

# **Chapter 10**

## **Atomic Emission Spectroscopy (AES, OES)**

## Introduction to AES:

- Atomic emission spectroscopy (AES or OES) uses quantitative measurement of the optical [emission](#) from excited atoms to determine analyte concentration.
- Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized, and atomized by a flame, discharge, or plasma.
- These high-temperature atomization sources provide sufficient energy to promote the atoms into high energy levels.
- The atoms decay back to lower levels by emitting light. Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow.
- The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer.
- Since all atoms in a sample are excited simultaneously, they can be detected simultaneously, and is the major advantage of AES compared to [atomic-absorption \(AA\) spectroscopy](#).

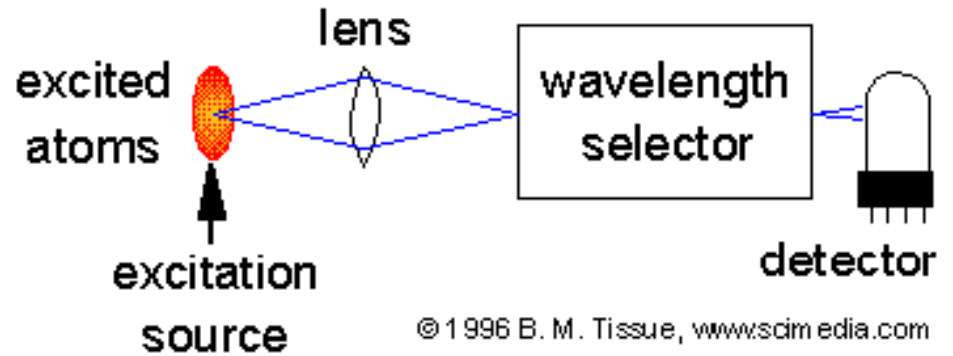
Instrumentation:

**NO LIGHT  
SOURCE  
FOR  
EXCITATION**

Sample Introduction

Atomization  
&  
Excitation

Detection



## Sample Introduction:

- Liquid samples are nebulized and carried into the excitation source by a flowing gas.
- Solid samples can be introduced into the source by a slurry or by laser ablation of the solid sample in a gas stream.
- Solids can also be directly vaporized and excited by a spark between electrodes or by a laser pulse.

## Atomization and Excitation:

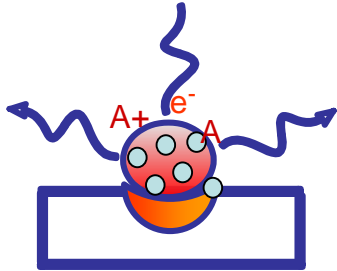
- In AE spectroscopy, the sample must be converted to free atoms, usually in a high-temperature excitation source
- The excitation source must desolvate, atomize, and excite the analyte atoms. A variety of atomization and excitation sources are;
  - Flame
  - Arc / Spark
  - Plasma
    - Inductively-coupled plasma (ICP)
    - Direct-current plasma (DCP)
    - Microwave-induced plasma (MIP)
    - Laser-induced plasma, Laser-induced breakdown (LIBS)

## Detection

- \* Emission spectra are often complex and frequently comprise hundreds, or even thousands, of lines,
- \* Spectra for many elements can be recorded simultaneously, and multielement analysis is possible.
- \* therefore, requires higher resolution wavelength selectors and sensitive detectors.

## AES based on Plasma Sources:

- \* Plasma sources are the most important and most widely used sources for AES
- \* Plasma is an electrical conducting gaseous mixture containing significant amounts of cations and electrons ( net charge approaches zero)



1) increased atomization/excitation

2) wider range of elements;

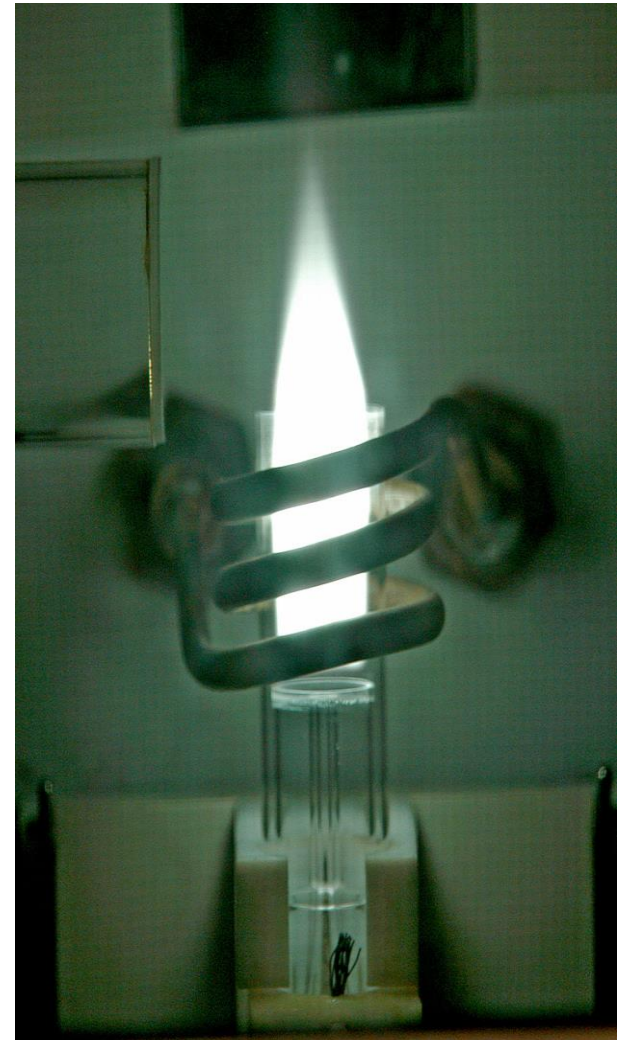
elements that tend to form refractory compounds that is, compounds that are highly resistant to thermal decomposition, such as the oxides of boron, phosphorus, tungsten, uranium, zirconium, and niobium).

In addition, plasma sources permit the determination of nonmetals such as chlorine, bromine, iodine, and sulfur.

