CHEM 517

Fundamentals And Applications Of Laser Induced Breakdown Spectroscopy, LIBS

Liquid Analysis by Laser Induced Breakdown Spectroscopy (LIBS)

LIQUID ANALYSIS by LIBS:

Bulk Liquids

- ✓Splashing
- ✓Buble formation
- ✓Shock wave formation

- ✓Shot-to-shot fluctuations
  - ✓Poor signal quality
  - ✓Reduced plasma emission
  - ✓Low limits of detection

APPROACHES :

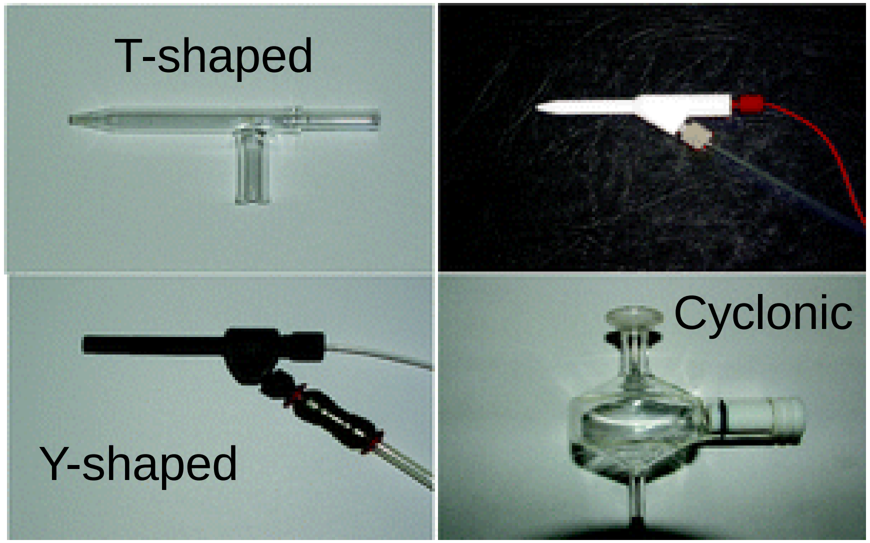
- ✓ use of double pulses
- ✓ formation of the plasma on
  - ✓ liquid surfaces
  - ✓ droplets
  - ✓ flowing-jet liquids
- ✓ use of common Atomic Spectroscopic *sample introduction techniques* for *aerosol* formation: (mist of very fine droplets)

Sample Introduction Techniques :

- ✓ electrospray ionization techniques (ESI)
- ✓ nebulization
  - ✓ pneumatic
  - ✓ ultrasonic
- ✓ Chemical Derivatization
  - ✓ Hydride Generation (HG)

Pneumatic Nebulization :

Hudson type



most commonly used → Low cost, simplicity gas flow (~1-8 L/min)

Drawbacks:

- ✓ Low analyte transport efficiency
- ✓ High sample consumption
- ✓ memory effect

Ultrasonic Nebulization :

piezo ceramics convert the electrical signal to mechanical vibration

- ✓ The average nebulized particle size
  - ✓ surface tension (T),
  - ✓ density (ρ) and
  - ✓ the frequency (f) of the liquid.

$$d_h = 0.73\sqrt[3]{\frac{T}{\rho . f^2}}$$

In the case of water,
T= 0.0729N/m,
ρ =1000kg/m^3
f= 50kHz,
the size of the particles centers around 22.5 microns

