CHEM 517

Fundamentals And Applications of Laser Induced Breakdown Spectroscopy, LIBS

CHAPTER I

INTRODUCTION and HISTORY of LIBS

LIBS Acronyms:

- LIBS: Laser Induced Breakdown Spectroscopy
- LIPS: Laser Induced Plasma Spectroscopy
- LSS: Laser Spark Spectroscopy
- LPS: Laser Plasma Spectroscopy

- Laser Oluşturmalı Plazma Spektroskopisi ,LOPS

1960-1970 Atomic Absorption Spectroscopy, (AAS)

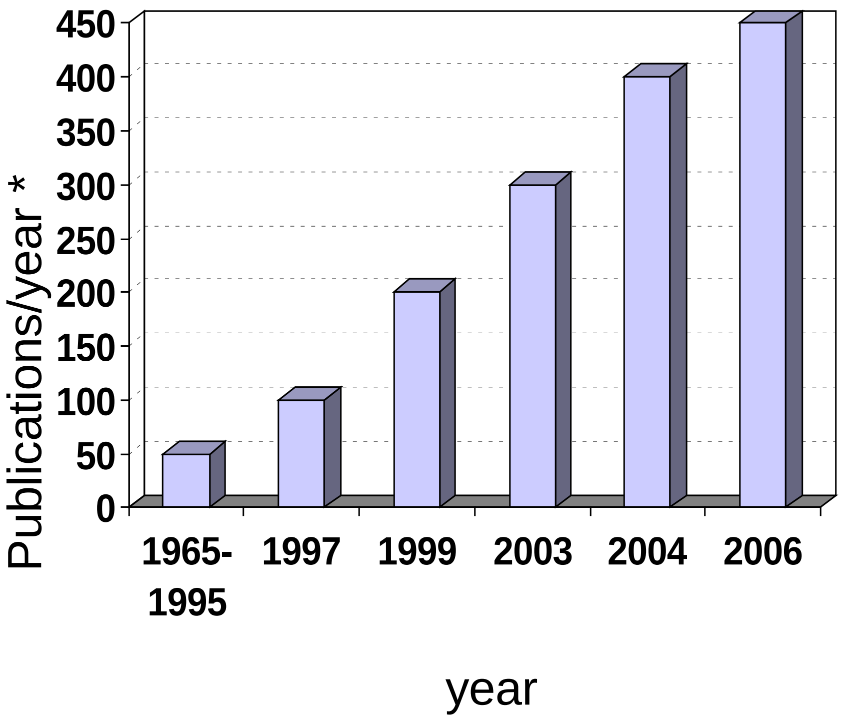
1970-1980 Inductively Coupled Plasma Atomic Emission Spectroscopy, (ICP-AES)

1980-1990 Inductively Coupled Plasma Mass Spectrometry, (ICP-MS)

OVERVIEW:

Radziemski and Cremers, 1981

- LIBS sessions
  - PITTCON, FACS
- LIBS conferences
  - EMSLIBS- odd years
  - LIBS – even years



* Data is from Handbook of Laser Induced Breakdown Spectroscopy, Wiley, 2006

What is Plasma?

•Plasma is considered to be a distinct state of matter, apart from gases, because of its unique properties.

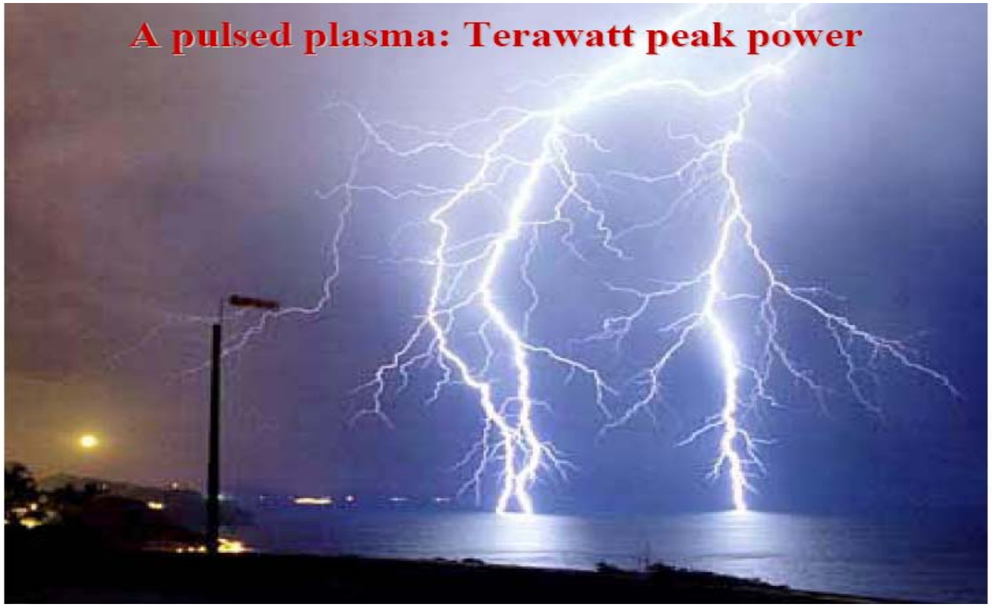
• A **plasma** is typically an ionized gas ⟶ physics and chemistry,