3) simultaneous multielement analysis

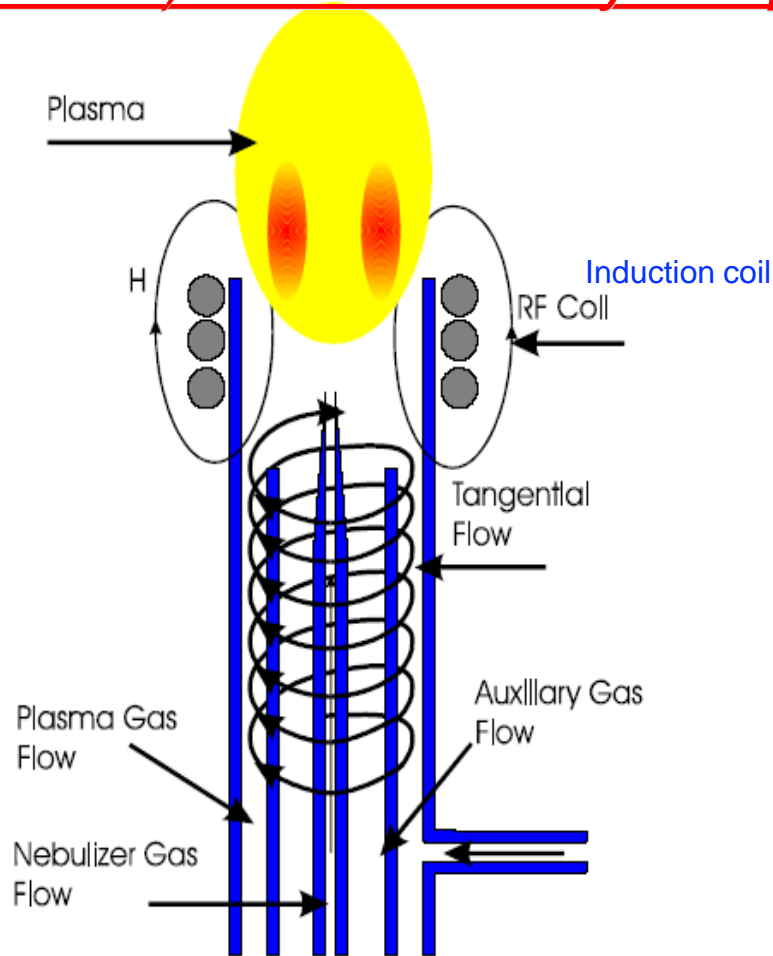
4) wide dynamic range

- \* In the argon plasma frequently used for emission analyses, argon ions, and electrons are the principal conducting species, although cations from the sample are also present in small amounts.
- \* Argon ions, once formed in a plasma, can absorb sufficient power from an external source to maintain the temperature at a level where further ionization sustains the plasma indefinitely. Such plasmas achieve temperatures as high as 10,000 K.





## 10A-1) The Inductively Coupled Plasma, ICP-OES:



-A typical ICP consists of three concentric quartz tubes through which streams of argon gas flow at a rate in the range from 5-20 L/min.

- The outer tube is about 2.5 cm in diameter and the top of this tube is surrounded by a radio frequency (RF) powered induction coil producing a power of about 2 kW at a frequency in the range from 27-41 MHz. This coil produces a strong magnetic field as well.

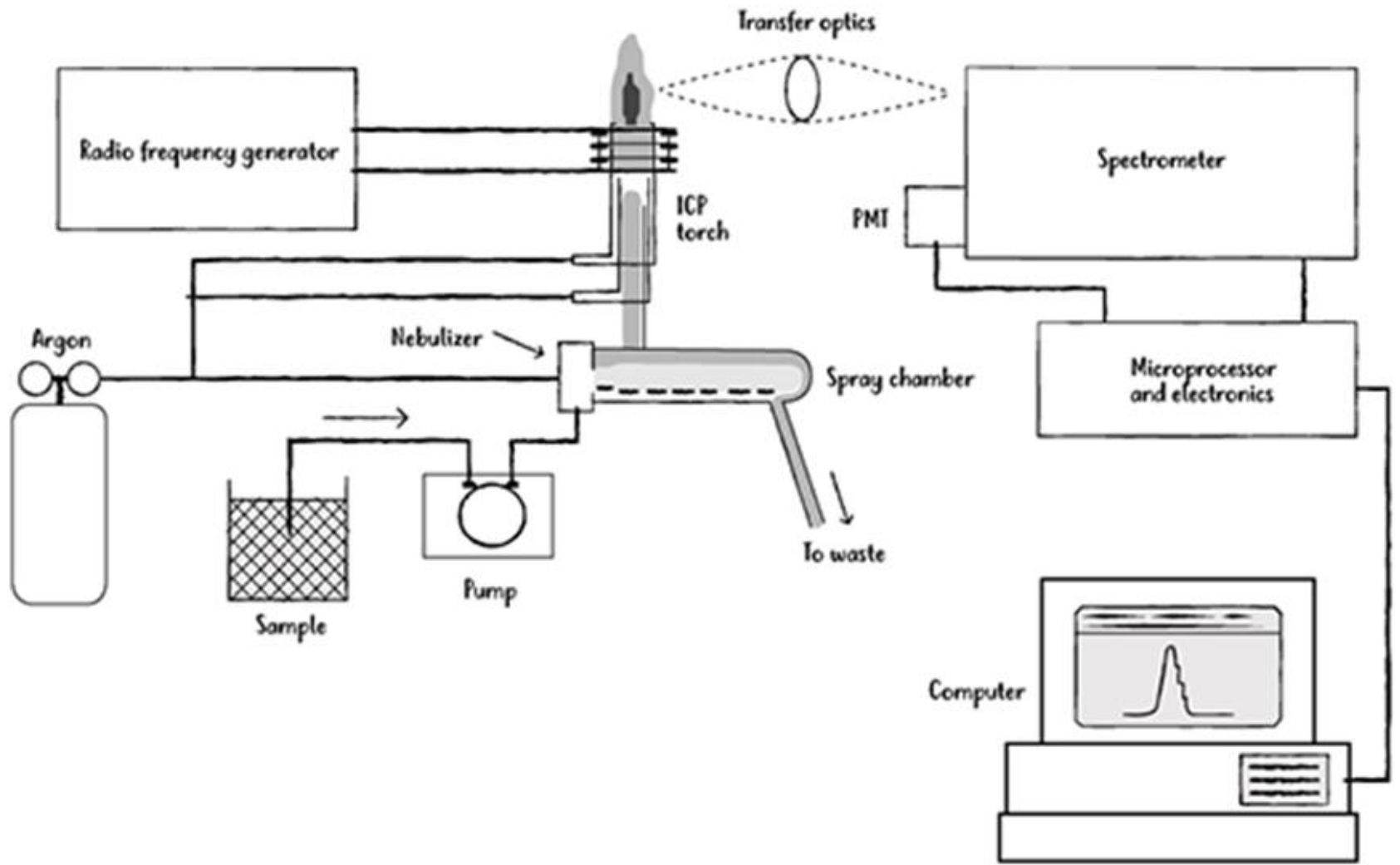
- Ionization of flowing argon is achieved by a spark where ionized argon interacts with the strong magnetic field and is thus forced to move within the vicinity of the induction coil at a very high speed.

- A very high temperature is obtained as a result of the very high resistance experienced by circulating argon (ohmic heating).

-The top of the quartz tube will experience very high temperatures and should, therefore, be isolated and cooled. This can be accomplished by passing argon tangentially around the walls of the tube