EXPERIMENTAL SET-UP

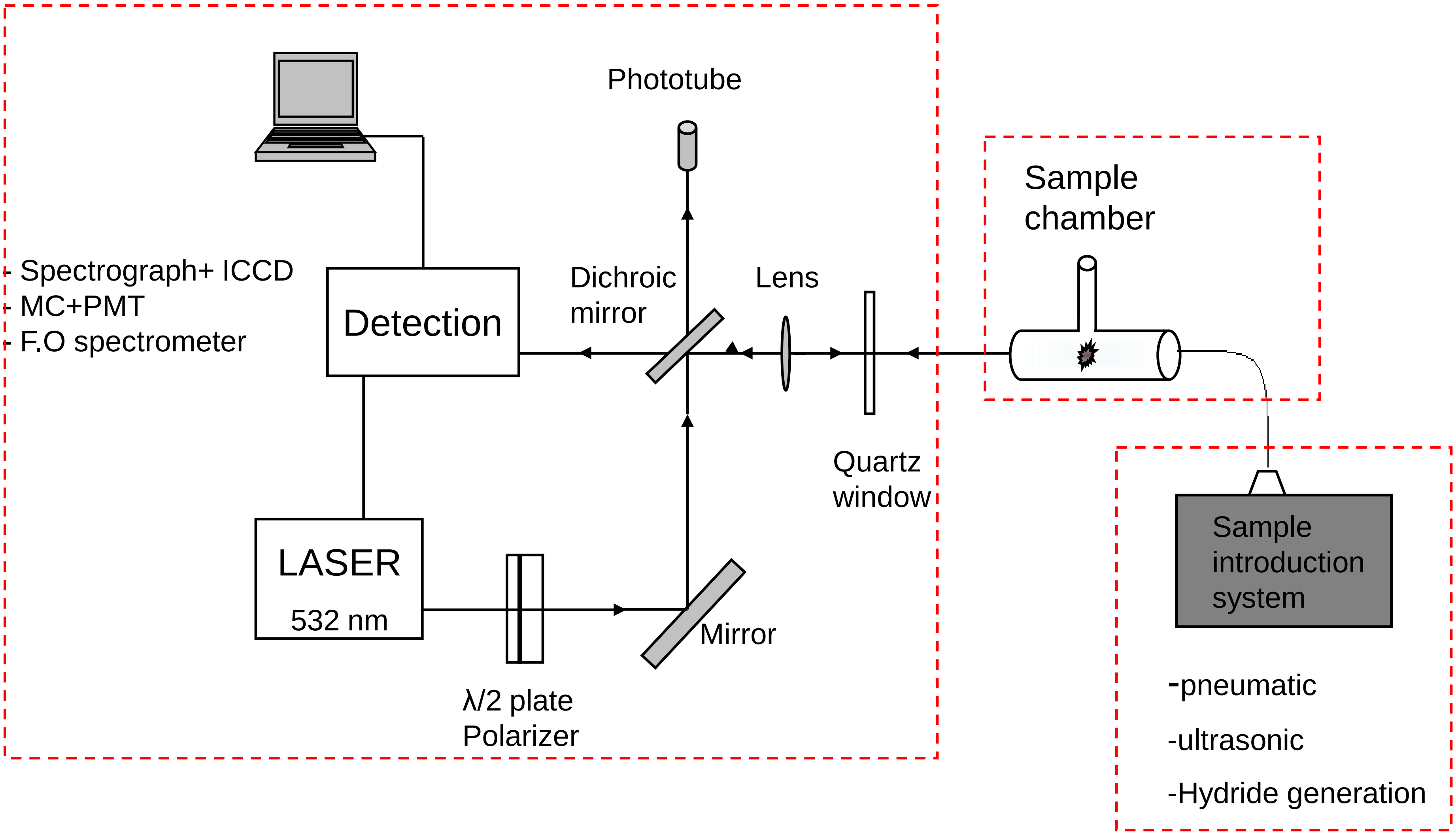


Figure 1. Schematical LIBS diagram

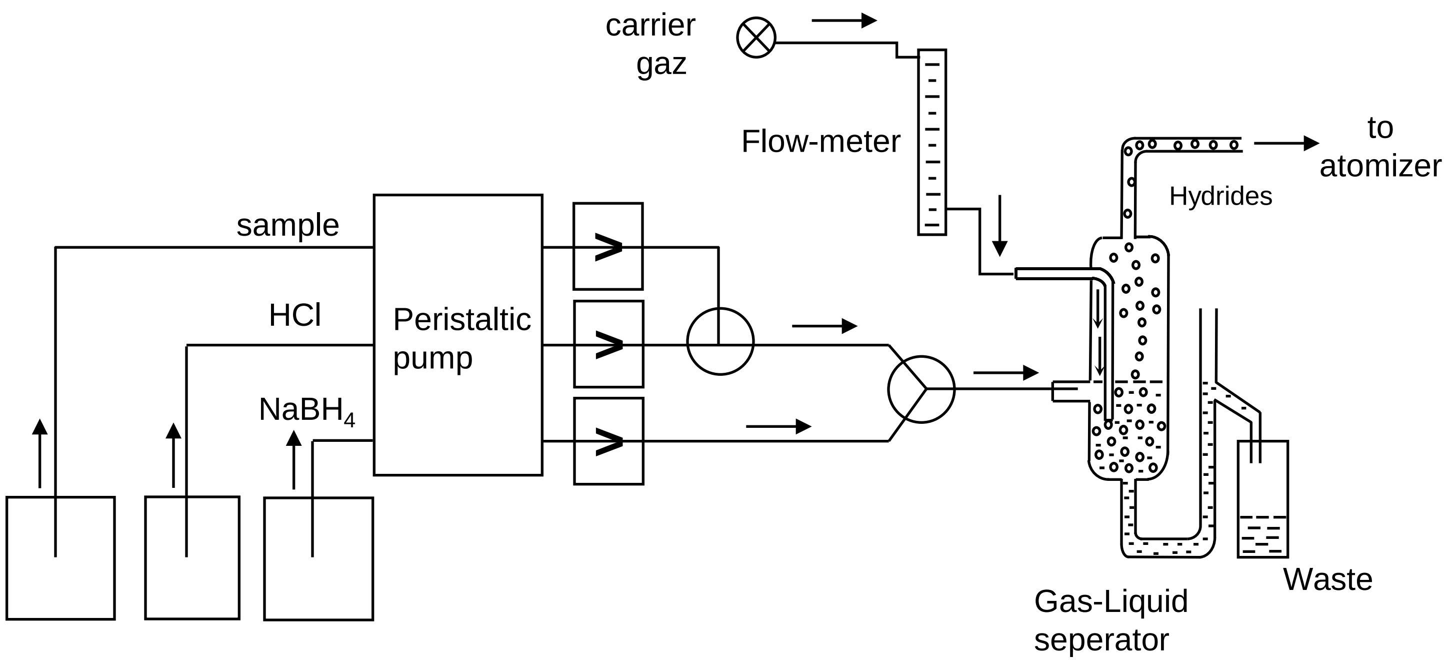
Hydride generation (HG):

- volatile hydrides of some elements (As, Sb, Pb, Te, Se, Bi, Ge, Sn)
- react with strong reducing agent such as sodium borohydride, $NaBH_4$

$$3BH_4^- + 3H^+ + 4H_3AsO_3 \rightarrow 3H_3BO_3 + 4\,AsH_3\uparrow + 3\,H_2O$$

- enhances sensitivity by 10–100 folds
- spectral and chemical interferences can be eliminated.

Hydride generation (HG):



LIBS signal

- ✓ Pulse Energy
- ✓ Gate / delay time
  - ✓Monitoring of ions / neutral species
- ✓ *Number of particles in the focal volume*

Efficiency of the aerosol generation system

- ✓ Carrier gas flow rate (1-8 ml min^{-1})
- ✓ Sample flow rate
- ✓ $NaBH_4$ and HCl flow rate (for HG-LIBS)