•Ionized refers to presence of one or more free electrons, which are not bound to an atom or molecule. The free electric charges make the plasma electrically conductive so that it responds strongly to electromagnetic fields.

•Plasma typically takes the form of neutral gas-like clouds (e.g. stars) or charged ion beams, but may also include dust and grains (called dusty plasmas)They are typically formed by heating and ionizing a gas, stripping electrons away from atoms, thereby enabling the positive and negative charges to move more freely.

•Plasmas are by far the most common phase of matter in the universe, both by mass and by volume. All the stars are made of plasma, and even the space between the stars is filled with a plasma,

What is Plasma?

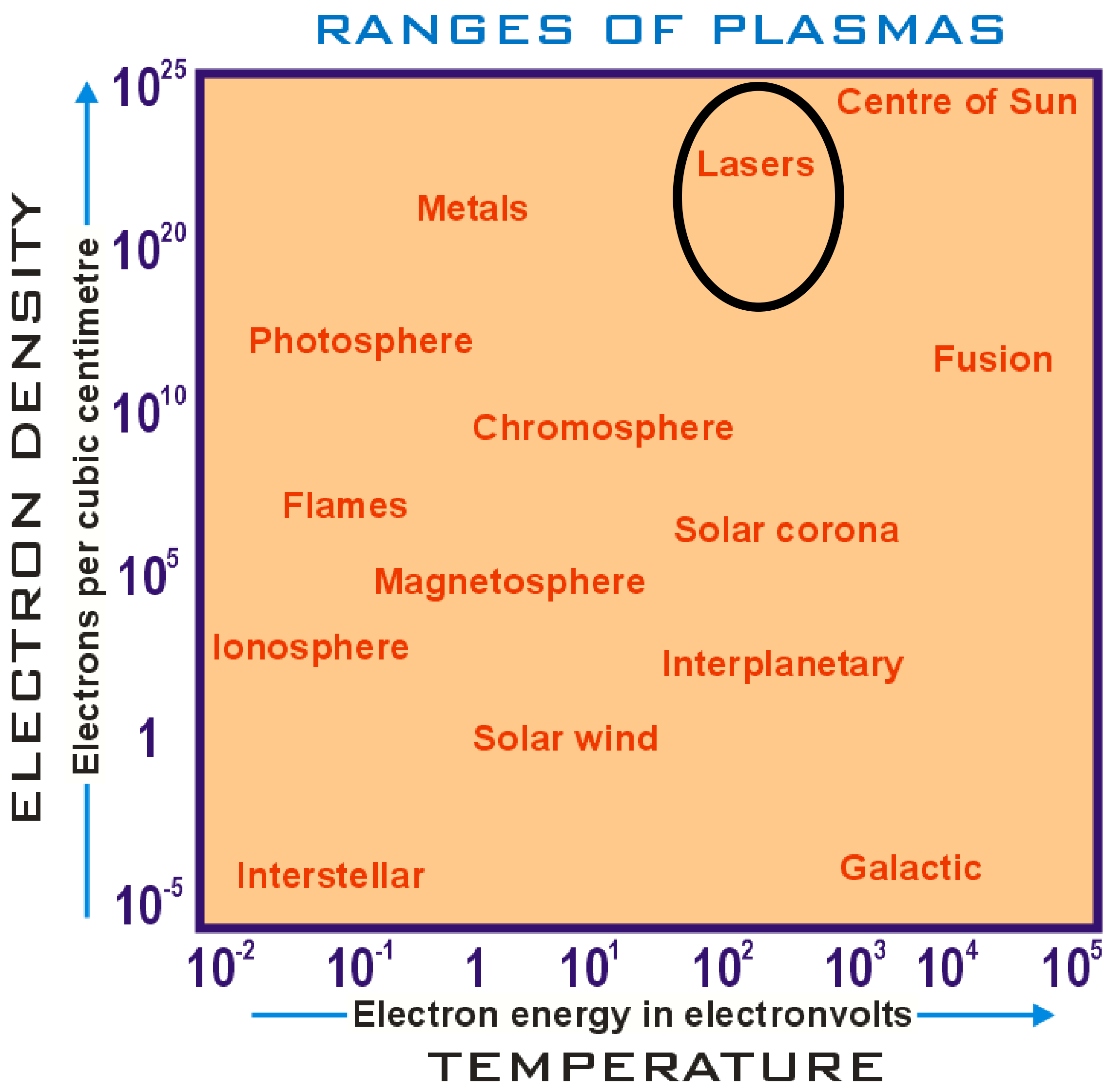


Lightning is an example of plasma present at Earth's surface. Typically, lightning discharges 30,000 amperes, at up to 100 million volts, and emits light, radio waves, x-rays and even gamma rays. Plasma temperatures in lightning can approach ~28,000 kelvin (~27,700^{o}C) and electron densities may exceed 10^{24}/m³.

From Wikipedia, the free encyclopedia

Typical ranges of plasma parameters: orders of magnitude (OOM)

Characteristic	Terrestrial plasmas	Cosmic plasmas
Size (in meters)	10^{-6} m (lab plasmas) to 10^{2} m (lightning) (~8 OOM)	10^{-6} m (spacecraft sheath) to 10^{25} m (intergalactic nebula) (~31 OOM)
Lifetime (in seconds)	10^{-12} s (laser-produced plasma) to 10^{7} s (fluorescent lights) (~19 OOM)	10^{1} s (solar flares) to 10^{17} s (intergalactic plasma) (~17 OOM)
Density (in particles /cubic metre)	10^{7} m^{-3} to 10^{32} m^{-3} (inertial confinement plasma)	10^{0} (= 1) m^{-3} (intergalactic medium) to 10^{30} m^{-3} (stellar core)
Temperature (in kelvin)	~0 K (crystalline non-neutral plasma) to 10^{8} K (magnetic fusion plasma)	10^{2} K (aurora) to 10^{7} K (solar core)
Magnetic fields (in tesla)	10^{-4} T (lab plasma) to 10^{3} T (pulsed-power plasma)	10^{-12} T (intergalactic medium) to 10^{11} T (near neutron stars)



Laser plasma:

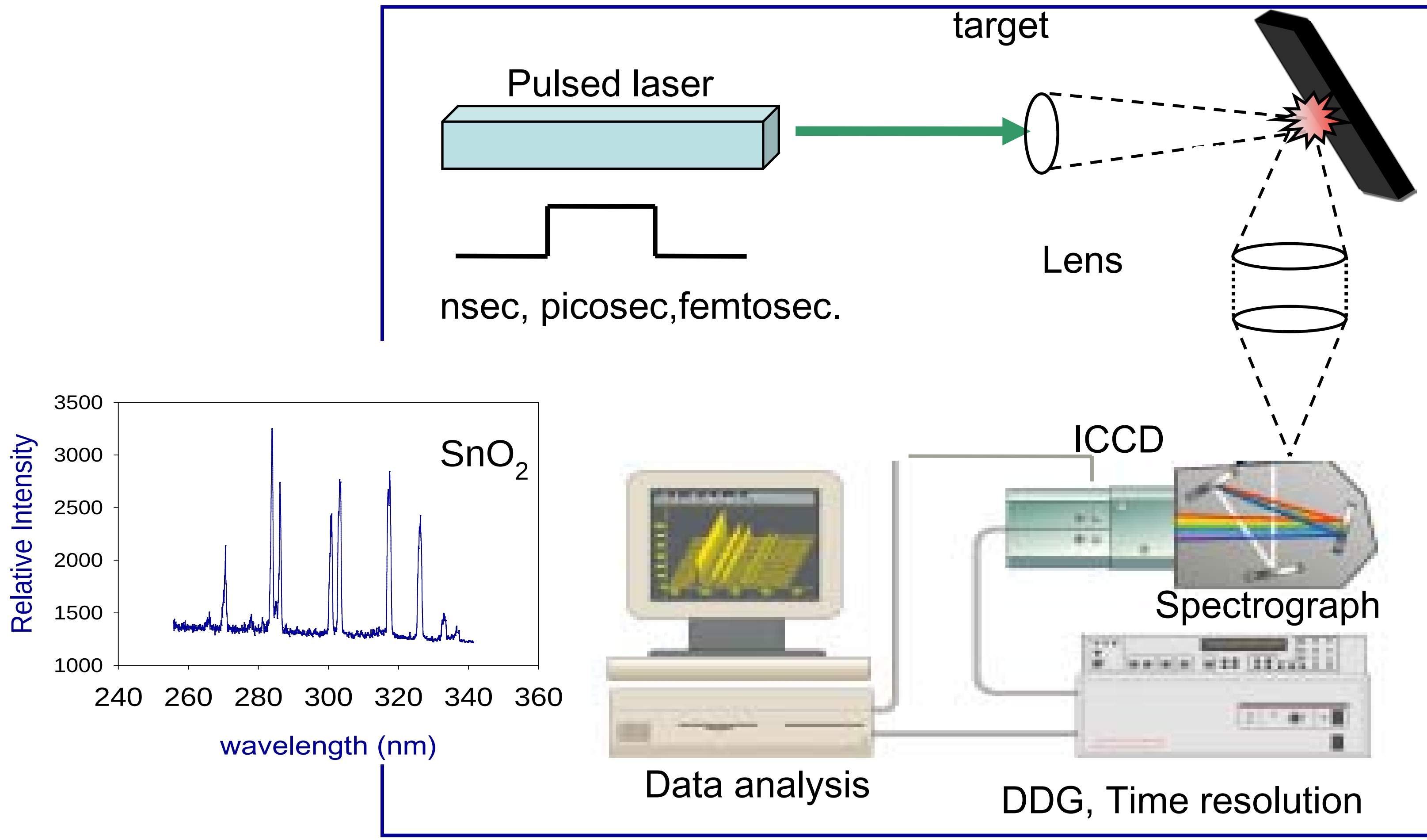
T~ 20.000 K

N_e ~ 1×10^{18} cm^{-3}

What are the parameters that define Plasma ?

- Size
- Lifetime
- Electron Density
- Temperature

Experimental Set-up:



The principle of the method:

•LIBS is an optical emission technique using a high peak power pulsed laser beam to form a small spark (i.e., breakdown) directly in/on the sample.

•This spark creates a plasma state hot enough to dissociate molecules into their constituent atoms and to excite the electrons in the neutral atoms and ions formed in the plasma out of the ground state and into excited electronic states.

•As the plasma cools, excited electrons and ions relax back into their ground states, emitting light at characteristic atomic wavelengths.

•The principle of the method:

•Material identification is accomplished by detecting the atomic emission using a spectrometer.

•Concentrations can be determined through relative light intensities. Elements that can be sensitively measured using LIBS include Al, Ba, Be, Ca, Cd, Cr, Cs, Fe, Mg, Mn, Na, Ni, Pb, Se, Ti, and V, among others.

•Multielemental analysis can be applied to different types of samples and matrices, i.e. gas, solids, liquids

•*LIBS is the only technology that can provide distinct spectral signatures characteristic of all chemical species in all environment*

LIBS Advantages:

- No or only minor sample preparation is needed

- small amount of material is consumed during the LIBS process the technique is considered essentially non-destructive or minimally-destructive