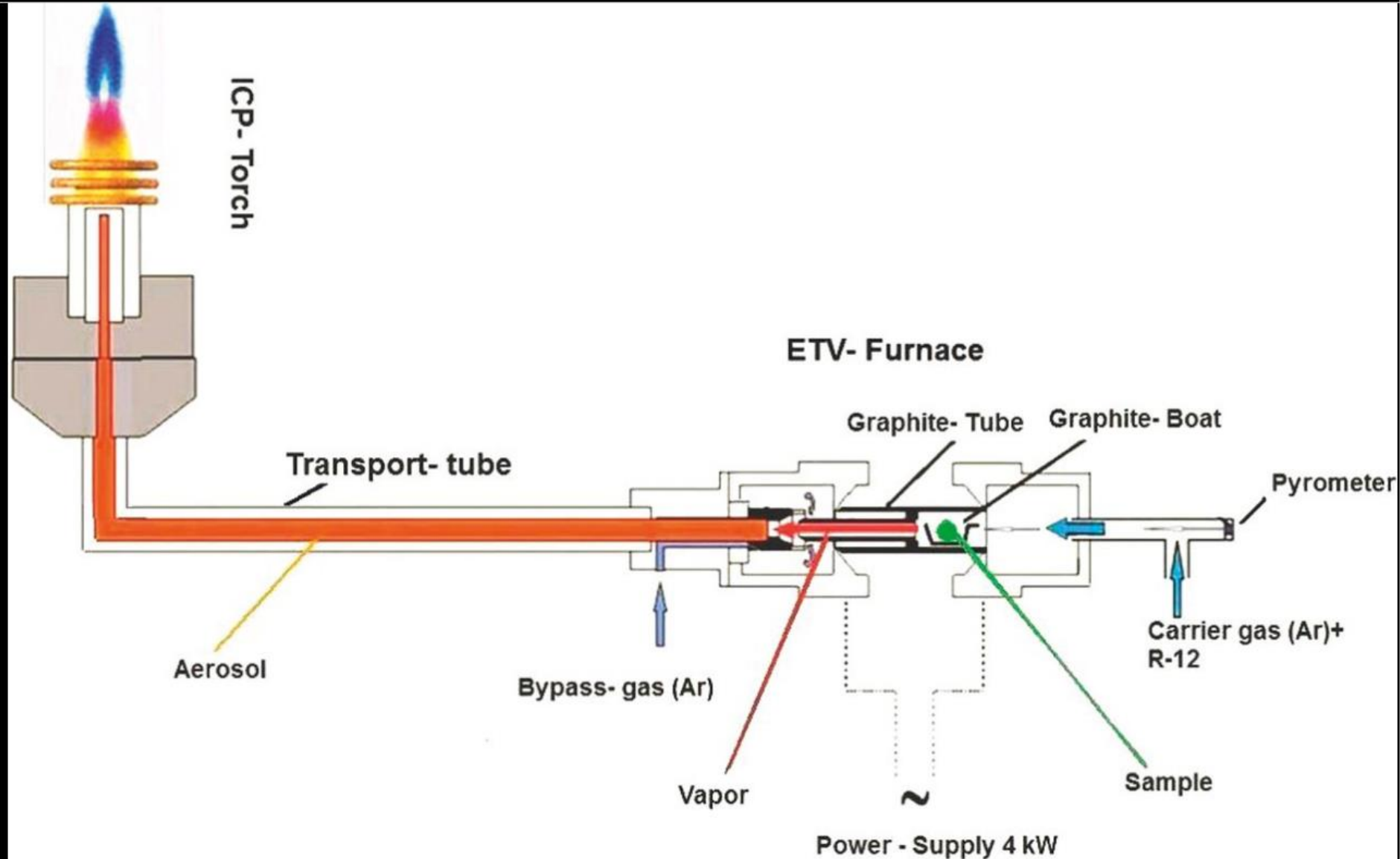
- Torch up to 1" diameter
- Ar cools outer tube, defines plasma shape
- Radio-frequency (RF) up to 2 kW
- Ar flow up to 20 L/min

# LIQUIDS:



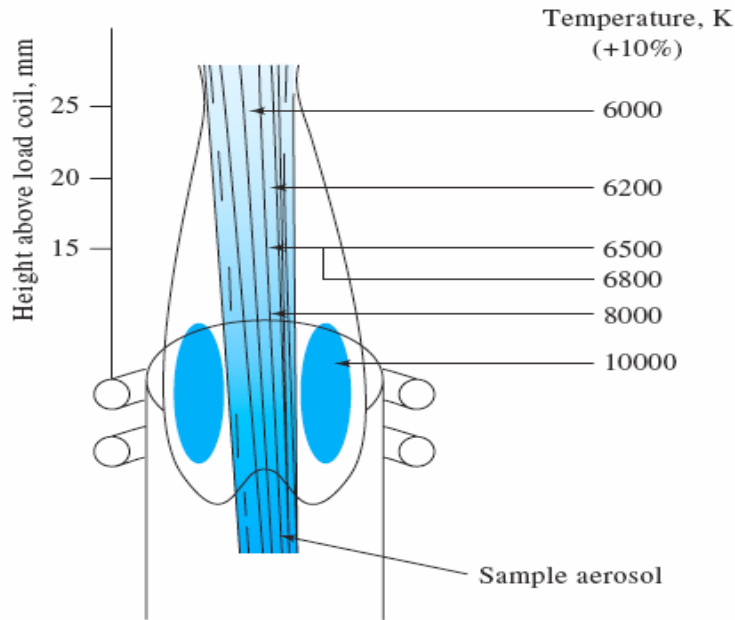
# SOLIDS:

Fig. 2. Schematic diagram of ETV principles of operation (modified from Perzl 2009).



**Solid sampling ETV-ICP-OES to study the distribution of elements in clay and soil samples for mineral exploration,**  
Geochemistry: Exploration, Environment, Analysis, Volume 13, Pages 11 - 20 <https://doi.org/10.1144/geochem2012-129>

## ICP Plasma Structure

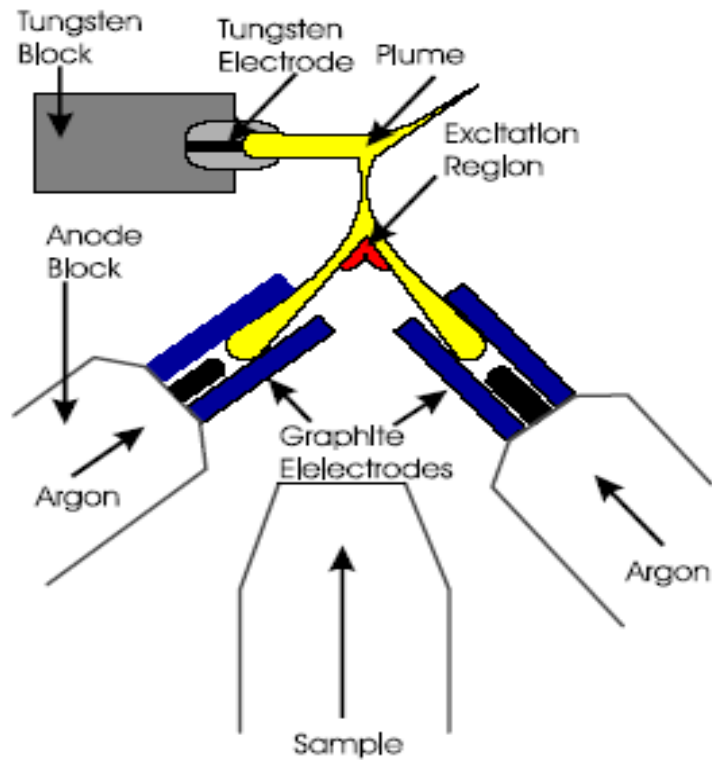


- Brilliant **white core** - Ar continuum and lines
- **Flame-like tail** up to 2 cm
- **Transparent region** - measurements made
- **Hotter than flame** (10,000 K) - more complete atomization/excitation
- **Atomized in "inert" atmosphere**
- **Little ionization** - too many electrons in plasma

- The viewing region used in elemental analysis is usually about 6000 °C, which is about 1.5-2.5 cm above the top of the tube.
- It should also be indicated that argon consumption is relatively high which makes the running cost of the ICP torch high as well.
- Argon is a unique inert gas for plasma torches since it has few emission lines. This decreases possibility of interferences with other analyte lines.

- A plasma torch looks very much like a flame but with a very intense nontransparent brilliant white color at the core (less than 1 cm above the top).
- In the region from 1-3 cm above the top of the tube, the plasma becomes transparent.
- The temperatures used are at least two to three orders of magnitude higher than that achieved by flames which may suggest efficient atomization and fewer chemical interferences.