optimization

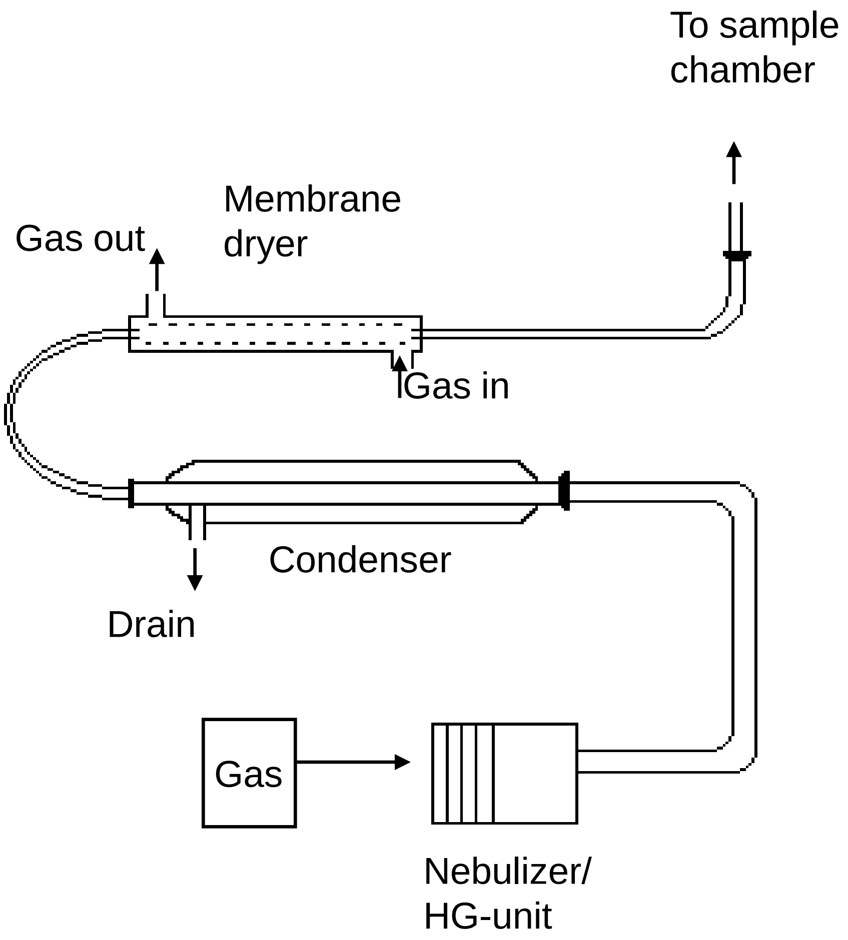
Desolvation/Dry Aerosol Generation:

aerosols particle size

✓ *Number of particles in the focal volume*

✓ *efficiency of vaporization, atomization, ionization*

Teflon membrane selective to water only



DESOLVATION UNIT
(Solvent Removal and membrane drying)

Table 1. LOD values for some of the elements

	Liquid LIBS	Hydride Generation LIBS (HG-LIBS)
As	0.5 mg/L (nebulizer)	Not given
	400 µg/m^3 (pneumatic nebulizer)	1.0 mg/L (hydride gas from their standards)
	5.0 mg/L (liq. evaporation on graphite)	1.0 mg/L (chemical hydride formation)
Bi	350 mg/L (Liquid on filter)	-
Ge	-	-
Pb	0.21 mg/L (aerosol)	-
	190 µg/m^3 (pneumatic nebulizer)	-
	12.5 mg/L (solution)	-
	0.2 mg/L (direct liquid)	-
	0.3 mg/L (liquid-jet)	-
	2.0 mg/L (liq. on graphite)	-
Sb	120 µg/acm	-
Se	-	-
Sn	-	Not given
		0.9 mg/L (chemical hydride formation)
Te		1.0 mg/L (chemical hydride formation)

- ✓Hydride Generation Atomic Absorption Spectrometry (HG-AAS),
- ✓Atomic Fluorescence Spectrometry (AFS),
- ✓Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES),
- ✓Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

- ✓sensitive measurements,
  - ✓ expensive to operate, to maintain, and
  - ✓ require laborious and time consuming data collection procedures
  - ✓ there is a risk of loosing chemical identity of the sample during its delivery from field to the laboratory.

- ✓ rapid,
- ✓ real time,
- ✓ in situ and
- ✓ economic

analysis techniques for environmental research applications

LIBS is a very suitable technique to develop environmental sensors

Conclusions:

✓ Versatility, operational simplicity, relatively low cost are some of the advantages

✓ The results obtained in terms of accuracy are comparable to conventional techniques however, detection power and sensitivity are still at moderate levels compared to other atomic spectrometric methods. The LIBS sensitivity can be enhanced by different approaches but at additional cost.

✓Several LIBS instruments are commercially available, but the technology is still far from mass production.

✓In the near future LIBS will gain a wide acceptance for process control in a broad range of industrial applications.

✓The advent of new detectors and spectrometers promises a bright future for the LIBS technique.