- Spatially and depth-resolved analysis is possible with resolution in the µm range

- LIPS can be used for many process analytical applications for a fast and on-line analysis of various raw materials such as minerals, ores, clays, chalk

- Remote sensing is possible using mirror- or fibre-optical interfaces

- Recent improvement of laser and detector technology allows construction of mobile and robust systems well adapted for screening and process analysis

LIBS Disadvantages:

- Difficulty in obtaining suitable standards (semi-quantitative)
- Relatively high detection limits (high ppb- low ppm)
- Surface composition can be different than bulk composition
- Variations in laser puls energy, shot to shot variation
- Low analytical performances,
  - The accuracy of LIBS measurement is typically better than 10%
  - and precision is often better than 5%

LIBS Applications:

- Metallurgy (solid or molten metals,alloy composition, process monitoring etc …)
- Pharmaceutical (active agent, lubricant, in tablets, etc...)
- Mining and mineral industry (detection, mineral composition)
- Microanalysis (by sharp laser focusing composition measurement at the micron scale;
- measurement of composition below the surface:3D- composition profile
- Recycling (sorting of alloys or various grades...)
- Security: detection of explosives
- Polymers (rubber, pigments, stabilizing additives..)
- Soil contamination
- Papers (pigment distribution, homogeneity)
- Art and archeology
- Biological samples(classification of bacteria: antrax)