## 2) Direct Current DC-Plasma

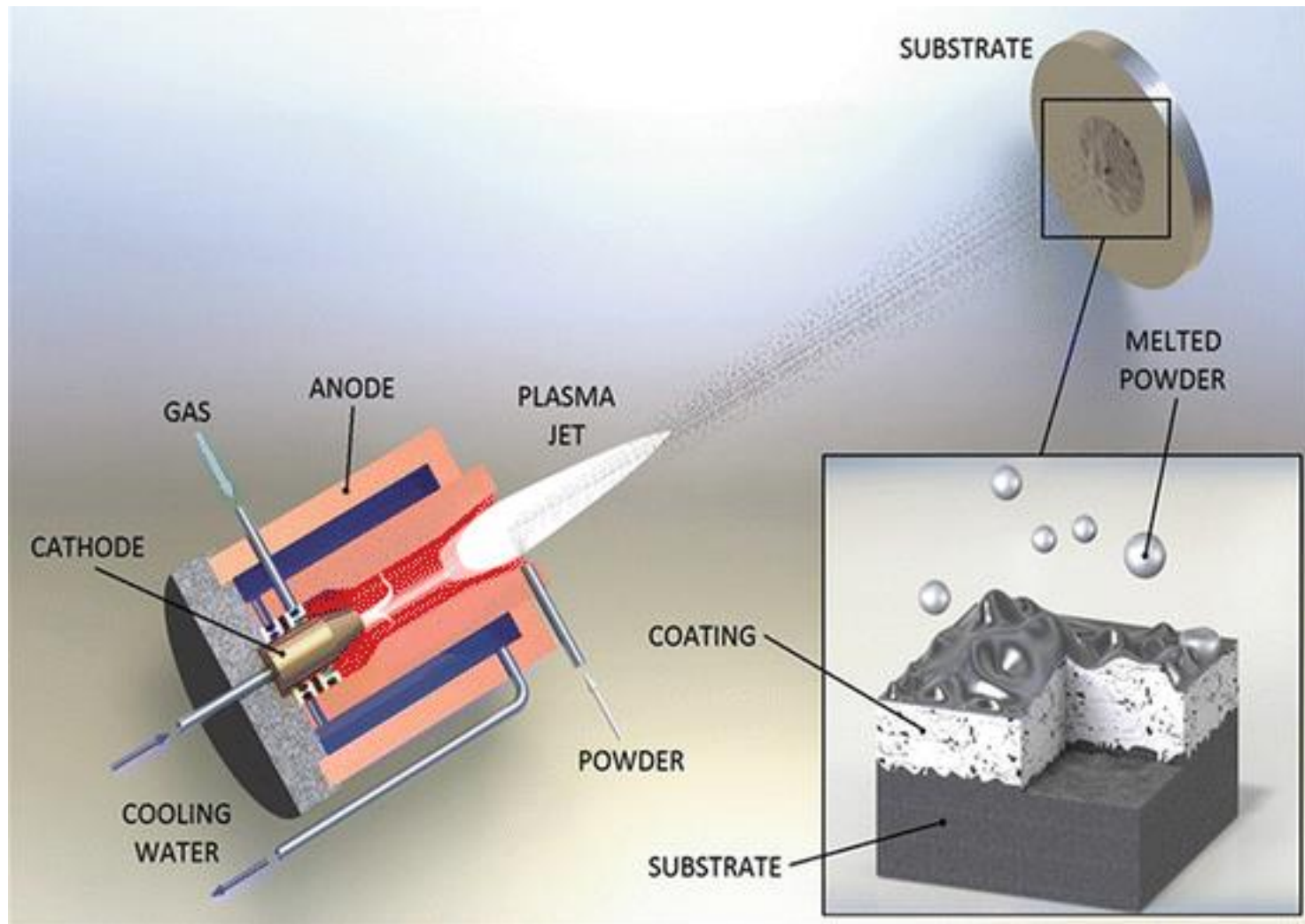


- DC current (10-15 A) flows between C anodes and W cathode
- Plasma core at 10,000 K, **viewing region at ~5,000 K**
- **Simpler, less Ar than ICP - less expensive**

<http://www.plasnix.co.kr/eng/html/sub0207.html>

- The DCP is composed of three electrodes arranged in an inverted Y configuration.
- A tungsten cathode resides at the top arm of the inverted Y while the lower two arms are occupied by two graphite anodes.
- Argon flows from the two anode blocks and plasma is obtained by momentarily bringing the cathode in contact with the anodes.
- Argon ionizes and a high current passes through the cathode and anodes.

- It is this current which ionizes more argon and sustains the current indefinitely.
- Samples are aspirated into the vicinity of the electrodes (at the center of the inverted Y) where the temperature is about 5000 °C.
- DCP sources usually have fewer lines than ICP sources, require less argon/hour, and have lower sensitivities than ICP sources.
- In addition, the graphite electrodes tend to decay with continuous use and should thus be frequently exchanged.



# Comparison of DCP and ICP

A DCP has the advantage of less argon consumption,

- simpler instrumental requirements, and
- less spectral line interference.

However,

- ICP sources are more convenient to work with,
- free from frequent consumables (like the anodes in DCP's which need to be frequently changed), and
- are more sensitive than DCP sources.

## *Advantages of Plasma Sources over Flame and Electrothermal Atomization*

1. No oxide formation due to
  - A) very high temperature
  - B) inert environment inside the plasma (no oxygen)
2. Minimum chemical interferences
3. Minimum spectral interferences except for higher possibility of spectral line interference due to exceedingly large number of emission lines (because of high temperature)
4. Uniform temperature which results in precise determinations
5. No self-absorption is observed which extends the linear dynamic range to higher concentrations
6. No need for a separate lamp for each element
7. Easily adaptable to multichannel analysis

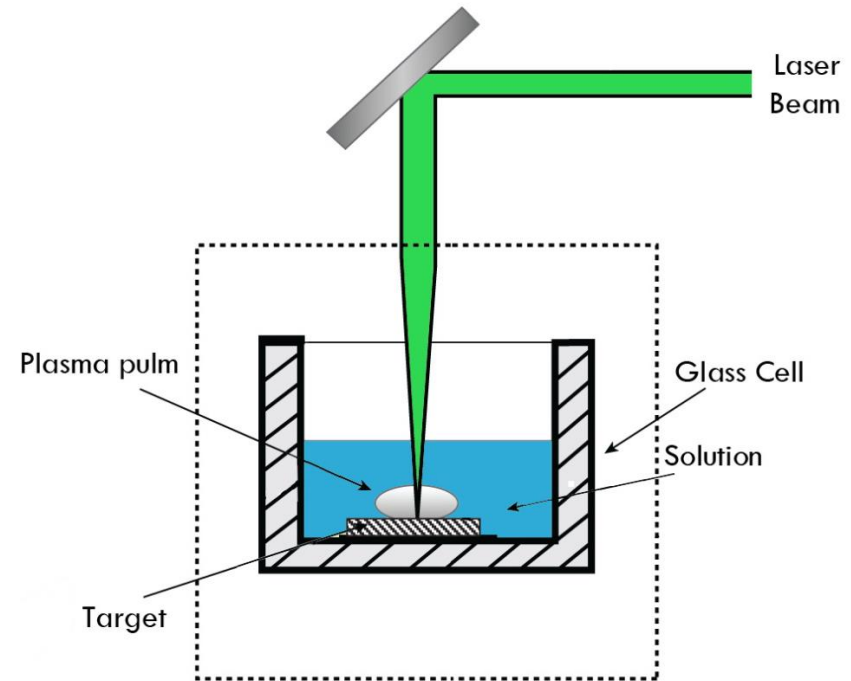


### 3) Laser-Induced Plasmas

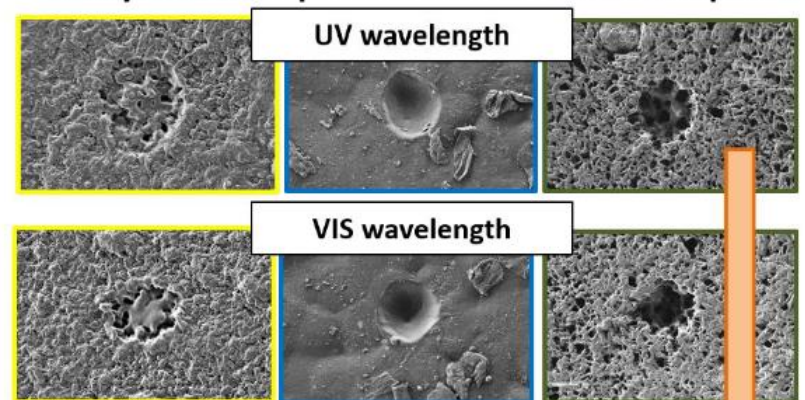
We consider here laser ablation and laser-induced breakdown spectroscopy (LIBS)

