grow (1997); Brodie et al., 1991 (Analytical methods for the Liberty Spectrometer system, Varian Instruments; Chapter 1).*

**Principles of Spectrochemistry (1920’s):**

* Relies on excitation of sample and short-lived ionization of its atoms followed by return to the ground state with subsequent emission of energy in the form of waves in the UV, visible, and/or near IR regions.
* Excited vs. ground state (Fig. 1).
* Electron transitions and characteristic wavelengths (lines; Fig. 2)

ΔE = h . ν

* Wavelength of emitted line useful for qualitative analysis; intensity of line for quantitative analysis.

**Components of a spectrochemical instrument:**

1. Excitation source
2. Dispersing unit
3. Detection unit

**Methods of excitation:**

1. Flame
2. Arc (AC or DC): atomic excitation
3. Spark (AC): ionic excitation; better precision than arc, but lower sensitivity
4. Laser ablation/ laser induced plasma
5. DC plasma (direct current)
6. IC plasma: superior sensitivity

**Dispersing units:**

* Prisms: useful in the UV and visual regions; no overlap of spectral orders.
* Gratings: constant dispersion at all wavelengths.

**Methods of detection:**

* Photographically
* Electronically: photomultiplier tubes
* Mass Spectrometry

**Types of Spectrochemical Instruments**

1. Flame photometer
2. DCP-AES
3. MIP-AES (microwave induced plasma atomic emission spectrometer)
4. ICP-AES
5. AAS: several methods including GF-AAS
6. ICP-MS
7. LA-ICP-MS (Laser ablation ICP mass spectrometer).

**Comparison of the Different techniques of spectrochemistry commonly used in geochemical analysis:** Uses, limitations, and detection limits (Table 1).

**Inductively Coupled Plasma Atomic Emission Spectroscopy:**

***Definition of “Plasma”*:**

A partially ionized gas in which some electrons are free. Overall, it has a neutral charge, is electrically conductive, and responds to electromagnetic fields. Characterized by T of 1000’s of degrees Celsius.

***Components of an ICP-AES (Fig. 3)***

* Nebulizer (Fig. 4)
* Torch and radiofrequency source (Fig. 5). Note the different zones within the flame. Two methods of mounting (orientation):
  + Vertical (Radial): better for organics, better linearity.
  + Horizontal (Axial): offers greater sensitivity, lower maintenance costs.
* Detectors:
* Simultaneous: measure specific λs at multiple (fixed!) positions simultaneously ⇒ polychromator
* Sequential: uses gratings ⇒ monochromator (time consuming, but more flexible!)

***Precautions for quantitative analysis***

* Standard selection
* Concentration ranges for standards
* Interferences:
  + Spectral
  + Background
  + Matrix effects
  + Ionization

***Detection Limits***

***Precision and Accuracy of the technique:***

***Laser Techniques*** (Fig. 6): CO2 laser sputters or “ablates” solid samples.