Development of the LIBS technique

- 1962 to 1980: First experiments
  - Inadequate instrumentation (lasers, detectors)
  - Quantitative measurement difficult
- 1980 to 1990: Evolution in laboratory
  - Lasers and detectors become more reliable
  - Better analytical performances
  - Quantitative analysis demonstrated
- 1990 to date: Applications emerge
  - Industrial lasers, intensified detectors and echelle spectrometers enter commercial market
  - Growth in research activity

Highlights of LIBS

1960 First Laser demonstrated

1962 First useful laser-induced plasma on a surface

1963 First report of a laser plasma in a gas

1964 Time-resolved laser plasma spectroscopy was performed

1970 Q-switched and non-Q-switched lasers used

1984 Analysis of Liquid samples demonstrated

1993 Underwater solid analysis via dual-pulse LIBS

1995 Demonstration of LIBS using Fiber Optic delivery of laser pulses

1997 Use of LIBS for pigment identification in painted artworks

2000 Demonstration of LIBS on NASA Mars rover

2012 First LIBS data from Mars

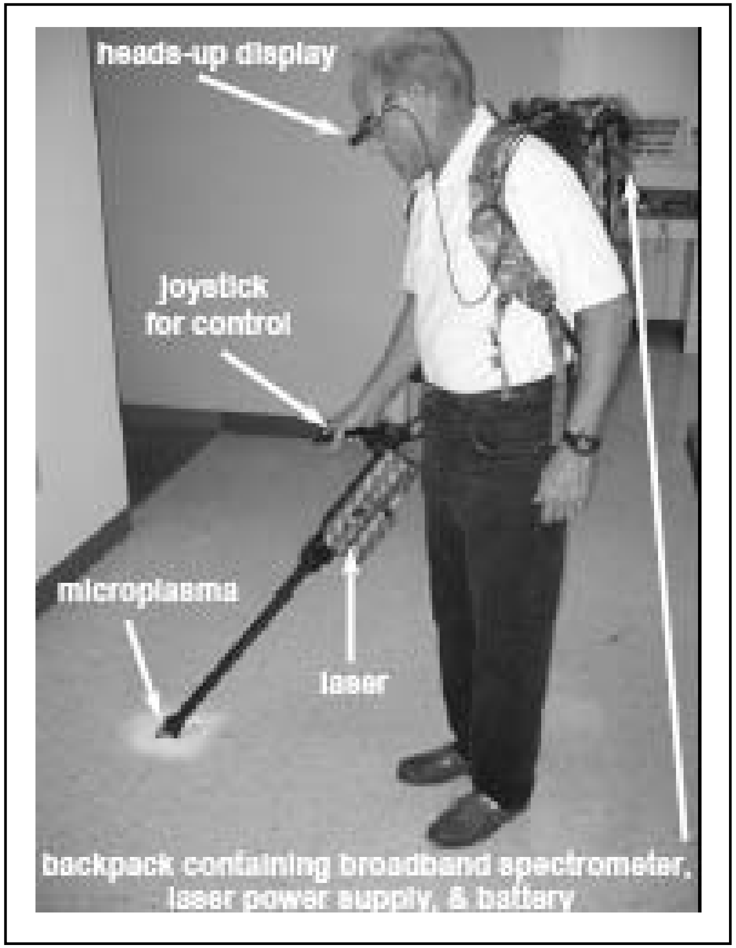
Portable LIBS

PORTA-LIBS-2000-

StellarNet Inc.