#### Laser Ablation.

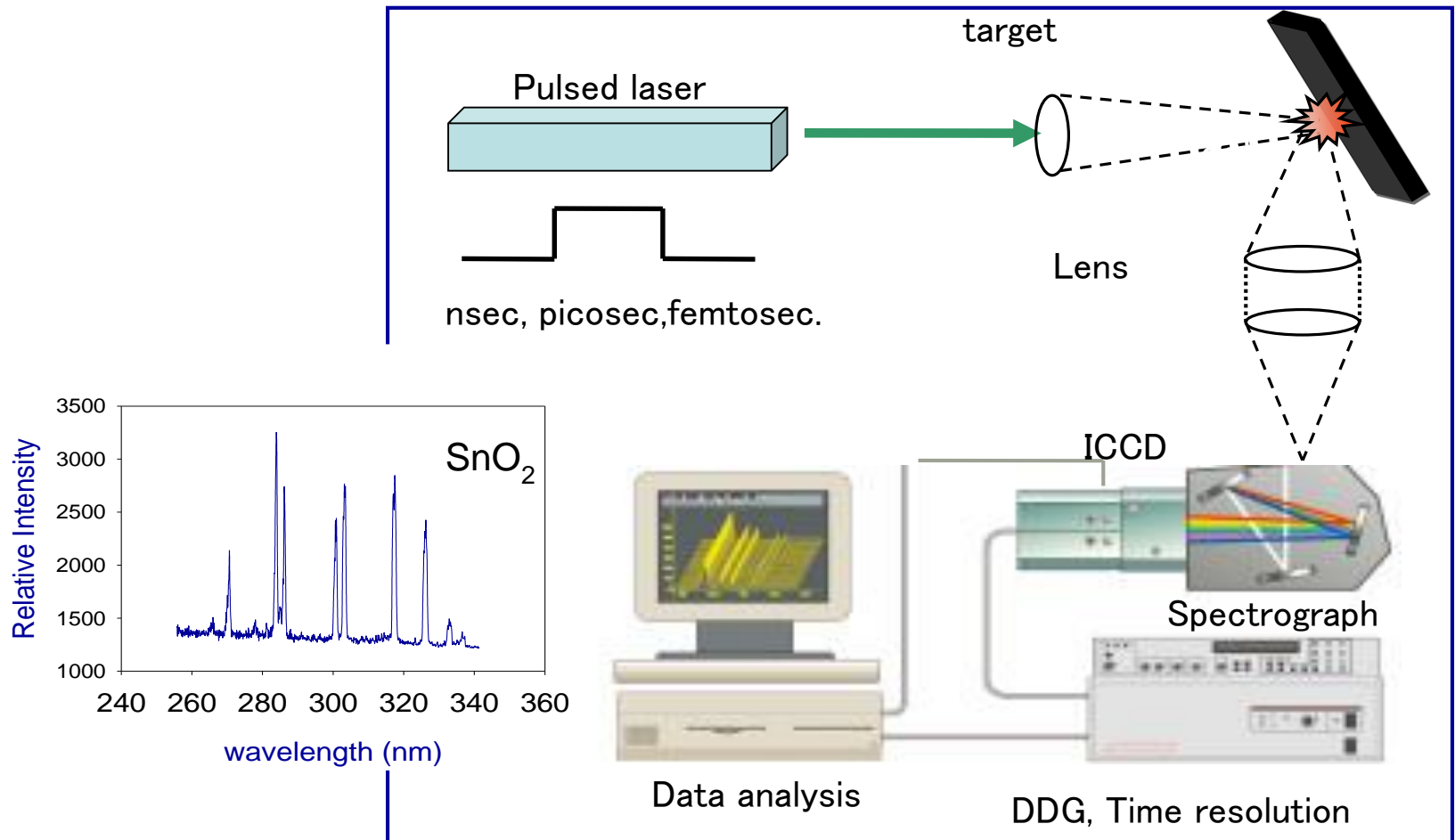
- Ablation is the removal of material from a surface by vaporization or some other process.
- In laser ablation, the beam irradiates the surface, which is usually a solid but occasionally a liquid, and causes localized heating and vaporization.
- Usually, a high-powered, pulsed laser is used, but continuous wave laser beams have also been used. Double pulse ablation is sometimes used.
- With high enough laser intensity, the material ablated can be converted into plasma.
- The laser plasma can emit radiation that is useful for AES, or it can produce ions that can be analyzed by mass spectrometry.
- In some techniques, a laser produces only a plume of atoms and ions, while a second device provides excitation. For example, with a laser microprobe, the contents of the plume formed by laser irradiation are excited by a spark discharge between a pair of electrodes located immediately above the surface
- The emitted radiation is then focused on a suitable spectrometer system. With a laser microprobe source, the trace element
- With some solids, the laser can be scanned across the surface to obtain a spatial representation of surface composition



#### Analysis of laser parameters and material response



# Laser-Induced Breakdown Spectroscopy:

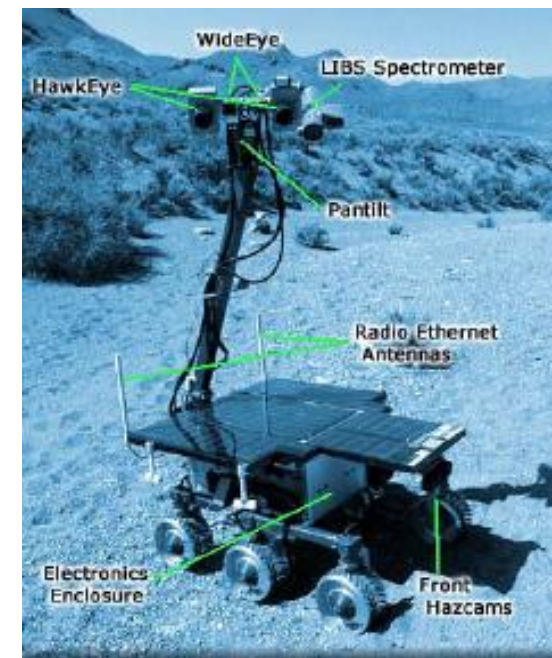


## ***Laser-Induced Breakdown Spectroscopy:***

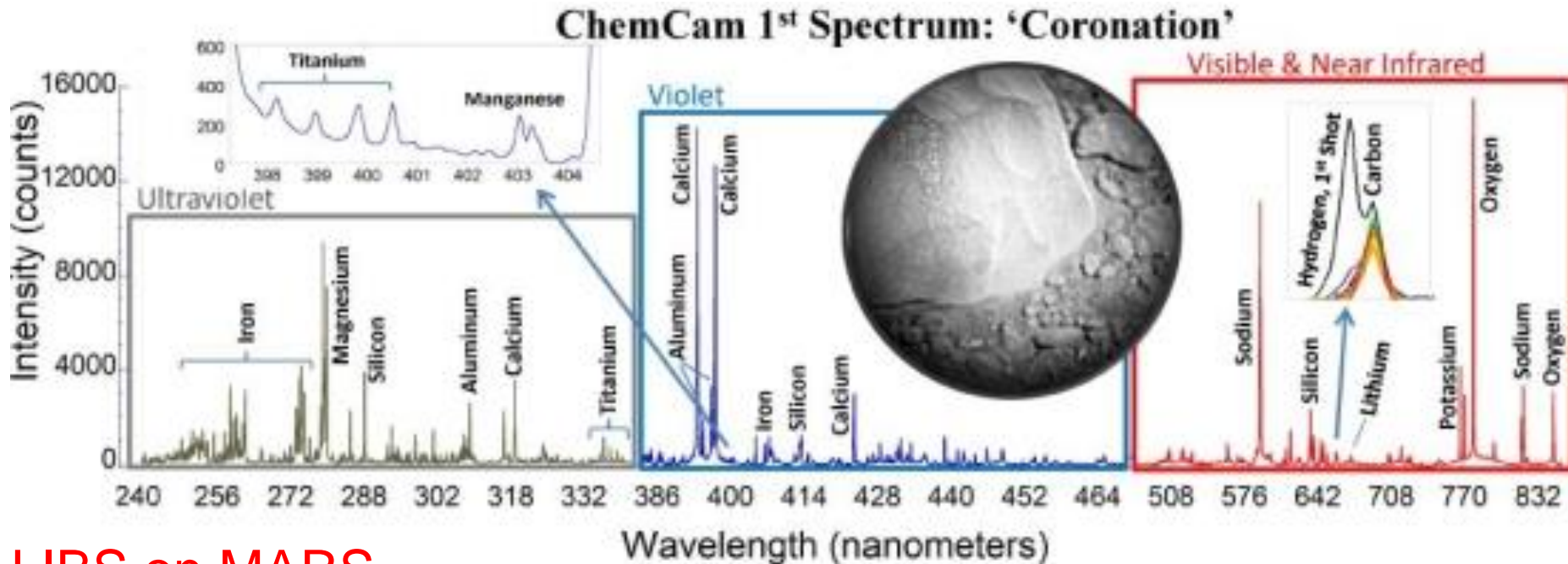
- The LIBS technique is closely related to laser ablation.
- Lasers used in LIBS are so powerful that dielectric breakdown of the atmosphere surrounding the ablated sample occurs, producing a highly luminous plasma.
- Typically, a short pulse of perhaps a few nanoseconds duration, such as that from a Nd:YAG laser, produces the plasma.
- Near the end of the laser pulse, the plasma cools, and radiation from excited atoms and ions can be detected.
- A spectrometer is used to collect the emission at the appropriate time so that the intense continuum radiation produced by the breakdown dies away before measurement of appropriate atom or ion lines.
- In addition to single-pulse LIBS, two-laser LIBS has also been successful. In two-laser LIBS, one laser ablates the sample while the second laser produces the plasma.
- The LIBS technique has been applied in several different areas. Metals, semiconductors, ceramics, coals, polymers, and pharmaceuticals are among these application areas.
- In addition to solid samples, gaseous and liquid samples have also been investigated. In fact, the first applications of LIBS were for the remote analyses of hazardous gases in industrial environments.

# Laser-Induced Breakdown Spectroscopy, .....Cont'd

- Various process liquids, biological solutions, aqueous environmental solutions, and pharmaceutical preparations have also been analyzed.
- LIBS instrument package in the Mars Science Laboratory is now active on Mars.
- The ChemCam system consists of a camera with a telephoto lens and the LIBS system. The LIBS laser enables the Martian soil or a rock of interest to be sampled remotely, without contamination from a robotic arm, and analyzed with the on-board spectrometer.



Laser Focus World August, 2000



LIBS on MARS

## Plasma Emission Measurement: Spectrometers

**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  $500 \times$  the detection limit)
7. High stability with respect to environmental changes
8. Easy background corrections
9. Computerized operation: readout, storage data manipulation, etc.

# AES:Spectrometers

Three classes of plasma emission instruments can be presented including:

- *Sequential, Simultaneous multichannel, and Fourier transform.*
  - Fourier transform instruments have not been widely used in AES.

## 1. Sequential instruments

\* *In this class of instruments a single channel detector is used*

\* *the signal for each element is read using the specific wavelength for each element sequentially.*

*Two types of sequential instruments are available:*

*a) Linear sequential scan instruments* where the wavelength is linearly changed with time. Therefore, the grating is driven by a single speed during an analysis of interest

*b) Slew scan instruments* where the monochromator is preset to provide specific wavelengths; moving very fast in between wavelengths while moving slowly at the specific wavelengths. Therefore, a two-speed motor driving the grating is thus used.

# Sequential MC

Sequential monochromators:

Slew-scan spectrometers - even with many lines, much spectrum contains no information

- rapidly scanned (**slewed**) across blank regions
- slowly **scanned** across lines
- computer control/preselected lines to scan

Sequential instrument - PMT moved behind aperture plate, or grating+prism moved to focus new  $\lambda$  on exit slit

- **Cheaper**
- **Slower**
- Pre-configured exit slits to detect up to 20 lines, slew scan

## 2. Simultaneous Multichannel instruments

- A simultaneous multichannel instrument incorporates either a polychromator or a spectrograph.
- Polychromators contain a series of photomultiplier tubes for detection, but
- Spectrographs use two-dimensional charge-injection devices (CIDs) or charge-coupled devices (CCDs) as transducers.