Portable LIBS Instrument
Model No. 0117

APPLIED PHOTONICS



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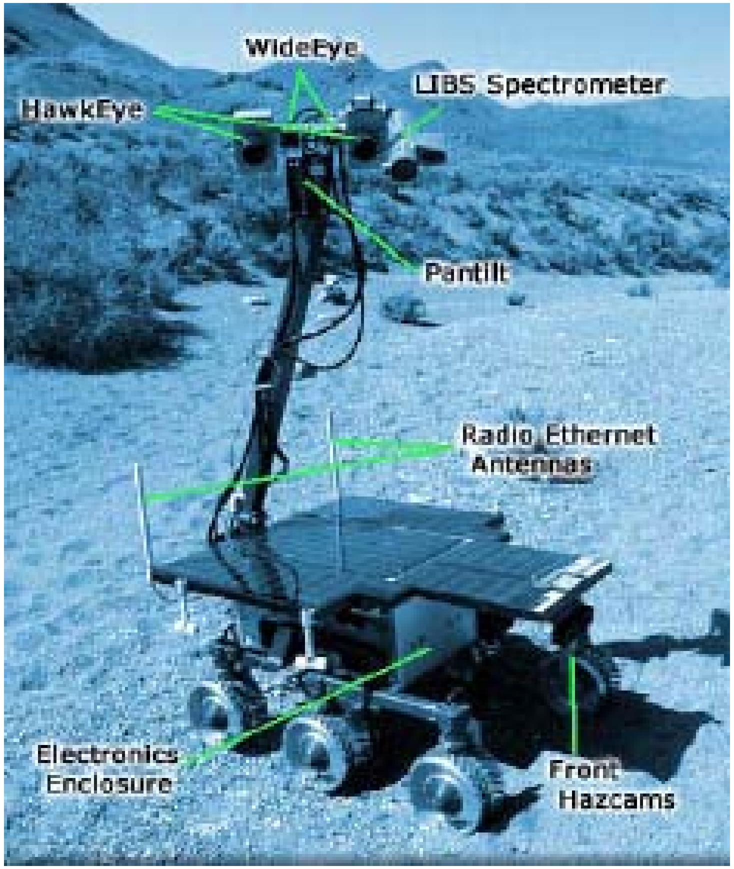
LIBS on MARS

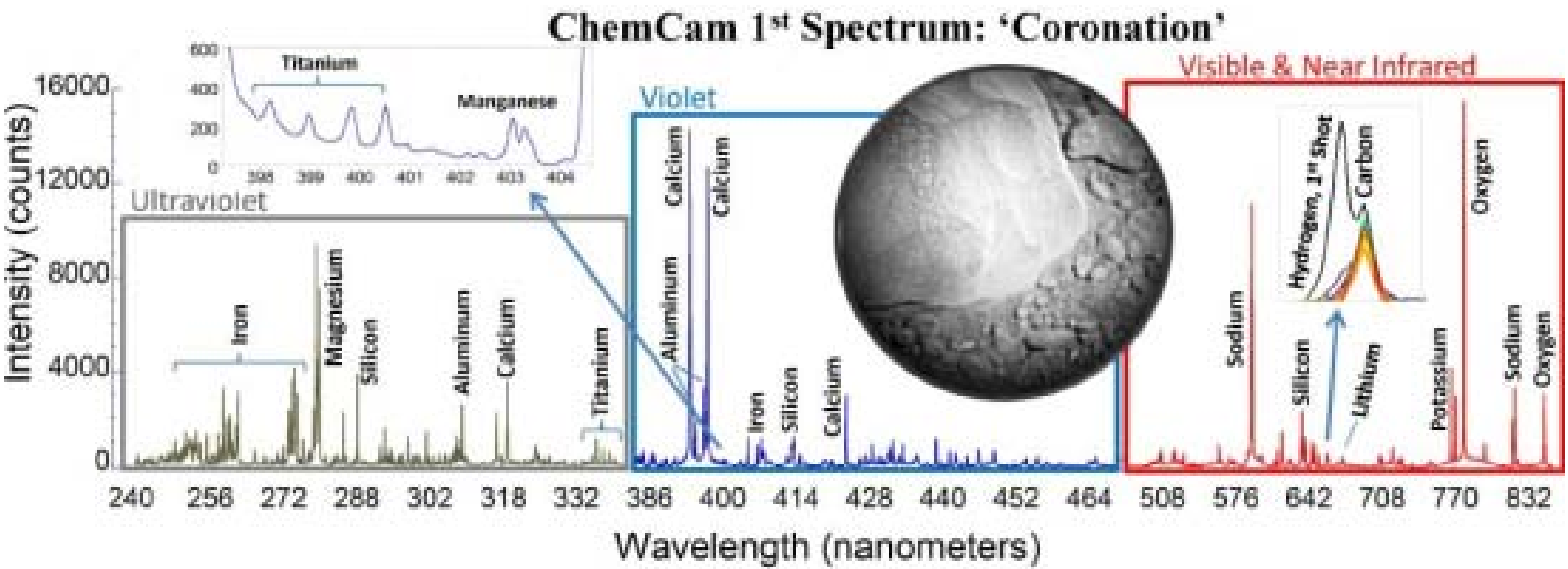


Rover Mounted LIBS system

Los Alamos National Laboratory, USA

Laser Focus World August, 2000

LIBS on MARS



(the larger version can be found at http://www.nasa.gov/mission_pages/msl/multimedia/gallery-indexEvents.html)