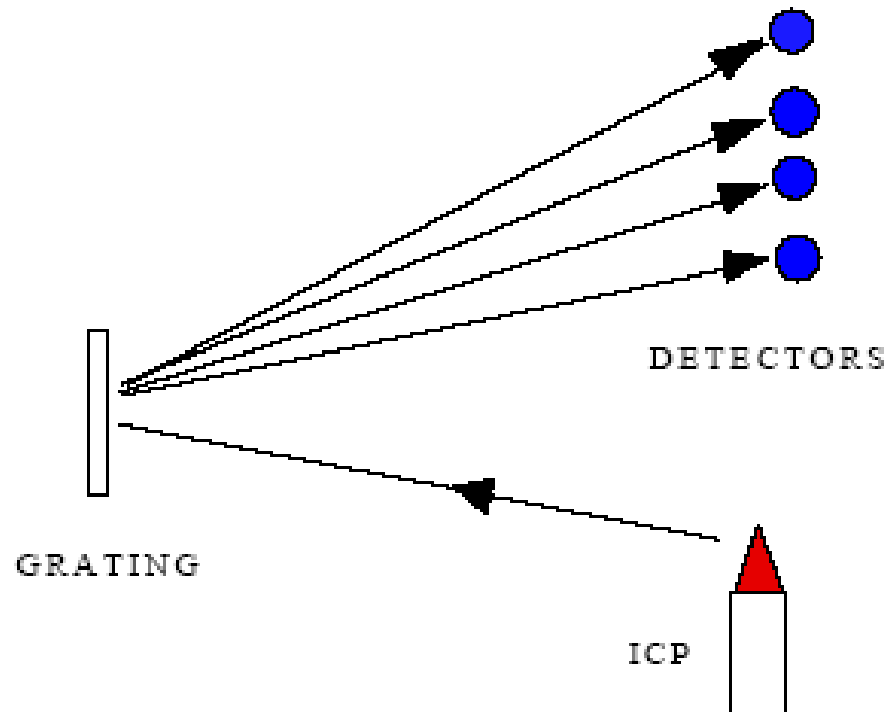
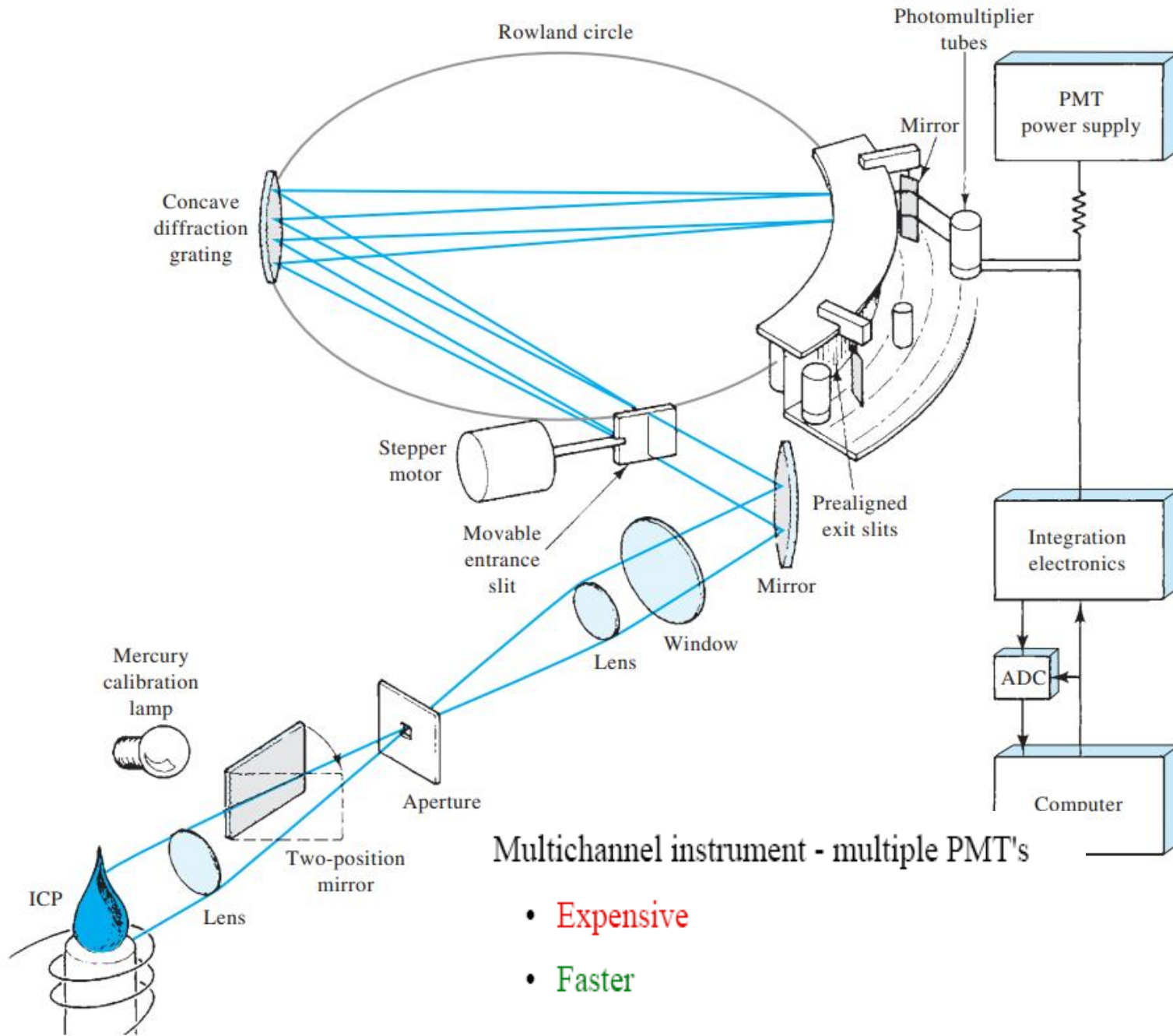


FIGURE 13. A POLYCHROMATOR FOR SIMULTANEOUS ANALYSIS OF RADIATION.

POLYCHROMATOR: MULTIPLE DETECTOR FOR EACH WAVELENGTH DISPERSED



## 2. Simultaneous Multichannel instruments



Multichannel instrument - multiple PMT's

- Expensive
- Faster

# SPECTROGRAPH : WIDE EXIT SLIT + ARRAY DETECTOR

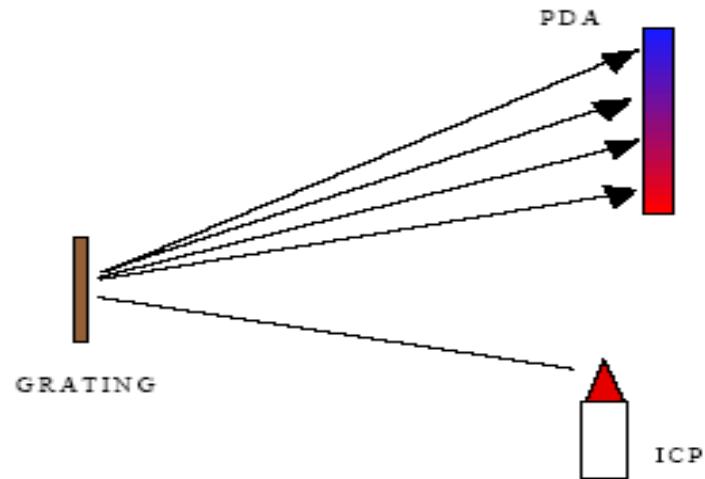


FIGURE 14. A PHOTODIODE ARRAY FOR SIMULTANEOUS ANALYSIS OF RADIATION.

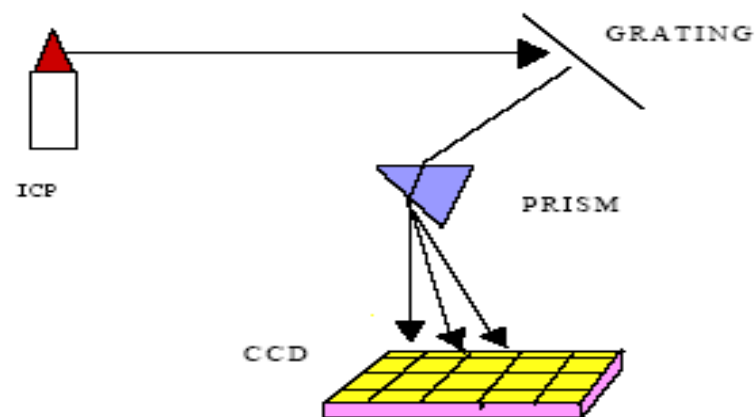
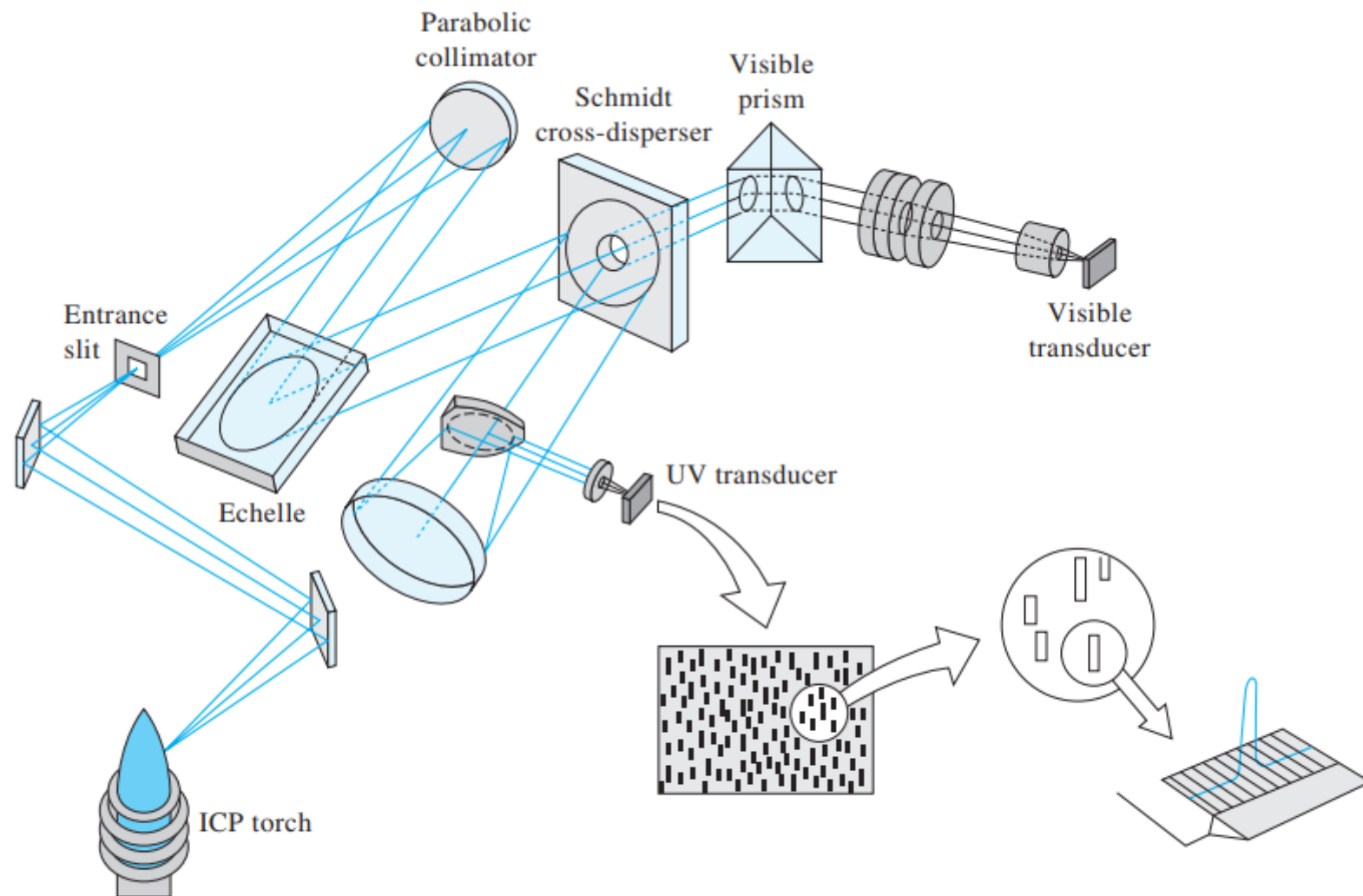


FIGURE 15. TWO-DIMENSIONAL DISPERSION AND DETECTION OF RADIATION USING A CHARGE-COUPLED DEVICE (CCD).



**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.)

# ICP TORCH POSITIONS

AXIAL



RADIAL

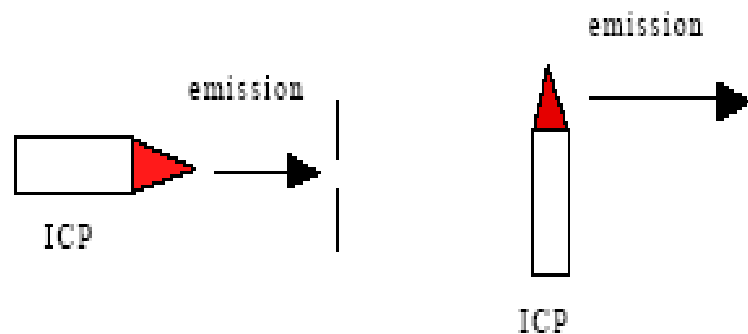
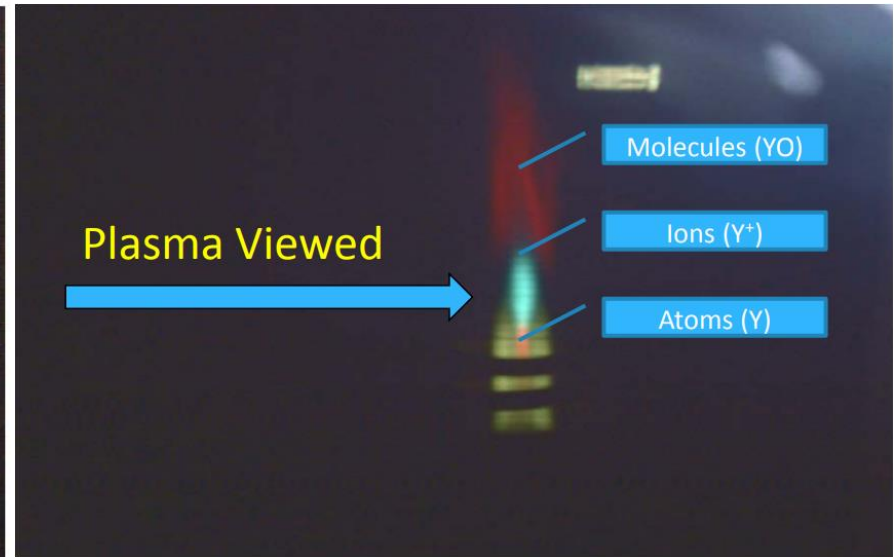


FIGURE 16. ICP TORCH POSITIONS INCLUDE A HORIZONTAL MOUNT (LEFT) AND THE MORE TRADITIONAL VERTICAL MOUNT (RIGHT).

*One should try to answer the following questions to decide on a technique that is right for your analysis*

- Number of samples to be analyzed
- Required sample digestion technique
- Which elements are required to be analyzed and their concentration levels
- Quantity of samples available for analysis
- Requirement for reporting isotope ratios of species present
- Initial cost and cost per analysis
- Special training requirements for operation and analysis of data.

# Flame Atomic Absorption Spectroscopy

## Benefits

- Lower price in comparison to ICP – OES and ICP – MS
- Mature technique with large base of established methods
- Analysis time per element is around 10 seconds
- Concentration range sub- ppm – ppm levels
- Simple to operate and not requiring specialized skills
- Lower cost of operation
- Can handle up to 5% dissolved solid samples
- Sample size requirement from about 5 to 8 ml

## Disadvantages

- Analysis of elements is possible one at a time.
- Only fraction of sample reaches the flame and residence time in flame is also small
- Linear dynamic range around  $(10^3)$ . Dilutions would be necessary for concentrated solutions
- Isotopic studies not possible
- Unattended operation not possible

# **Graphite furnace atomic absorption spectroscopy**

## **Benefits**

- Higher sensitivity of up to sub–ppb levels
- Low sample volume requirement 0.2 – 1 ml
- Unattended operation possible
- Can handle higher concentrations of dissolved solids up to around 10%

## **Disadvantages**

- Cost higher than flame AAS and involves additional operational expenses
- Analysis time per element is longer than flame AAS
- More interferences than flame AAS

# ICP – OES

## Benefits

- High detection limits from sub-ppb – ppm levels
- Simultaneous analysis of more than 40 elements in each sample per minute
- Cost higher than flame AAS but lower than ICP- MS
- Large linear dynamic range  $(-10^6)$
- Unattended operation possible
- Capacity to handle high dissolved solid samples up to 20%

## Disadvantages

- Time of analysis 1 – 5 min/sample
- More interferences than flame AAS
- Isotopic studies not possible



# ICP- MS

## Benefits

- Ultra trace detections up to sub-ppt levels are possible
- Linear dynamic range is highest up to  $(10^8)$
- Multi-element analysis up to about 40 elements at the same time as for ICP-OES analysis
- Isotope ratio studies possible
- Low sample volume consumption 0.02 – 2 ml/min

## Disadvantages

- Higher initial cost and cost of operation
- Can handle only up to 0.2% level of dissolved solids
- Special operational skills are required for good quality results